Chemical sensors clustering with the dynamic moments approach

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Abstract

One of the most important steps in pattern recognition is the definition of features describing the entities that have to be assigned to classes. From the point of view of chemical sensors, the extraction of features consists in the selection of some characteristics of the temporal sequence of sensor signal taking place during the interaction between the sensors and the compound present in the environment.

In this paper, the morphological descriptors of the sensor trajectory in the phase space are introduced and investigated. The performance of these new features has been compared with the usual features in three typical electronic nose applications.

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1. Introduction

In recent years, the role of data analysis in chemical sensing has been steadily growing. This is partly due to the emergence of subjects like electronic noses and tongues where data analysis is necessary to extract any analytical information from sensor signal. Also the interpretation of signals related to single sensors has shown to be enhanced when a little bit more than conventional data analysis is used. Among the various data analysis tools those devoted to the definition of novel features are particularly interesting. To this regard, it is of great interest the fact that increasing the number of features makes possible to perform typical recognition applications in a fashion usually reserved to sensor arrays but using only one sensor [1].

The extraction of features from a chemical sensor consists in the selection of some characteristics of the temporal sequence of sensor signal taking place during the interaction between the sensors and the compound present in the environment. From a general point of view, a chemical sensor is a dynamic system whose signal temporally evolves following, with its proper dynamics, the concentration of the analytes at which it is sensitive.

When a sensor is considered as a dynamic system any of the currently available tools usually employed to study the properties of dynamics systems may be utilized [2]. For instance, this approach has been followed adopting a non-linear dynamics model to calibrate the response of an array of quartz microbalances [3] and to develop a drift counteraction strategy [4]. In another application the time series expansion coefficients were considered, for instance by Eklov et al. [5], as sensor features.

Beside the dynamic modelling, a number of methods aimed at providing a graphical representation of a system have also been developed in the system theory realm. They are quite useful due to the immediate information display. Such methods usually define suitable spaces where the state of the system corresponds to a point and the time evolution is represented by trajectories [6].

The use of this approach for chemical sensors has been outlined in a recent paper where a phase space, suitable for thickness shear mode resonators, has been introduced [7]. This space was simply formed by the signal and its first time derivative. The description of sensor signals in these spaces may give rise to novel features that can alternatively be used to build more accurate sensor models. For instance, the area spanned by the trajectory of the signal when it undergoes a state transition has been proposed as an alternative feature to estimate both gas concentration (in the frame of quantitative analysis) and class membership (in qualitative analysis) [7].

Generally speaking, the area spanned by the trajectory, namely the sum instant by instant of the product of the signal by its first derivative, condenses the magnitude of the interaction with its velocity while standard
features usually considers only the magnitude of the signal shifts.

Nonetheless, the area being an obvious integral operation neglects the characteristics proper of the signal evolution. On the other hands, it is reasonable to expect that different interactions may take place when a sensor is exposed to different compounds and that such differences should be reflected in the sensor signal evolution namely on its dynamic properties. This makes important not merely the magnitude of the signal shift or its integral combination with the interaction velocity (as in the area case) but also the shape of the trajectory in the phase space; so that, the interactions with different compounds are expected to result in trajectories differently shaped.

The trivial way to describe a trajectory is to provide its analytical representation, nonetheless actual sensor trajectories may be difficult to be fitted with simple analytical functions. Furthermore, trajectories could change making impossible the use of a unique analytical function.

A better approach consists in the definition of a set of descriptors able to capture general morphological properties of the trajectories like the symmetries with respect to some fixed directions such as the axis and their bisectors.

In this paper, the sensor response will be studied in a phase space and the dynamic moments will be introduced as descriptors of the sensor trajectories.

The use of moment descriptors as features in pattern recognition problem will be illustrated and discussed in practical electronic nose applications. Once a novel feature is introduced, in order to evaluate its performance it is necessary to compare its properties in a comparison test. This is not a straightforward operation because this kind of tests is naturally influenced by the choice of the cases. Even so, these tests provide an indication about the potentiality of a feature extraction procedure, which, from a practical point of view, is offered to the chemical sensors practitioners as an additional tool to be considered when chemical sensors applications are considered.

In this paper, dynamics moments features will be considered as input of typical pattern recognition applications. Therefore, features will be judged according to their capability to increase the distance between the samples belonging to different classes and to decrease the distance between samples of the same class.

Feature extraction is only the first step of pattern recognition so in order to make the comparison effective it is necessary that the whole pattern recognition sequence of algorithms will remain unchanged. Nonetheless, the results may be different according to the kind of pattern recognition classifier following the feature extraction procedure. The choice of the pattern recognition classifier has been driven by the consideration that an optimal feature extraction should also tend to reduce the complexity of the data analysis. So that good results can be achieved using classifiers of low complexity. For this reason in this paper all the comparisons have been performed using a simple discriminant analysis solved by partial least square discriminant analysis (PLS-DA) and cross-validated by leave-one-out.

In the next section, an alternative phase space is introduced along with the definition of the dynamic moments. Both the concepts are applied to an array of thickness shear mode resonators coated by various chemically sensitive layers.

2. Phase space, dynamic moments and chemical sensors

Given a scalar observable quantity \( s(t) \) of a generic system, it is possible to define a \( k \)-dimensional vector space, here-with called phase space, with a defined orthonormal base. The fundamental property of the phase space is the correspondence between each point and the instantaneous state of the system.

A generic phase space can be defined considering the Taken’s Embedding theorem \([6]\). Given an observable quantity \( s(t) \) and defining a time delay \( \tau \), the space coordinates are

\[
[s(t), s(t + \tau), \ldots, s(t + (k-1)\tau)]
\]

the time evolution of the signal \( s(t) \) results in a trajectory containing the dynamical properties of the system.

Depending on the nature of the phenomena, trajectories assume a large variety of shapes. Disregarding scale effects the shapes of trajectories are expected to be associated to the properties of the physical phenomena. From this point of view, it is interesting to define some morphological descriptors able to encode the shape of the trajectories. These morphological descriptors can then be used to obtain information about the system dynamics. Here sets of morphological descriptors representing the parameters analogous to the second moments of the area of a geometrical figure in a 2-D space are considered. These quantities are sometimes called dynamic moments \([8,9]\). They are calculated considering both the coordinates and bisectors of the space

\[
\text{MD}_2 = \frac{1}{n} \sum_{i=1}^{n} x_i y_i
\]

\[
\text{MD}_3 = \frac{\sqrt{2}}{2n} \sum_{i=1}^{n} (x_i^2 y_i - x_i y_i^2)
\]

\[
\text{MD}_5 = \frac{\sqrt{2}}{2n} \sum_{i=1}^{n} [2x_i^3 + 3x_i^2 y_i + x_i y_i^2]
\]

\[
\text{MD}_3 = \frac{1}{2n} \sum_{i=1}^{n} (x_i^3 + 3x_i^2 y_i)
\]

\[
\text{MD}_3 = \frac{1}{2n} \sum_{i=1}^{n} (x_i^3 + 3x_i^2 y_i)
\]
each term is labelled according to the notation used in [8].
the number gives the degree of the moment. The subscript
indicates the direction along which the moment is calculated:
PB and SB are principal and secondary bisectors, x and y
are the phase space axis. The quantities x and y are related
to the observable quantity s(k) by the following relations
\( x_k = s(k); \quad y_k = s(k + \tau) \) (7)
each moment describes different morphological features of
the trajectory, so that the collective use of more than one
moment is required for an exhaustive description. It is also
important to remark that the moments value depends on the
time lag generating the phase space.

In order to apply dynamic moments to chemical sensors,
let us consider a typical absorption–desorption experiment
where the sensor is abruptly exposed to a fixed concentra-
tion of some analyte. Assuming a proportion between the
amount of the absorbed analyte and the sensor signal, sim-
ple absorption models leads to exponential behaviours of
the sensor signal with time. In real cases, multi-exponential
functions are more likely found[10,11].

The discerning property of dynamic moments can be il-
lustrated considering the response of a sensor exposed to
two analytes producing sensors signals very close one each
other as shown in Fig. 1. These signals follow the following
function
\[ s(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + c \] (8)
the two signals differ for a little variation of one of the time
constants.
The standard features extracted from this kind of signal
is the net variation between the signal measured before the
exposure and after the transitory. Obviously according to
this definition these signals result in the same feature and
therefore they are not distinguishable.
The same signals can be represented in a phase space built
from the signal and its delayed value. The two trajectories
are shown in Fig. 1b. Here the differences become more
evident with respect to the time domain.

Fig. 2a–c show three dynamic moments plotted versus the
time lag. In order to improve the recognition between the
two signals the choice of both MD and the time lag are of
primary importance.

In this simple case, for MD2 (Fig. 2a) the largest differ-
ence between the two signals occur for \( \tau_L = 1 \) s; for MD3PB
and MD3SB the separation is maximized considering \( \tau_L =
4 \) s. This simple example puts in evidence that dynamic mo-
ments can emphasize the subtle differences between signals
that appears rather similar in time domain. However, opti-
mization of moment order and the time lag on which the
phase space is built is necessary to maximize the features
performance.
In the next section, the potentialities of MD will be investigated in two practical cases.

3. Experimental

The performances of the dynamic moments strategies with respect to standard features have been evaluated in two typical electronic nose applications. These experiments were typical pattern recognition application aimed, in particular, at classifying between populations of kiwi-fruits and peaches.

The first experiment considers the difference of headspaces of kiwi-fruits of the same cultivar (hayward) but farmed in conventional and biological agriculture. Since biological agriculture avoids the use of pesticides this is expected to result in the headspace composition.

The second experiment represents a classic ripening stage discrimination, a number of peaches with three different storage time were measured in order to detect the differences in post-harvest processes.

The experiments involved 45 kiwi-fruits and 19 peaches.

The chemical sensor array used for the experiments was one of the prototypes of the LibraNose series (University of Rome “Tor Vergata” and Technobioschip) [12]. This electronic nose is based on thickness shear mode quartz resonators (TSMR). Sensors sensitivity is provided by a molecular film of metalloporphyrins coating the surface of TSMR sensors [13,14].

The sensors signal is a sequence of frequencies sampled at the constant interval of 10 s. Time lags multiple of 10 s have been utilized in the phase space building.

Measurements have been performed enclosing individual fruits in glass jars. Jars were then sealed and held at a constant temperature for 20 min in order to establish a steady headspace composition. Headspace was fluxed in the electronic nose measurement chamber by the LibraNose proper pumping system.

Partial least square discriminant analysis has been used as classifier. Models have been cross-validated with leave-one-out technique. In order to evaluate the identification performances of the dynamic moments have been compared with the frequently shift between the steady frequencies in measuring and cleaning phase. Features has been calculated and used without any additional pre-processing except autoscaling (zero mean and unitary variance). All calculations have been performed in matlab.
4. Results and discussion

4.1. Kiwi-fruits experiment

For this experiment we have used as feature MD2 with $\tau_L = 20$ and 30 s and MD3 with $\tau_L = 20$ s. The dynamic moments have been extracted by sensor responses.

In Table 1 the confusion matrices obtained by PLS-DA models built considering as input either the frequency shift (Table 1a) or the MD2 (Table 1b) are shown. It is relevant to note that in the case of the shift of frequency the errors are not equally distributed between the two classes. This effect is mainly due to the fact that the data set is not balanced (only 31% of the data are related to the biological cultivar) and as a consequence due to the scarce discrimination property of the frequency shift, the classifier results biased towards the most populated class.

This effect disappears when MD is used as input of the classifier. In this case being the feature more discriminant the inequality in class population does not give any effect of the classification and an almost perfect recognition is obtained.

As usual with PLS-DA models, classification can be shown plotting the scores of the PLS model resolving the classification problem. Fig. 3 shows the score plot of the first two latent variables of PLS-DA model built from MD features. Only 68% of the variance is explained in this plot, nonetheless the tendency to separate the two classes is clearly visible. It has to be remarked that the cross-validated PLS-DA model is formed by four latent variables.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Confusion matrix of PLS-DA in the kiwi experiment obtained using as input</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) The shift of frequency</td>
<td>Industrial</td>
</tr>
<tr>
<td>Industrial</td>
<td>29</td>
</tr>
<tr>
<td>Biological</td>
<td>6</td>
</tr>
<tr>
<td>(b) The dynamic moment</td>
<td>Industrial</td>
</tr>
<tr>
<td>Industrial</td>
<td>30</td>
</tr>
<tr>
<td>Biological</td>
<td>0</td>
</tr>
</tbody>
</table>

The classification rates are 82 and 97% for frequency shift and dynamic moments, respectively.

4.2. Peaches experiment

For this dataset the dynamic moments MD2 with $\tau_L = 10$ s and $\tau_L = 20$ s was considered. In Table 2 the confusion matrices resulting from the PLS-DA models obtained with these dynamic moments and the standard features are shown. Also in this case the dynamic moment outperforms with respect to the standard frequency shift. The percentage of correct classification is around 89% with only two misclassified samples and the performance improvement respect to the PLS model built with the shift of frequency is around 16%. The cross-validation gives a minimum of the classification errors using four latent variables. The classification
Fig. 4. Score plot of the second and fourth latent variables of PLS-DA evaluated using the dynamic moments as input, in the case of the peaches dataset. Ripeness states are indicated by integer numbers from 1 to 3 indicating the pre-ripe, ripe and over-ripe fruits. The plot explains only 15% of the total variance of the data.

is spread over the four latent variables so that the better separation between classes is obtained plotting the second and the fourth latent variables as shown in Fig. 4, only 15% of the total variance is represented in this plot. Evidently, the process of ripening in this population of peaches is not straightforward and the ripening stage is not the only variance source in the data.

Although in both the cases the dynamic moments outperform the standard frequency shift the performance of the method depends on the phase space (through the time lag) and the particular selected moment requiring in practice an adjustment of these parameters.

Table 2
Confusion matrix of PLS-DA for the peaches dataset calculated using as input

<table>
<thead>
<tr>
<th></th>
<th>Pre-ripe</th>
<th>Ripe</th>
<th>Over-ripe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-ripe</td>
<td>2</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>Ripe</td>
<td>0</td>
<td>8</td>
<td>0</td>
</tr>
<tr>
<td>Over-ripe</td>
<td>0</td>
<td>2</td>
<td>4</td>
</tr>
</tbody>
</table>

The difference in optimized parameters is not completely clear; likely they depend on the different kinds of experimental conditions that could mask the intrinsic dynamic information of the sensors. The time lag in particular, can be expressed only as multiple of the sampling rate of the sensor signal, in the experiments here described the signal rate was large (10 s). A shorter sampling time could bring to a better prediction capability.

5. Conclusions

In this paper, a novel feature extraction procedure for chemical sensors has been illustrated and the properties have been investigated in the case of an array of thickness shear mode resonators. The explored feature consists in a set of synthetic descriptors of the morphological properties of the sensor signal trajectory in a proper phase space.

Such quantities are the dynamic moments that describe the symmetry properties of curves towards a number of fixed directions such as the coordinate axis and their bisectors. The properties of these features have been investigated mainly comparing the performances of a PLS-DA classifier fed alternatively with the standard frequency shift and the dynamic moments. Comparisons have been performed with two data sets related to typical electronic nose experiments aimed at grading fruits according to different cultivars or ripening stage. In both cases, the PLS-DA models built from...
dynamic moments have obtained the best classification rates. Moreover in the kiwi-fruit dataset the discrimination was not influenced by the unequal population of the two classes. The results obtained reveal that these features contain tangible part of the information related to the essential characteristics of the system under measurement.

It is important to note that the optimal choice and the number of MD and the time lags can be depending on the specific application as seen in the cases here under studied. Therefore, in general it could be necessary to use different dynamic models at different time lags to maximize the discrimination of the classification model. In particular, the definition of the phase space is important for the overall quality of the features. In this paper, a space defined by delayed signal coordinates has been used. The amount of time lag is important both for the definition of the trajectory and for the associated dynamic moment.

Dynamic moments have been shown to be rather sensitive to small changes in the sensors dynamics, this makes the evaluation very sensitive to the chemical information but also to the disturbances as for example temperature and flow rate fluctuations that, very likely, are expected to influence the sensor dynamics. Although the influence of such parameters necessitate of a deep investigation, we can conclude that the control of the measurement protocol parameters is of great importance. Finally, the abundance of features that is possible to extract from the morphological description of trajectories in the phase space, makes this approach interesting to study from a different point of view the mechanisms that characterize the adsorption–desorption process of chemical sensors.

References