Fast Transient Classification With a Parallelized Temperature Modulated E-Nose
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Abstract

In this thesis work, a novel operating principle for a temperature modulated electronic nose is introduced. The main goal is to perform gas discrimination with metal oxide gas sensors in natural, uncontrolled environments where the sensors are exposed to patches of gas only for short periods of time.

The proposed Parallelized Temperature Modulated electronic nose (PTM e-nose) allows to speed-up discrimination of gases by measuring in parallel the response of $n$ gas sensors of the same type but with a phase-shifted temperature modulation cycle. The basic idea is to replicate the base sensor $n$ times with each sensor instance measuring one different $nth$ of the modulation cycle. In this way the response to the full modulation cycle for one sensor can be recovered from $n$ different sensors in one $nth$ of the time while the chemical response of the individual sensors is not compromised by a too fast temperature change.

The PTM e-nose operating principle is evaluated with an array of four commercially available tin oxide gas sensors, which are modulated with sinusoids of the same amplitude but phase-shifted by 90 degrees. By addressing gas discrimination in the early stages of the transient response and in the steady state, it is demonstrated that the information contained in one entire modulation cycle can be sufficiently recovered from the responses of the individual sensors.
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Many thanks to my close friends for these two years at the Örebro University.

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Víctor Hernández Bennetts.
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Contents

1 Introduction .................................................. 17
  1.1 Background ................................................. 17
  1.2 Motivation .................................................. 18
  1.3 Thesis Outline ............................................ 19

2 Background .................................................. 21
  2.1 Introduction ................................................ 21
  2.2 The Sense of Smell ....................................... 21
  2.3 Electronic Nose Concept ................................. 23
    2.3.1 Early Development ................................. 23
  2.4 E-nose Architecture ..................................... 24
    2.4.1 Delivery and Sampling Systems ..................... 24
    2.4.2 Sensor Array ....................................... 26
    2.4.3 Signal Pre-processing .............................. 27
    2.4.4 Feature Extraction ................................ 28
    2.4.5 Pattern Recognition and Classification .......... 29
  2.5 Current Developments .................................. 30

3 Gas Sensing and Selectivity Enhancement ............... 33
  3.1 Introduction .............................................. 33
  3.2 Gas Sensing Technologies ............................... 34
    3.2.1 Chemocapacitor Sensors (CAP) ..................... 34
    3.2.2 Gravimetric Odour Sensors ....................... 34
    3.2.3 Optical Odour Sensors ............................. 35
    3.2.4 Thermal Odour Sensors ............................. 35
    3.2.5 Amperometric Gas Sensors ....................... 35
    3.2.6 Potentiometric Odour Sensors ..................... 35
    3.2.7 Conducting Organic Polymers ..................... 35
  3.3 Metal Oxide Gas Sensors ................................ 36
    3.3.1 Operation Principles ............................... 36
  3.4 Selectivity Enhancement ................................ 38
3.4.1 Material Technology .................................. 38
3.4.2 Operation in Dynamic Mode .......................... 39
3.5 Temperature Modulation ................................. 39
  3.5.1 The “Virtual Sensor” Concept ....................... 41
  3.5.2 Temperature Modulated E-noses ..................... 42

4 The PTM E-Nose .............................................. 45
  4.1 Introduction ............................................. 45
  4.2 The PTM E-Nose Concept ................................ 45
    4.2.1 Four Sensor PTM E-Nose .......................... 46
  4.3 Implementation ......................................... 48
  4.4 The Sensor Array ....................................... 48
  4.5 Data Acquisition (DAQ) .................................. 49
  4.6 Pattern Recognition Block .............................. 50
  4.7 Signal Preprocessing ................................... 50
    4.7.1 Prefiltering ....................................... 50
    4.7.2 Baseline Correction ................................. 52
    4.7.3 Segmentation ..................................... 52
    4.7.4 Odour Signature Reconstruction ................... 53
  4.8 Feature Extraction ..................................... 56
    4.8.1 Feature Extraction in Dynamic Equilibrium ........ 56
    4.8.2 Feature Extraction in Transient Response ......... 57
    4.8.3 Dimensionality Reduction ........................... 58
  4.9 Classification Algorithm .............................. 58
  4.10 Validation .............................................. 58
    4.10.1 Cross-Validation .................................. 59
    4.10.2 K-Fold Validation ................................. 59

5 Experimental Results ...................................... 61
  5.1 Test Setup ............................................. 61
    5.1.1 Gas Sources ....................................... 61
    5.1.2 Sampling in Controlled Environments .............. 61
    5.1.3 Sampling in Natural Environments .................. 63
  5.2 Parameter Selection .................................... 64
    5.2.1 DC Level and Amplitude ............................ 64
    5.2.2 Modulation Frequency ............................... 65
  5.3 Results and Discussion ................................ 68
    5.3.1 Controlled Environments ........................... 68
    5.3.2 Natural Environments ............................... 72

6 Conclusions and Future Work ............................. 75
## List of Figures

2.1 The Human Olfactory System ........................................... 22
2.2 Block Diagram of a Typical Electronic Nose .......................... 24
2.3 Sensor response using a traditional three phase sampling process. The phases of the sampling are as follows: 0-Baseline. 1-Transient response. 2-Steady state. 3-Recovery [1].................. 25
2.4 Sensor readings obtained with an electronic nose mounted on a mobile robotic platform [1]........................................ 26
2.5 Feature extraction for a temperature modulated TGS2620 gas sensor. Feature “slope” and feature “AUC” denote the first derivative of the sensor response and the area under the curve, respectively........................ 29

3.1 Commercial gas sensors from Figaro Engineering...................... 33
3.2 The basic construction of a Metal Oxide Sensor ....................... 37
3.3 Resistance changes due to the interaction of a volatile compound with the surface of a MOX sensor................................. 37
3.4 Basic measurement circuit for a MOX gas sensor......................... 40
3.5 Left: Sensitivity-temperature profile for Pt- and Pd-doped tin-oxide sensors. Right: conductance-temperature response of a tin-oxide gas sensor in (a) air, (b) methane, (c) ethane, (d) propane, (e) n-butane, (f) isobutene, (g) ethylene, (h) propylene, and (i) carbon monoxide [2]........................................... 41
3.6 Conductivity response of a temperature modulated TGS2620 gas sensor exposed to 2-Propanol. (a) Modulating signal. (b) Sensor Response.............................. 42
3.7 Typical response of a tungsten oxide micro-hotplate sensor to ammonia (500 ppm), nitrogen dioxide (1 ppm) and ammonia + nitrogen dioxide (500 + 1 ppm) in the phase-space domain [3]........ 43
3.8 Hilbert transform decomposition applied to the response of a temperature modulated e-nose in presence of CH₄ [4].................... 44
4.1  Responses in dynamic equilibrium to different analytes recorded with a single TGS2620 sensor modulated by a sinusoidal signal of 1.7V DC Level, 3.3V amplitude voltage and a modulation frequency of 0.05hz. ................................................. 46
4.2  A PTM e-nose composed by four gas sensors. A) Modulation signals. B) to E) Outputs from the replicated sensors. F) Odour signature obtained from the four replicated sensors. ............... 47
4.3  Block diagram of the PTM e-nose used in this work. ................. 48
4.4  Electric diagram of a TGS2620 Figaro gas sensor [5]. ................. 49
4.5  Schematic diagram of the pattern recognition block. ................. 50
4.6  Comparison between the raw signal coming from the DAQ and the output from a 6th order averaging FIR filter. ............................... 51
4.7  Finite state machine used for the segmentation of the signal. ....... 52
4.8  Signal segmentation of a temperature modulated sensor. A) Averaged sensor response. B) Individual output from one sensor of the array. The start of the dynamic equilibrium response is denoted by the label “Rise end”. ............................... 53
4.9  Odour signature reconstruction in dynamic equilibrium response. A) to D) Individual sensor readings. E) Appended readings. F) Signal approximation. ............................................................... 54
4.10 A). Phase shift $\Psi$ between the reference sinusoid and the modulating signal $V_1$. B) Shift correction applied to the replicated odour signature. ............................................................... 55
4.12 Signal decomposition using discrete wavelet transform. .......... 57
4.13 K-Fold cross validation. ...................................................... 60

5.1  Setup and measurement process for the controlled environment scenario. A) The electronic nose is exposed to the reference gas (ambient air at room temperature). B) The electronic nose is exposed to one of the target analytes. ............................................. 62
5.2  Setup for natural environment experiments ......................... 63
5.3  TGS2620 response with different DC levels. A) and B) DC level $= 0V$ and the corresponding sensor response. C) and D) DC level $= 3.75V$ and the corresponding sensor response .......... 64
5.4  Modulation Frequency vs. $MD_3$ chart. ................................. 66
5.5  Obtained LDA plots in dynamic equilibrium with working parameters $V_a=1.3V$, $V_b=3.7V$ and A) $f=0.05Hz$, B) $f=0.1Hz$, C) $f=0.2Hz$, D) $f=0.25Hz$, E) $f=0.33Hz$ F) $f=0.5Hz$, G) $f=0.66Hz$, H) $f=1.00Hz$. ......................................................... 67
LIST OF FIGURES

5.6 LDA plots obtained in dynamic equilibrium (f=0.50Hz, \( V_a = 1.3V, V_b = 3.7V \)): A) Classical method, one sensor collecting data during T. B) Proposed PTM e-nose operating under the same working parameters collecting data during T/4. 68

5.7 Transient response obtained with a modulation frequency equal to 0.5Hz. Labels “0”, “1” and “2” are explained in the text. 69

5.8 Error bar chart at different exposure times \( t_e \) in controlled environments with a PTM nose with configuration parameters \( V_a = 1.3V, V_b = 3.7V \) and f=0.5Hz. 70

5.9 LDA plots obtained with a PTM nose in controlled environments with configuration parameters \( V_a = 1.3V, V_b = 3.7V \) and f=0.5Hz at different \( t_e \). A) \( t_e = 0.5s \). B) \( t_e = 2.5s \). C) \( t_e = 3.5s \). D) \( t_e = 4.5s \). 71

5.10 A) Sensor response when exposed to an Ethanol patch of gas in natural environments. B) Transient response segment where “0” denotes the detected rising edge, “0” to “1” delimits \( t_t \) and the exposure time is given from “0” to “2”. 72

5.11 Error bar chart at different exposure times \( t_e \) in natural environments with a PTM nose with configuration parameters \( V_a = 1.3V, V_b = 3.7V \) and f=0.5Hz. 73

5.12 LDA plots obtained with a PTM nose in natural environments with configuration parameters \( V_a = 1.3V, V_b = 3.7V \) and f=0.5Hz at different \( t_e \). A) \( t_e = 0.5s \). B) \( t_e = 2.5s \). C) \( t_e = 3.5s \). D) \( t_e = 4.5s \). 74
Chapter 1
Introduction

All living organisms (from simple bacteria to the human being) are immersed in a world of chemical signals that carry information about the environment. These signals play a key role in almost every aspect of their life such as feeding, territorial recognition, reproduction and detection of possible harmful conditions. In complex organisms, special chemical sensing systems have developed into the sense of smell or olfaction.

Historically, the human nose has been used as an analytical sensing tool to assess the quality of food, drinks, perfumes and several other household products. However, it is not practical to think about the human nose as a smell assessment instrument for certain industrial applications where it is needed to monitor a given volatile for prolonged periods of time or detect hazardous chemicals in the environment. Consequently, the interest for instrumentation devices that could overcome the limitations of the human nose has made possible the emerging of gas sensing technologies.

1.1 Background

A gas sensor is a device capable of generating an electrical signal in the presence of a target volatile. For many applications, such as gas monitoring alarms, it is desirable to have a low cost gas sensor that is able to discriminate between different substances (selectivity), at fast response times. There are several technologies and materials for gas sensor fabrication [2], here we focus on the utilization of metal oxide (MOX) gas sensors. They are low cost with acceptable response time, but they suffer from lack of selectivity, response drift (age factor) and are heavily influenced by environmental factors such as humidity and temperature [6].

One approach to partially overcome such limitations is the use of an array of gas sensors combined with pattern recognition algorithms. This devices are commonly referred as electronic noses. Gardner et al. defined in 1994 the electronic nose (e-nose) as an instrument that comprises an array of partially
selective chemical sensors with an appropriate pattern recognition algorithm capable of recognizing simple or complex odours [7].

To improve the gas sensor selectivity, the operating temperature dependence of the MOX sensors has been widely investigated and it has been shown that, by modulating the operational temperature, the information content of the response can be improved. Temperature modulation can be performed by connecting the heating element of the gas sensor to a waveform generator that periodically changes the working temperature of the device. When the sensor operating temperature is modulated, the kinetics of adsorption and reaction that occur at the sensor surface are altered [8]. Therefore, a cycle of the modulation signal (of period $T$) generates a characteristic pattern (i.e. an “odour signature”) of a target analyte present in the environment [9].

Over the past two decades, e-nose systems have been used in a wide range of applications under laboratory conditions (i.e. controlled environments), from wine brand discrimination [10] and food quality control [11] to medical applications for bacteria detection [12]. In a typical laboratory setting, measurements are performed inside a chamber where temperature, humidity and gas concentrations are controlled and the sampling process comprises of three phases. The sensors are first exposed to a reference gas, then to the gaseous analyte until the sensors reach the steady state response in which, the analysis is usually performed. Finally, the gas analytes are flushed away and the sensors recover.

1.2 Motivation

It is desirable to use e-noses, especially based on inexpensive sensor technology, also outside the laboratory. There are several potential applications in outdoor areas (i.e. natural environments) that can be implemented with the use of an e-nose combined with a mobile robot platform. Examples of such applications are environmental exploration [13], gas distribution modelling [14], buried land mine detection [15] or pollution monitoring [16]. Three phase sampling techniques cannot be applied straight forward when the e-nose is mounted on a mobile robotic platform due to constraints related to weight, space, power consumption [17] and response time. Furthermore, for MOX gas sensor, the steady state is hardly reached due to the intermittent nature of turbulent airflow [18] along with the movement of the robot. Consequently, data analysis (i.e. classification) has to be performed in the transient response of the sensory array.

In this thesis work, we introduce a novel operating principle for a temperature modulated e-nose aimed to be used in natural environments where the e-nose is exposed to gas patches for short periods of time. The proposed system uses cycling temperature modulation to increase the selectivity of the sensors

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1 In the case of temperature modulated sensors, until they reach a dynamic equilibrium (i.e. a semi stationary response) with the environment.
and the transient response can be used to perform discrimination. The particular characteristics of our approach is that a single sensor is instantiated $n$ times, each of them measuring one different $nth$ of the modulation cycle. By considering the transient response and the parallel operation of the replicated sensors, the required exposure time can be reduced. To the author's best knowledge, parallelized operation of gas sensors of the same type in an e-nose (PTM e-nose) has not been previously explored.

The experiments were based on a discrimination problem of three organic solvents (namely Acetone, Ethanol and 2-Propanol). We used a PTM e-nose composed of an array of four commercially available TGS2620 metal oxide gas sensors modulated with sinusoids of the same amplitude but phase shifted by 90 degrees. The experiments were carried out under laboratory conditions and in natural environments. Gas discrimination was addressed in dynamic equilibrium state (when available) and in the early stages of the transient response. It is demonstrated that the information contained in one entire modulation cycle can be sufficiently recovered from the responses of the individual sensors and thus, the exposition time can be significantly reduced with the PTM e-nose configuration.

1.3 Thesis Outline

The organization of this work is as follows:

- **Chapter 2**: Introduces key concepts related to e-nose technology and presents a brief summary of the current trends and directions in this field.

- **Chapter 3**: Presents a review about different gas sensor technologies, focusing on metal oxide sensors and selectivity enhancement by temperature modulation.

- **Chapter 4**: Introduces the PTM e-nose operation principle along with the signal processing and pattern recognition algorithms used in this work.

- **Chapter 5**: Describes the sampling processes in controlled environments and natural environments as well as the results and performance of the PTM e-nose in both scenarios.

- **Chapter 6**: Presents a summary of this thesis, along with the final remarks and directions for future work.
Chapter 2
Background

2.1 Introduction

Chemical signals, that are present in the environment, play a key role in almost every aspect of life for all organisms. These signals contain valuable information about several aspects of life such as feeding, territorial recognition, reproduction and detection of possibly harmful conditions such as fire or poisonous food. In higher organisms, special chemical sensing systems have developed into the sense of smell or olfaction. However, due to its complexity, the sense of olfaction is far from being fully understood.

Over the past decades, scientists and engineers have been interested in building systems that mimic the human olfactory system for industrial and commercial applications. An important class of these systems, known as electronic noses (e-nose), is composed by an array of gas sensors together with a pattern recognition mechanism. Currently, e-nose systems have become commercially available for applications such as quality assurance of food and drugs, medical diagnosis, and environmental monitoring [19]. There exist other sensing technologies such as gas chromatography and mass spectrometry which are superior in quantifying the concentration of certain gas compounds, but they require trained personnel, are time consuming and expensive. Thus, for certain applications, e-nose systems are a viable and cost effective alternative.

This chapter provides a theoretical background on electronic nose technology, starting from a brief description of the human olfactory system to the concept of electronic noses and their main components. The chapter closes with a brief review of the current trends and developments in electronic nose research.

2.2 The Sense of Smell

The sense of smell can be remarkably sensitive and respond to very low concentrations of chemicals. It is estimated that only 2% of the volatile compounds available in a single “sniff” will reach the olfactory receptors, and as
CHAPTER 2. BACKGROUND

few as 40 molecules of an odourant are sufficient to stimulate the olfactory system [20,21]. Odourants are volatile, hydrophobic compounds that have molecular weights of less than 300 Dalton\textsuperscript{1}, they vary widely in structure and include many chemical classes, for example organic acids, alcohols, a dehydes, amides, amines, aromatics, esters, etc. [22].

The human olfactory system is very complex, and is not yet fully understood. A simplified schematic view of the olfactory system can be seen in Figure 2.1. The process of smell starts with a simple sniff, where an air sample that contains odourants is transported towards the epithelium in which the olfactory receptors lie. In this layer, nervous stimuli are generated by the binding of the odour compound with receptor proteins and transmitted towards the olfactory bulb in the brain. In the olfactory bulb, the odour information is first processed by a set of approximate 2000 spherical cell structures that generates different “odour patterns” which, activate different brain regions with different degrees of intensity [19].

![Figure 2.1: The Human Olfactory System](image)

Even though the human nose is used to assess goods such as wines or perfumes, by nature it is subjective and fragile. It is not practical to think about the human nose as a sensing device for industrial applications where dangerous components are present in the air or when it is needed to monitor certain volatile for prolonged periods of time. Thus, new instrumentation devices and chemical sensor have been developed in order to overcome the human limitations.

\textsuperscript{1}The Dalton (Da) or “unified atomic mass unit” (u) is not an International System of Units (SI) unit for mass, however it is accepted for use with SI. 1Da = 1.66053 x 10^{-24} \text{g}
2.3 Electronic Nose Concept

An electronic nose (e-nose) is a system that, just like the human nose, is able to characterize different gas mixtures. It uses a number of individual sensors (typically 5–100) whose selectivity towards different molecules overlap. Since the number of sensors is relatively small and the sensors are often carefully chosen, the overlap is usually much smaller than for the receptors in the human nose. The response from a chemical sensor is measured as the change of some physical parameter (e.g. conductivity). The response time of gas sensors typically ranges from seconds up to a few minutes. This can be considered as a drawback for certain applications and reducing the response time is a topic of ongoing research and it is the main goal of this thesis work.

2.3.1 Early Development

We can date back to 1919-1920 the first attempts to develop instruments for odour detection when Zwaardemaker and Hogewind [23] proposed that odours can be detected by measuring the electrical charge on a fine spray of water that contained odourant solution. However, this early work lacked of a serious attempt to process the generated patterns due to the computing limitations at the time. In 1954 and 1964, Hartman et al. [24, 25] developed an amperometric gas sensor composed of an array of eight different electrochemical cells that gave different patterns of response for different odourant samples but still, no attempt was made to process the obtained patterns.

It was until 20 years later that the concept of an e-nose as an intelligent chemical sensor array system emerged, when Persaud et al. [26] and Ikegami et al. [27, 28] proposed in separate works a system composed of a sensor array and a stage of pattern recognition. (i.e. odour classification). Substantial advances in chemosensory technology were made in the early 1980’s when researchers at the University of Warwick in Coventry England, developed sensor arrays for odour detection. These experiments were focused on the use of metal oxide devices together with conducting polymers, where sensing was based on conductivity changes [19].

In 1989 and 1990 the first workshops and conferences dedicated to the topic of chemosensory information and e-noses were held [29–31], and in 1994, the most widely accepted definition of an e-nose was coined by Gardner and Bartlett, which states:

“An electronic nose is an instrument which comprises an array of electronic chemical sensors with partial specificity and an appropriate pattern recognition system capable of recognizing simple or complex odours” [7]
2.4 E-nose Architecture

An e-nose, as the human olfactory system, is not intended to discriminate one specific volatile. The idea is that an e-nose can learn to discriminate new patterns and associate them to specific odours by training the system using a set of data samples. Figure 2.2 presents a block diagram of an e-nose system. It consists on a delivery/sampling system that conducts the target substances towards an array of gas sensors, that is combined with several feature extraction and pattern recognition methods for the detection and identification of specific volatile compounds [32].

2.4.1 Delivery and Sampling Systems

Delivery system are designed to transfer the odour from the source material (typically by a vacuum pump) to a sensor chamber in which an array of selected gas sensors lies. The process of odour delivery can be summarized as follows:

At the beginning of a sampling process, the odour delivery system drives each sensor to a known state by a reference gas (for example, fresh air) to the sensor chamber. The readings of the sensors in this state are known as baseline level. Then, the delivery system exposes the sensors to a given odourant, producing first a transient response as the compounds starts interacting with the surface and bulk of the sensor’s active material. After a few seconds to a few minutes, the sensors reaches a steady state and, finally, the analyte (i.e.
2.4. E-NOSE ARCHITECTURE

odourant) is flushed away from the system by pumping the reference gas to prepare the system for a new measurement cycle.

The above mentioned steps are known in the e-nose literature as a “three phase sampling process” and they are usually carried out in chambers where humidity, temperature and exposure to the analyte are controlled [1]. Figure 2.3 shows a typical response of a given array of gas sensors to a three-phase sampling process.

![Figure 2.3: Sensor response using a traditional three phase sampling process. The phases of the sampling are as follows: 0-Baseline. 1-Transient response. 2-Steady state. 3-Recovery [1].](image)

The three phase sampling process has been widely used in laboratory-based applications with an important amount of success. Around a thousand articles on this subject have been published over the last years, mainly in relation to the food and beverage industry [33–36].

However, the interest in having continuously monitoring gas systems in uncontrolled environments has grown. Applications such as on-line pollution monitoring or exploration of hazardous areas using mobile robots, require a different strategy than the classical three phase sampling process due to factors such as:

- In mobile platforms, there exist weight, space and power consumption constraint, hence it is complicated to mount a delivery sampling system.
- Due to the chaotic nature of the uncontrolled environments (i.e. natural environments), the sensor array is exposed to patches of gas for short
periods of time and it is not guaranteed that the sensors will reach a steady state.

Figure 2.4 shows the readings obtained with an e-nose mounted on a mobile platform to collect data in natural environments. As can be seen from the figure, the sensors never reach the steady state phase. Therefore, gas discrimination has to be performed in the transient response. Ultimately, a measurement devices is needed that collects information in a way which allows to discriminate odourants based on the response of the gas sensors to a short exposure to the gas. This is the main motivation in this thesis work.

![Figure 2.4: Sensor readings obtained with an electronic nose mounted on a mobile robotic platform [1].](image)

**2.4.2 Sensor Array**

In general, the sensor array is composed of a selected group of non specific gas sensors, which means that two or more sensors in the array may have similar responses or selectivity to certain compound. The different response rates and intensity levels of the sensors in the array will produce a characteristic response pattern (i.e. “finger print”) when exposed to volatiles with similar chemical content, whereas a different response pattern will be produced when the array is exposed to a volatile with different chemical characteristics.

A sensor array is composed of $n$ sensors, where each sensor will produce a response $x_{ij}$ during a given experiment $j$. This response can be represented by a vector:
When $M$ experiments are repeated with the same sensor array, the response can be represented as a response matrix $X$ given by:

$$X = \begin{pmatrix} x_{11} & x_{12} & \ldots & x_{1M} \\ x_{21} & x_{22} & \ldots & x_{2M} \\ \vdots & \vdots & \ddots & \vdots \\ x_{n1} & x_{n2} & \ldots & x_{nM} \end{pmatrix}$$

(2.2)

Where each column represents a response vector associated with a particular experiment, whereas the rows are the responses of an individual sensor.

### 2.4.3 Signal Pre-processing

In this stage, several operations are carried out to condition the signal for further processing. First, the raw measurements $X$ are converted from analogic readings to a digital signal that can be interpreted by a computer. Several other preprocessing operations are performed such as baseline manipulation or data normalization.

Baseline manipulation aims to minimize the effects of temperature, humidity and short term drift \[37, 38\]. As previously defined, the baseline is the set of the first initial readings, when the nose is exposed to a reference gas and no significant change is reported in the sensor response. The following techniques are commonly employed for baseline manipulation:

- Differential
- Relative
- Fractional

Differential manipulation aims to remove any sensor drift or additive noise ($\delta_A$) present in the sensors response. It consist on subtracting the baseline level $x_0$ from the full sensor response $x$ as shown below:

$$x_{bm} = (x + \delta_A) - (x_0 + \delta_A) = x - x_0$$

(2.3)

Relative baseline manipulation removes any multiplicative drift $\delta_M$ and provides a dimensionless response by dividing the full sensor response $x$ by the baseline $x_{S0}$ as shown below:

$$x_{bm} = \frac{(x)(1 + \delta_M)}{(x_0)(1 + \delta_M)} = \frac{x}{x_0}$$

(2.4)

A dimensionless and normalized response (i.e. fractional manipulation) can be obtained by subtraction and then dividing the sensor response $x$ by the baseline $x_0$ as shown in the following equation:
\[ x_{bm} = \frac{x - x_0}{x_0} \] (2.5)

The selection of a proper baseline manipulation technique is highly dependent on the sensor technology and the particular application. For example, Gardner et al. [39, 40] propose to use fractional manipulation (eq. 2.5) to compensate the temperature cross-sensitivity and non-linearities for MOX sensors. Several authors have proposed ad-hoc baseline manipulation techniques for specific applications as described in [41–43].

The data normalization step is aimed at smoothing sample to sample variations, providing a more regular input for the subsequent computations [1]. Data normalization can be divided in two groups: local and global methods. Local methods compensate for sample to sample variations by operating on a single sample. Global methods operate across the full database in order to compensate for differences in sensor scaling.

2.4.4 Feature Extraction

The goal of feature extraction is to find a vector of features \( F \) that is particularly informative for the classification process.

One common approach is the use of the signal dynamics as features. Consider for example, a temperature cycled tin oxide sensor TGS2620 modulated by a sinusoidal signal with frequency of 0.5Hz and amplitude range from 2.5-5V exposed to an Ethanol gas sample. As shown in Figure 2.5, the slope of the signal (i.e. first derivative) and the area under the curve of the response (“AUC” in Figure 2.5) can be used to describe the transient response of the sensor when exposed to the sample.

Another approach is to perform a transformation of the data to obtain descriptors of the phenomena in a different space. Feature extraction methods such as the fast Fourier transform, multi resolution analysis, curve fitting and phase space descriptors [3] have been proposed by several authors in order to discriminate between different analytes.

It is preferable for the subsequent classification stage to work with a reduced number of features. A small but informative set of features significantly reduces the complexity of the classification algorithm, the time and memory requirements to run this algorithm, as well as the possibility of overfitting. In fact, the detrimental effects of a large number of features are well known within the pattern recognition community, and referred as “the curse of dimensionality”.

The process of dimensionality reduction consists of selecting \( m \) features out of a possibility of \( D \) (\( m < D \)), which provide the most discriminative information.

A criterion used to assets the feature selection is the performance of a subsequent classifier trained with a subset of features and the subset that gives a better generalization performance is kept. However, an exhaustive search of
2.4. E-NOSE ARCHITECTURE

each subset and the consequent evaluation of the generalization performance is computationally expensive. Dimensionality reduction can be carried out by a transformation that projects the feature vector in a less dimensional space where only the most significant features are kept. These techniques are known as filter based feature selection [44]. The most widely used are Principal Component Analysis (PCA) and Linear Discriminant Analysis (LDA).

![Figure 2.5: Feature extraction for a temperature modulated TGS2620 gas sensor. Feature “slope” and feature “AUC” denote the first derivative of the sensor response and the area under the curve, respectively.](image)

2.4.5 Pattern Recognition and Classification

Pattern recognition and classification can be seen as a function approximation problem (e.g. finding a function that maps a \(d\)-dimensional input to appropriately encoded class information). The stage of pattern recognition and classification determines the relationship that exists between a set of independent variables (the feature vector) and a set of dependent classes (odour classes) [38].

A classifier takes an input feature vector \(F\) and assigns it to one of the \(K\) discrete classes \(C_k\) where \(K = 1, 2, \ldots, K\). In the most common scenario, the classes are taken to be disjoint, so that each input is assigned to one and only one class. The input space is thereby divided by decision boundaries or decision surfaces [45].

The classifier returns a vector \(D_k\) of length \(K\) for each element of the vector \(F\) where, if a given \(F_a\) belongs to the class \(C_j\), then all elements in \(D_a\) are zero, except for the element \(j\) which takes the value of 1. For example, consider a classification problem where \(K = 5\) and that \(F_a\) belongs to class \(j = 3\), then, \(D_a\) is given by:
Classification techniques are divided in statistical approaches and neural network approaches. The most common are Bayes classifiers, KNN classifier, Support vector machines and multi layer perceptrons.

\[ \mathbf{D}_a = (0, 0, 1, 0, 0)^T \]

2.5 Current Developments

So far in this chapter, we have reviewed the main concepts related to e-noses. In this section we will provide a brief summary of current works related to gas discrimination under laboratory conditions and in natural environments by means of e-nose systems.

Panigrahi and co-workers [46] successfully detected spoiled meat samples by using an e-nose that used an array of nine commercially available MOX gas sensors. The authors analysed the volatile compounds that emanates from the meat samples stored at 4°C and 10°C. The samples and the e-nose were placed inside a chamber, where the sensors were first exposed to clean air for 20s to measure the baseline level and then the chamber was closed to expose the sensors to the gases emanating from the meat samples in order to measure the microbial population. As features, the authors considered the area under the curve of the sensors responses and resistance values of the sensors at predefined time intervals of the response. By using linear discriminant analysis and a linear classifier, spoiled samples of meat were detected with an accuracy of 92%.

E-noses have been used also for medical applications. In [12], an e-nose is used to identify bacteria in human blood culture samples. The authors used an array of 22 gas sensors and experiments were performed using a three phase sampling process. For each of the samples of the training set, the experiment was repeated ten times in order to improve the reliability of the discrimination results. The authors applied a classifier built with a Support Vector Machine (SVM) to each of the ten consecutive samples and concluded that through ensembling the decisions on consecutive samples, the accuracy of an e-nose can be improved.

As previously mentioned, in natural uncontrolled environments the steady state is hardly reached. Hence, it is required to perform the data analysis in the rising edge of the sensors response. Transient response classification has been proved feasible in many works. Osuna et al. [37] proposed in 1999 that the transient response of a gas sensor can be modelled as a summation of exponential functions where, the obtained model parameters can be used as feature vectors for gas discrimination purposes.

In 2007, Muezzinoglu et al. [47] proposed a method to extract features that are available in early stages of the sensor response and that are correlated with those present in the steady state. The authors extracted the peak value of the exponential moving average \( E_{\alpha} \) in the transient response and the maximum
resistance value in steady state ($\Delta R$). The authors performed their experiments in a 3-class gas discrimination problem, and it was demonstrated that odour processing can be accelerated by substituting the steady state feature $\Delta R$ with the transient feature $E_\alpha$. By using this method, and with a single gas sensor, the authors obtained success rates of 82.9% and 89.5% at exposure times of 10.0s and 17.5s respectively.

Gas source localization by means of an e-nose in a mobile robot has been proved feasible in previous works. In [48], the authors combined two e-noses composed by four MOX sensors with a directional thermal anemometer to estimate the localization of an odour source. Features were extracted from the transients of the gas sensors by using wavelet analysis. The authors tested the effectiveness of the pattern recognition algorithm by performing gas discrimination of six different gas mixtures inside a closed chamber. The algorithm’s averaged performance was 83% of successful classification using the first four seconds of the transient response.

Trincavelli et al. [1] compared different feature extraction methods and classification algorithms to successfully discriminate between three odour sources using the transient response of the sensors. The data set was collected with an e-nose composed by five tin oxide sensors mounted on a mobile robotic platform.
Chapter 3
Gas Sensing and Selectivity Enhancement

3.1 Introduction

A gas sensor is a device that generates an electrical signal in the presence of a target odourant. Gas sensors (Figure 3.1) are intended for the identification and quantification of gaseous chemical volatiles. They are routinely used to characterize samples of odourant species under laboratory conditions.

Analytical equipment, such as IR spectroscopy, gas chromatography and mass spectrometry constitute an alternative for the use of gas sensors, however, these instruments are very expensive and require trained personnel to operate them [49]. Therefore the development of less expensive equipment based on chemical sensors is of high interest.

Figure 3.1: Commercial gas sensors from Figaro Engineering.

There exists several materials to build gas sensors (i.e. conductive polymers, metal oxides, etc.) and operational principles such as optical, thermal or amperometric sensing. Metal oxide (MOX) sensors are one of the most widely
spread devices used for e-nose applications due to their low cost, acceptable response and recovery times. However, there are challenges to overcome in MOX sensing technologies such as poor selectivity. It has been demonstrated that by modulating the operational temperature of the sensors, the information content and hence the selectivity can be improved.

In this chapter we briefly introduce the different types of gas sensor technologies available, specifically we focus on MOX sensors. A review of different techniques for selectivity enhancement is also presented in this chapter. The focus is particularly on the temperature modulation technique. The chapter closes with a brief summary of research regarding temperature modulated e-noses.

3.2 Gas Sensing Technologies

In table 3.1, a summary of different sensors and their corresponding operational principle is shown. In the following sections a brief introduction for each of these devices is presented.

<table>
<thead>
<tr>
<th>Principle</th>
<th>Measurands</th>
<th>Sensor Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductometric</td>
<td>Conductance</td>
<td>Chemoresistors (MOX, CP)</td>
</tr>
<tr>
<td>Capacitive</td>
<td>Capacitance</td>
<td>Chemocapacitors (Polymer)</td>
</tr>
<tr>
<td>Potentiometric</td>
<td>Voltage, I-V/C-V</td>
<td>Chemdiodes, Chemotransistors (MOSFET)</td>
</tr>
<tr>
<td>Caloriometric</td>
<td>Temperature</td>
<td>Thermal chemosensor</td>
</tr>
<tr>
<td>Gavirometric</td>
<td>Piezoelectricity</td>
<td>Mass sensitive chemosensor (QCM, SAW)</td>
</tr>
<tr>
<td>Optical</td>
<td>Refractive index</td>
<td>Resonant type chemosensor (SPR)</td>
</tr>
<tr>
<td>Amperometric</td>
<td>Current</td>
<td>Toxic gas sensor (electrocatalyst)</td>
</tr>
</tbody>
</table>

Table 3.1: Classification of chemosensors based on their operation principle.

3.2.1 Chemocapacitor Sensors (CAP)

Polymer technology can be used to build chemocapacitors. When these devices are exposed to a given gaseous analyte, the polymer changes its electrical and physical properties (dielectric constant $\epsilon$ and volume $V$ respectively) producing a reversible deviation $\Delta C$ of its nominal capacitance $C$.

3.2.2 Gravimetric Odour Sensors

This family of sensors operate by detecting the effect of absorbed molecules on the propagation of acoustic waves. The basic device consists of a piezoelectric substrate, such as quartz, lithium niobate and ZnO, coated with a suitable
membrane. Absorption of vapour molecules produces changes in the propagation of the acoustic wave thus, the resonant frequency and the wave velocity are altered.

### 3.2.3 Optical Odour Sensors

Optical odour sensors are based on a phenomenon called “Surface Plasmon Resonance” (SPR) in which incident light excites a charge density wave at the interface between highly conductive metal and dielectric material. Optical SPR sensors are sensitive to the changes in the refractive index of a sample surface when it interacts with a given analyte.

### 3.2.4 Thermal Odour Sensors

A thermal odour sensor consists of a tiny bed of catalyst that surrounds a coil of thin, Pt wire thermometer. At proper conditions, when these devices enter in contact with hydrocarbon volatiles, temperature increments are produced due to the catalytic oxidation of the sensor surface. This sudden temperature rise is registered by the Pt wire in form of a change in resistance ($\Delta R$). The larger $\Delta R$, the higher the concentration of hydrocarbon present in the environment.

### 3.2.5 Amperometric Gas Sensors

Amperometry is an electro-analytical technique that encompasses coulometry, voltammetry, and constant potential techniques, and it is widely used to identify and quantify electroactive species in liquid and gas phases. In Amperometric gas sensors, the measurements are made by recording the current in the electrochemical cell between the working and counter electrodes as a function of the analyte concentration.

### 3.2.6 Potentiometric Odour Sensors

Potentiometric odour sensors are based on two technologies: Schottky diodes and MOSFET gas sensors. The first type are based on a change in the work function because of the presence of chemical species on their surfaces and the latter ones use metal-insulator-semiconductor structures in which the metal gate is a catalyst for gas sensing. Depending upon the concentration of the target gas, the MOSFET sensors exhibit a shift in the gate voltage threshold.

### 3.2.7 Conducting Organic Polymers

This type of sensors is made of semiconducting materials, aromatic or heteroaromatic (e.g. polypyrrole, polyanilite, polythiophene) deposited onto a substrate and between two gold plated electrodes. The selectivity and sensitivity
of these devices can be modified by the use of different polymers and doping ions [50]. When interacting with odour molecules, a reversible change in the conductivity occurs.

### 3.3 Metal Oxide Gas Sensors

Metal Oxide (MOX) sensors are a low cost option for constructing gas detectors or e-noses and currently, they remain the most widely spread [32]. The development of the MOX sensor technology started when Wagner and Hauffe studied how the interaction of volatile compounds with semiconductor surfaces affects the electrical conductances of the semiconductor. These studies allowed Seiyama and Taguchi to produce the first chemoresistive semiconductor gas sensor [51]. In this early stage, the semiconductors used underwent irreversible chemical transformations by forming stable oxide layers. It was later found that the most suitable semiconductor materials for gas sensors are metal oxides, which bind oxygen on their surfaces in a reversible way. This effect was investigated by Heiland [52], Bielanski et al. [53] and Seiyama et al. [54]. A decisive step was taken when Taguchi turned semiconductor sensors based on metal oxides into an industrial product (Taguchi-type sensors [55]). Nowadays, there are many companies offering this type of sensors, such as Figaro, FIS, e2v, MICS, UST, CityTech, Applied-Sensors, NewCosmos, etc. [56–60].

#### 3.3.1 Operation Principles

As shown in Figure 3.2, a MOX sensor comprises of a sensitive layer deposited on a substrate provided with electrodes for the measurement of the electrical characteristics of the device. MOX sensors comes with an in-built heater, separated from the sensing layer and the electrodes by an electrically insulating layer, which allows the sensor to operate in temperature ranges of 200°C–400°C.

The conductivity changes in a MOX sensor are due to surface reactions that involve changes in the concentration of oxygen species such as $\text{O}_2^-$ or $\text{O}^-$. Figure 3.3 shows typical changes in conductivity of n-type MOX sensors. The y-axis of the plots in the lower part of the image represents the sensor electrical resistance. In (a) and (c) when oxygen dissolves in the sensors surface, the resistance converges to the reference or background level. In (b), a volatile compound, in this case methane, reacts with the surface creating a conductivity change.
3.3. METAL OXIDE GAS SENSORS

Figure 3.2: The basic construction of a Metal Oxide Sensor.

From the electrical point of view, in the case of an n-type MOX sensor, the oxygen can be seen as a trap of electrons from the bulk of the solid. Electrons are drawn from ionized donors via the conduction band, so the charge carrier density at the interface is reduced and a potential barrier to charge transport, \( \Delta G \), is developed. As the charge in the surface rises, the ionosorption of further oxygen is limited by the potential barrier that has to be overcome by the electrons in order to reach the surface. The adsorption rate slows down because the charge must be transferred to the adsorbate over the developing surface barrier, and the coverage saturates at a rather low value. At the junctions between the grains of the solid, the depletion layer and associated potential barrier make high resistance contacts, which dominate the resistance of the solid.

Figure 3.3: Resistance changes due to the interaction of a volatile compound with the surface of a MOX sensor.
3.4 Selectivity Enhancement

There are three main drawbacks to overcome in MOX technology: poor selectivity, sensitivity and stability. Also, it is a well known phenomenon that MOX gas sensors are influenced by water vapour, so changes in the moisture content of the atmosphere being monitored interfere with the sensing process [61].

Selectivity describes the degree to which a sensor responds to only the desired target gases, with minimal interference from non-target components. Sensitivity refers to the minimal concentration and concentration changes that can be successfully and repeatedly sensed by the device [62].

MOX gas sensor stability is heavily affected by environmental conditions such as temperature, pressure and humidity. Furthermore, the chemical reactions that occur at the sensors surface may lead to irreversible changes in the sensor itself (poisoning) or a degradation of the sensor over time (drift).

Several new techniques have been investigated to overcome the limitations on selectivity: the development of new materials and technologies, the use of pattern recognition algorithms along with gas sensor arrays and dynamic mode operation.

3.4.1 Material Technology

Regarding material technology, so far the most studied metal for MOX sensor construction is SnO₂. The specific selectivity of sensors built with this material can be increased by selecting an appropriate operation temperature, making structural modifications or by using different dopants and catalysts. As an example, in table 3.2 a list of metal oxides and their corresponding target gas is shown.

<table>
<thead>
<tr>
<th>Oxide type</th>
<th>Detectable gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO₂</td>
<td>H₂, CO, NO₂, H₂S, CH₄</td>
</tr>
<tr>
<td>WO₃</td>
<td>NO₂, NH₃</td>
</tr>
<tr>
<td>TiO₂</td>
<td>H₂, O₂, C₂H₅OH</td>
</tr>
<tr>
<td>In₂O₃</td>
<td>NO₂, O₃</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>CO</td>
</tr>
<tr>
<td>LaFeO₃</td>
<td>NO₂, NOₓ</td>
</tr>
<tr>
<td>Cr₁.₈Ti₀.₂O₃</td>
<td>NH₃</td>
</tr>
</tbody>
</table>

Table 3.2: Semiconductor oxides and their corresponding target gases.
3.4.2 Operation in Dynamic Mode

Selectivity and sensitivity improvements in MOX sensors can also be achieved by operating them in dynamic mode and characterizing their transient responses. Dynamic mode operation techniques can be grouped to three categories:

- AC operation mode.
- Modulation of the gas concentration.
- Modulation of the working temperature of the sensors.

In AC operation mode, a periodic waveform (e.g. a sinusoidal) is applied to the sensor input as a reference voltage \( V_C \) in Figure 3.4) instead of a fixed DC power supply, while the voltage in the sensor heater \( V_H \) is kept constant. Gas discrimination is enhanced in AC operation mode, by taking measurements of different electrical parameters (such as sensor capacitance, conductance or dissipation factor) at different frequency values of the reference voltage generator [63].

Concentration modulation is carried out by introducing abrupt changes in the gaseous concentrations presented to the sensors, in order to study the dynamic response of the sensor to sudden changes in the gas concentrations. It has been shown that this technique is able to increase the selectivity of a sensor array [64–66].

Temperature modulation consists of altering the kinetics of the sensor through changes in the operational temperature of the device. As the sensor response changes at different working temperatures, measuring the sensor response at \( n \) different temperatures is similar to have an array of \( n \) different sensors.

In the following section it is explained in detail the different principles and concepts regarding temperature modulation.

3.5 Temperature Modulation

The operating temperature dependence of the metal oxide sensors has been widely investigated [3, 66, 67], and it has been shown that the information content of the sensor response can be improved by modulating the operational temperature.

According to [37], temperature modulation can be grouped into two broad categories: thermal transients and temperature cycling. In the thermal transient approach, the heater voltage of the sensors consists of a step function or a pulse and the discrimination is performed in the transient response induced by the fast change in the temperature.
In the temperature cycling technique, the heating element of the gas sensor is connected to a waveform generator that periodically changes the working temperature of the device. In a typical measurement circuit for a MOX gas sensor (as shown in Figure 3.4), the input is connected to a constant reference DC voltage (denoted by $V_C$), and the output voltage $V_L$ is measured in the load resistance $R_L$. For temperature modulated sensors, the heating device is connected to a signal generator $V_H$, that provides for example, a sinusoid, square, sawtooth or triangular waveform.

During sensor operation, $V_H$ will cycle the sensors surface temperature rather than maintaining a constant operating point, thus generating an “odour signature” (i.e. a multivariate dynamic signature) when the sensor is exposed to a given analyte. The resulting “odour signature” has a duration equal to the period ($T$) of the cyclic signal applied to $V_H$.

![Figure 3.4: Basic measurement circuit for a MOX gas sensor.](image)

Figure 3.5.a illustrates the sensitivity profiles (i.e. sensor outputs in response to a fixed concentration over a range of operating temperatures) of several doped tin-oxide gas sensors at different temperatures when exposed to various analytes.

For e-nose applications it is advantageous to capture the response of the sensor over the entire temperature range. Figure 3.5.b shows the dynamic response to various analytes when a sinusoidal voltage (2-5 V, 0.04 Hz) is applied to the heater of a commercial SnO$_2$ sensor (Figaro TGS813). It can be observed that not only the magnitude of the conductance but also the shape of the dynamic response is unique to each analyte.
3.5. TEMPERATURE MODULATION

3.5.1 The “Virtual Sensor” Concept

The temperature dependence of MOX gas sensors can lead to the generation of “multiple virtual sensors”. This can be explained by the fact that temperature modulation generates different sensor responses for the same analyte.

An example of the virtual sensor concept can be seen in Figure 3.6 where a single tin oxide sensor TGS2620 is modulated by a sinusoid of 5V of amplitude, no DC level and a frequency of 0.05Hz. In this example, the measurements were conducted inside a Plexiglas chamber and the sensor is exposed to a sample of 2-Propanol. In Figure 3.6.(A), points A and B are segments in the modulation signal with the same temperature value but with different change dynamics (i.e. in A, the temperature value is decreasing while in B, the temperature value is increasing). As can be seen in the output plot in Figure 3.6.(B), this different change dynamics generate two different output responses that can be considered as two “virtual sensors”.

Figure 3.5: Left: Sensitivity-temperature profile for Pt- and Pd-doped tin-oxide sensors. Right: conductance-temperature response of a tin-oxide gas sensor in (a) air, (b) methane, (c) ethane, (d) propane, (e) n-butane, (f) isobutene, (g) ethylene, (h) propylene, and (i) carbon monoxide [2].
CHAPTER 3. GAS SENSING AND SELECTIVITY ENHANCEMENT

Figure 3.6: Conductivity response of a temperature modulated TGS2620 gas sensor exposed to 2-Propanol. (a) Modulating signal. (b) Sensor Response.

3.5.2 Temperature Modulated E-noses

Early research in temperature modulation was made by Clifford et al. [68, 69]. The authors investigated how different temperature levels affected the conductance of MOX sensors. They proposed that selective gas detection could be accomplished using either many sensors at different but fixed temperatures, or by sequential operation of a single sensor at several temperatures.

In 1983, Advani et al. [70] introduced the use of a square wave as a modulating signal in order to classify and quantify hydrogen sulphide (H₂S) with a single gas sensor. Sears and co-workers [71] used a modulating sinusoidal waveform to increase the selectivity of a tin oxide TGS 812 sensor. By performing experiments with three analytes (ethanol, carbon monoxide and propane), they concluded that the temperature range and the period of the modulation cycle determine the information that can be extracted from the conductance transients.

In [72], Sears et al. introduced the Fast Fourier Transform (FFT) as a feature extraction method. They used a tin oxide sensor modulated by a square waveform and the sensor was allowed to reach the steady state to discriminate between several gases.

Nakata and co-workers [73–79] applied the FFT as a feature extraction method to solve another discrimination problem with a temperature modulated tin oxide TGS 813 gas sensor. The authors also related the values of the high harmonics of the FFT to the characteristics of the molecular structure of the gases.

In 2007, Vergara et al. [3] proposed a method where features are extracted in the phase space for an array of gas sensors modulated by a multi level pseudo random sequence. The phase space concept was introduced in [80] and it can be
summarized as the time evolution of an observed quantity or signal. The time evolution can be seen as a trajectory (as shown in figure 3.7) which can be represented with a set of 2D descriptors called Dynamic Moments. This set of descriptors was used in [3] to discriminate ammonia, nitrogen dioxide and their binary mixtures at different concentrations. The authors used an array composed of Tungsten oxide sensors, temperature modulated by multiple sinusoids and the analysis was performed in both, the transient response and steady state.

![Figure 3.7: Typical response of a tungsten oxide micro-hotplate sensor to ammonia (500 ppm), nitrogen dioxide (1 ppm) and ammonia + nitrogen dioxide (500 + 1 ppm) in the phase-space domain [3].](image)

Guanfen et al. proposed in 2009 [4] an alternative method to classical FFT and multi resolution analysis called the Hilbert Transform to obtain features from an array of micro hot plate gas sensors modulated with a sinusoidal signal in order to discriminate methane, carbon monoxide and ethanol. The Hilbert transform is a newly developed method to decompose a signal into so-called intrinsic mode functions (IMF), and obtain instantaneous frequency data. Figure 3.8 shows the decomposition of one of the target gases by the Hilbert transform for feature extraction.
In [81], an alternative feature extraction method is proposed for an array of four MOX gas sensors modulated by a multi sinusoidal signal. The authors extracted a feature vector by computing the energy value for each sensor and the mutual energy between the binary combination of the sensors. This method was evaluated by solving a discrimination problem of three gases (namely Ammonia, Acetaldehyde and Ethylene) and a success rate of 100% was obtained when at least a response sequence of 1s in dynamic equilibrium was available.
Chapter 4
The PTM E-Nose

4.1 Introduction

The previous chapters introduced the main concepts related to e-nose technology as well as the use of temperature modulation to increase the selectivity of MOX gas sensors. Also, e-nose applications under laboratory conditions and in natural environments were reviewed. One interesting application in natural environments is the use of e-noses along with a mobile robotic platform to solve gas discrimination and gas source localization problems in which, a fast gas sensing device is a key component.

As the key contribution of this work, this chapter introduces a novel operational principle for an e-nose. It is based on cycling temperature modulation to increase selectivity. The distinctive characteristic of our approach is the use of an array of \( n \) replicated MOX sensors which, by sampling an odourant in parallel, can significantly reduce the exposure time. With this approach, the aim is to speed up gas discrimination.

The proposed principle is evaluated by solving a discrimination problem of three analytes (namely Acetone, Ethanol and 2-Propanol), under laboratory conditions and in natural environments. Data analysis is performed in both, the transient and the dynamic equilibrium (i.e. steady state) segments of the sensor response.

4.2 The PTM E-Nose Concept

The exposure time needed to record an “odour signature” is a function of the period \( T \) of the modulation signal. Figure 4.1 shows the responses in dynamic equilibrium (i.e. steady state) of a single TGS 2620 gas sensor exposed to Acetone, Ethanol and 2-Propanol. In this example the odour signatures are collected in a full modulation period \( T \). An approach to reduce the exposure time is to increase the frequency of the modulation signal. However, due to the physical limitations a of a gas sensor (i.e. the thermal time constant), fast changes in
the modulating temperature might not significantly alter the sensor’s conductance profile [82].

![Figure 4.1: Responses in dynamic equilibrium to different analytes recorded with a single TGS2620 sensor modulated by a sinusoidal signal of 1.7V DC Level, 3.3V amplitude voltage and a modulation frequency of 0.05hz.](image)

We propose a parallelized temperature modulated e-nose (PTM e-nose) with the aim to reduce the exposure time needed to perform classification without increasing the modulation frequency. A PTM e-nose consists of an array of $n$ gas sensors of the same type, individually modulated with sinusoids of the same amplitude and DC level but shifted in phase. The idea of this configuration is to replicate the sensor $n$ times, where each one of the sensor instances is measuring one different $nth$ of the modulation cycle. Thus, a full odour signature can be recovered from the replicated sensors in an $nth$ of the modulation cycle.

In the following sections we describe the particular implementation of a PTM e-nose comprised of four commercially available gas sensors that, according to the definition previously stated, could reduce the exposure time needed to perform classification to a fourth of the modulation period.

### 4.2.1 Four Sensor PTM E-Nose

The exposure time needed to collect an odour signature with a single temperature modulated sensor is $T$. To reduce this exposure time, we use four gas sensors independently modulated with sinusoids of DC level equal to $V_{a\text{i}}$, amplitude equal to $V_{b\text{i}}$ ($\text{i}=1,..,4$) and frequency $f$. Thus, the modulation signals ($V_{1}$ to $V_{4}$) are given by:
4.2. **THE PTM E-NOSE CONCEPT**

\[
V_1(t) = V_{a1} + V_{b1}\cos(2\pi ft) \quad (4.1a)
\]
\[
V_2(t) = V_{a2} + V_{b2}\cos(2\pi ft + \frac{\pi}{2}) \quad (4.1b)
\]
\[
V_3(t) = V_{a3} + V_{b3}\cos(2\pi ft + \pi) \quad (4.1c)
\]
\[
V_4(t) = V_{a4} + V_{b4}\cos(2\pi ft + \frac{3\pi}{2}) \quad (4.1d)
\]

For parallelized operation, the working parameters \(V_{ai}, V_{bi}\) and \(f\) are set to the same value for all the sensors in the array and the sinusoids are shifted in phase by 90 degrees. The four sensors in the array are able to collect data in parallel from \(t=0\) to \(t=T/4\), each one of them covering one quarter of the modulation period, effectively reducing the exposure time by four as shown in Figure 4.2.

*Figure 4.2: A PTM e-nose composed by four gas sensors. A) Modulation signals. B) to E) Outputs from the replicated sensors. F) Odour signature obtained from the four replicated sensors.*
4.3 Implementation

Figure 4.3 shows the block diagram of the PTM e-nose used in this thesis work. It consists of an array of four gas sensors, a waveform generator and a data acquisition (DAQ) system that transfers the samples taken to a pattern recognition subsystem for further analysis.

The waveform generator outputs are the four phase shifted sinusoids that modulates the sensor array. It has nine adjustable working parameters: $V_{a1}$ to $V_{a4}$, $V_{b1}$ to $V_{b4}$ and $f$. $V_{a1}$ and $V_{b1}$ are respectively the DC voltage and the amplitude of the sinusoids and both can be adjusted to values between 0-5V, under the constraint\(^1\) that $V_{a1} + V_{b1} \leq 5V$. The values of DC voltage and amplitude are always kept as $V_{a1} = V_{a2} = V_{a3} = V_{a4}$ and $V_{b1} = V_{b2} = V_{b3} = V_{b4}$ in order to parallelize the sensors operation.

The frequency of the modulating sinusoidal signal is given by the working parameter $f$ and, for this particular implementation, it is adjustable to eight possible values (0.05Hz, 0.1Hz, 0.2Hz, 0.25Hz, 0.33Hz, 0.5Hz, 0.66Hz and 1Hz).

Figure 4.3: Block diagram of the PTM e-nose used in this work.

4.4 The Sensor Array

The sensor array of the PTM e-nose implemented in this thesis work, consists of four TGS2620 gas sensors enclosed in an Aluminum tube of 0.05m diameter

\(^1\)According to the manufacturer, the maximum voltage that can be applied to the heater device is 5V. [5]
and 0.05m length. The sensors are mounted close to each other in order to have a gas exposure that is as similar as possible across the sensor array. A fan is placed at the opening of the tube in order to create a constant airflow towards the sensors.

According to the data sheets provided by the manufacturer, the TGS2620 gas sensors comprise a metal oxide semiconductor layer formed on an aluminium substrate of a sensing chip together with an integrated heater.

The TGS2620 is highly sensitive to the vapour of organic solvents (such as Ethanol, Acetone and 2-Propanol), and to a variety of combustible gases such as carbon monoxide [5]. In the presence of a detectable gas, the conductivity of the sensor is increased depending on the gas concentration in the environment.

The electrical diagram of a TGS2620 sensor is shown in figure 4.4. Two voltage inputs are required to operate the sensor. A circuit voltage that allows voltage measurements across a load resistor ($R_L$) connected in series with the sensor and a heater voltage $V_H$ that is applied to the heating device of the sensor. $V_H$ can be either a constant power supply or in case of temperature modulated applications a waveform generator.

![Figure 4.4: Electric diagram of a TGS2620 Figaro gas sensor [5].](image)

### 4.5 Data Acquisition (DAQ)

The DAQ block comprises an Atmel’s AT-MEGA16 microcontroller and its support circuitry. According to the manufacturers data sheet [83], the AT-MEGA16 is an 8-bit microcontroller which among other features is equipped with 8 embedded analog to digital converters (ADC’s) and a serial RS232 interface. The ADC’s are used to sample the voltage levels of the four modulating signals and the output of the gas sensors measured as the voltage at the load resistance connected in series with the sensors (as shown in figure 4.4). The sampling rate of the DAQ block is 10Hz (10 samples per second). The samples
obtained with the 8 ADC’s are transferred to a personal computer (PC) via the RS232 interface of the microcontroller.

4.6 Pattern Recognition Block

The pattern recognition block comprises three subsystems named: signal preprocessing, feature extraction, and classification as shown Figure 4.5.

In the signal preprocessing subsystem, the readings from the four sensors \( (x_1, \ldots, x_4) \) taken in one experiment are processed in several stages to reconstruct a full odour signature \( (x_R) \). In the next stage, the relevant features of \( x_R \) are extracted and stored in a vector \( F \) that is passed to the classifier to obtain a decision vector \( D \).

![Figure 4.5: Schematic diagram of the pattern recognition block.](image)

4.7 Signal Preprocessing

Signal preprocessing is performed in four stages named: prefiltering, baseline correction, segmentation and reconstruction. Most of the effort in the development of the signal preprocessing subsystem was dedicated to the reconstruction of the odour signature where, based on the operating principle explained in the previous chapter, the four sensors of the array are combined to obtain the information given by a full modulation cycle in a fourth of the period.

4.7.1 Prefiltering

The first stage of the preprocessing is filtering the raw readings coming from the DAQ in order to suppress the distortions produced by burst noise and quantization errors.

Burst noise consists of sudden step like transitions with amplitudes in the range of microvolts and with durations of several milliseconds. Quantization errors are produced due to the rounding and truncation of the reading values.
4.7. SIGNAL PREPROCESSING

during the discretization of the analog signal by the AD (analog to digital) converter.

Due to its simplicity and low computational cost, a moving average finite impulse response (FIR) filter is used. A FIR filter is given by:

\[
x_f[n] = \sum_{i=0}^{M} b_i x[n - i]
\]

(4.2a)

\[
b_i = \frac{1}{M + 1}
\]

(4.2b)

where \(M\) represents the order of the filter. A high order filter produces a smoother signal, however, it will also remove signal details that may contain valuable information for classification. In a systematic way, it was determined that a filter of order 6 smooths the signal enough without removing the information needed for classification.

Figure 4.6 shows the effect of the FIR filter over the sensor response. The blue plot corresponds to the raw signal and as can be seen in the amplified images 1 and 2, burst noise is present at the baseline and quantization errors do appear when the sensor reaches the dynamic equilibrium. The red plot corresponds to the filtered signal.

Figure 4.6: Comparison between the raw signal coming from the DAQ and the output from a 6th order averaging FIR filter.
4.7.2 Baseline Correction

Differential baseline correction was used to remove the additive drift $\delta_A$ present in the four sensors in the array. For each experiment, when the sensors are exposed to the reference gas, the baseline is measured for at least 800 seconds. The average of the readings during this period is considered as the baseline value $x_0$ and substracted to the full sensor response.

4.7.3 Segmentation

In this step, the sensor response is divided in three segments: rising edge, dynamic equilibrium state (i.e. steady state) and decay edge.

Based on the method proposed by Trincavelli et al. [84], a finite state machine (as shown in Figure 4.7) is used to segment the signal information. The signal is considered to be at the baseline level until the first derivative (denoted by $ds/dt$) of the sensor readings surpasses a threshold level $THR_R$. When $ds/dt$ stabilizes between $(THR_S^-, THR_S^+)$ after the rising edge has been detected, it is determined that the signal has reached the dynamic equilibrium. For this thesis work, the information contained in the decay edge of the signal is not used.

![Finite state machine used for the segmentation of the signal.](image)

In the proposed operational principle we consider the four sensors working in parallel to obtain a single odour signature. Therefore, instead of segmenting each baseline corrected sensor output ($x_{1C}, x_{2C}, x_{3C}, x_{4C}$) individually, the rising edge and the dynamic equilibrium starting points are obtained over an averaged response ($x_{avg}$) of the four sensors given by:

$$x_{avg} = \frac{x_{1C} + x_{2C} + x_{3C} + x_{4C}}{4}$$  (4.3)
The output of the signal segmentation process can be seen in Figure 4.8, where 4.8.A corresponds to the averaged sensor output \( (x_{avg}) \) and 4.8.B shows the rising edge and the dynamic equilibrium starting points detected and plotted over the response of a given sensor of the array.

![Figure 4.8: Signal segmentation of a temperature modulated sensor. A) Averaged sensor response. B) Individual output from one sensor of the array. The start of the dynamic equilibrium response is denoted by the label “Rise end”.](image)

### 4.7.4 Odour Signature Reconstruction

The odour signature reconstruction approximates the sensor response in a full modulation cycle \( (T) \) by using the information contained in the \( n \) replicated sensors. Since we are interested in solving a classification problem in both controlled and natural environments, we address the reconstruction of the transient response and the dynamic equilibrium response of the four sensor PTM e-nose.

#### 4.7.4.1 Reconstruction in the Dynamic Equilibrium Response

The first step to reconstruct an odour signature in dynamic equilibrium is to concatenate the readings of the four replicated sensors, from the sensor modulated by \( V_1 \) to the sensor modulated by \( V_4 \). However, differences in the response levels of the four sensors will create discontinuities in the appended signal (as shown in Figure 4.9). To remove the discontinuities, a fourth order Fourier curve approximation is used. This curve fitting is defined by:

\[
x_{\text{approx}}(t) = a_0 + \sum_{j=1}^{4} a_j \cos(j\omega t) + b_j \sin(j\omega t) \quad (4.4)
\]

where \( a_0, a_j, \) and \( b_j \) are the Fourier series coefficients and \( t \) is a discrete time sequence.
Figure 4.9: Odour signature reconstruction in dynamic equilibrium response. A) to D) Individual sensor readings. E) Appended readings. F) Signal approximation.

From experiment to experiment, the starting time when the sensor was exposed to the analyte source and therefore the time when the sensors reaches the dynamic equilibrium ($t_{\text{start}}$) can differ. Hence, the voltage value of the modulating signal $V_i$ at $t_{\text{start}}$ is not the same for all the experiments.

In other words, odour signatures were collected in the experiments starting with a different phase. In order to uniform a starting modulation level for all the experiments, it was defined a reference sinusoid which value at $t_{\text{start}}$ is:

$$V_{\text{ref}}(t_{\text{start}}) = V_{\text{ai}} + V_{\text{bi}}$$  \hspace{1cm} (4.5)

where $V_{\text{ai}}$ and $V_{\text{bi}}$ are the DC level and sinusoid amplitude values as in equations 4.1a to 4.1d.

As can be seen in Figure 4.10.A, there exists a phase $\Psi$ between the reference sinusoid and the modulating signal $V_1$. Since the response in dynamic equilibrium can be assumed as stationary, an intuitive solution to correct the phase shifting is to replicate the reconstructed odour signature and select the section of the signal that makes $\Psi = 0$ as shown in Figure 4.10.B.
4.7. SIGNAL PREPROCESSING

Figure 4.10: A) Phase shift $\Psi$ between the reference sinusoid and the modulating signal $V_1$. B) Shift correction applied to the replicated odour signature.

4.7.4.2 Reconstruction in the Transient Response

Since the transient edge is not given by a stationary function, in order to minimize $\Psi$, the modulating signals of the four sensors are compared with the reference sinusoid to determine the sensor with a higher temperature (the sensor with a modulating voltage level closer to $V_{ai} + V_{bi}$). This sensor response is then appended first to the combined sensors responses.

Figure 4.11.A shows four sub cycles of $T/4$ extracted from the four sensors $t_e$ after the transient response was detected. In Figure 4.11.B the four sensors responses are appended and the discontinuities are eliminated by fitting the appended curve with a fourth order Fourier curve approximation as given by equation 4.4.

Figure 4.11: Odour signature reconstruction in transient response. A) to D) Individual sensor responses. E) Appended readings. F) Signal approximation.
4.8 Feature Extraction

Two feature extraction methods are used in this thesis work: the discrete Fourier transform, for classification in the dynamic equilibrium response and the discrete wavelet transform, for classification in the transient response.

### 4.8.1 Feature Extraction in Dynamic Equilibrium

The Discrete Fourier Transform (DFT) is used for feature extraction in the dynamic equilibrium since the sensor responses in this stage are given by stationary signals. Hence, a series of sines and cosines can sufficiently describe the sensor responses.

The DFT and the Inverse DFT are given by the following set of equations:

\[
x[k] = \sum_{n=1}^{N-1} x[n] \cdot e^{-2\pi j k n / N} \tag{4.6}
\]

\[
x[n] = \frac{1}{N} \sum_{n=1}^{N-1} x[k] \cdot e^{2\pi j k n / N} \tag{4.7}
\]

where \( x[k] \) represents the sinusoidal components of the input signal \( x[n] \). The amplitude and phase \( A[k] \) and \( \phi[k] \) respectively can be expressed as:

\[
A[k] = ||x[k]|| = \sqrt{\Re(x[k])^2 + \Im(x[k])^2} \tag{4.8}
\]

\[
\phi[n] = \text{atan2}(\Im(x[k]), \Re(x[k])) \tag{4.9}
\]

Therefore, the feature vector \( F_i \) \((i=1,\ldots,M)\) for each of the \( M \) experiments is given by:

\[
F_i = [A_1, \Phi_1, A_2, \Phi_2, A_3, \Phi_3]^T \tag{4.10}
\]

where \( A_1 \) to \( A_3 \) and \( \Phi_1 \) to \( \Phi_3 \) denotes the amplitude and phase of the first three harmonics of the modulation signal frequency.

The feature matrix \( F \) obtained after \( M \) experiments can be represented by:

\[
F = \begin{pmatrix}
A_{11} & A_{21} & \ldots & A_{M1} \\
A_{12} & A_{22} & \ldots & A_{M2} \\
A_{13} & A_{23} & \ldots & A_{M3} \\
\Phi_{11} & \Phi_{21} & \ldots & \Phi_{M1} \\
\Phi_{12} & \Phi_{22} & \ldots & \Phi_{M2} \\
\Phi_{13} & \Phi_{23} & \ldots & \Phi_{M3}
\end{pmatrix} \tag{4.11}
\]

where each of the \( M \) columns of the matrix represents the features extracted in a single experiment.
4.8.2 Feature Extraction in Transient Response

In the case of transient response analysis, the readings are given by non stationary signals that evolve over time and contain transitory characteristics (e.g. drift, trends and abrupt changes) so that Fourier analysis is not suitable for representation [67]. In the transient case, the Discrete Wavelet Transform (DWT) is used in order to have features that describe the signal in the time domain and also the frequency domain.

The DWT captures both frequency and temporal information, and is defined as a multilevel decomposition technique that returns a series of descriptors (named approximation and detail coefficients) that are calculated for different scales of a generating function known as the mother wavelet.

Mathematically, the DWT consists of a bank of quadrature mirror filters (as shown in Figure 4.12) in which a function $f(t)$ is decomposed in a set of frequency bands. The low pass filters $h_n(k)$ generate the signal approximation coefficients ($A_1, A_2, A_3$) which are the high scale, low frequency components; and the high pass filters $g_n(k)$ generate the detailed coefficients ($D_1, D_2, D_3$) which are the low scale, high frequency components.

![Figure 4.12: Signal decomposition using discrete wavelet transform.](image)

We opted to keep only the coefficients that correspond to the frequency band where the modulating signal is located and disregard the rest. Hence, the feature matrix for transient analysis is given by:
CHAPTER 4. THE PTM E-NOSE

\[
F = \begin{pmatrix}
A_{j1}^1 & A_{j2}^1 & \ldots & A_{jM}^1 \\
A_{j1}^2 & A_{j2}^2 & \ldots & A_{jM}^2 \\
\vdots & \vdots & \ddots & \vdots \\
A_{j1}^n & A_{j2}^n & \ldots & A_{jM}^n
\end{pmatrix}
\quad (4.12)
\]

where each column \( M \) represents one experiment, \( n \) is the number of coefficients at the decomposition band \( j \) where the modulation frequency lies.

### 4.8.3 Dimensionality Reduction

To simplify the classification problem, we apply dimensionality reduction over the feature matrix \( F \) using Linear Discriminant Analysis (LDA). LDA is a transformation that projects the data into a \( C-1 \) dimensional space (\( C \) is the number of classes in the discrimination problem) where the within-class distance is minimized and the distances between classes are maximized [45].

### 4.9 Classification Algorithm

The classification algorithm uses the feature matrix \( F \) as an input and assigns each of the experiments contained in \( F \) to one three possible classes \( C_1, C_2 \) and \( C_3 \), namely Acetone, Ethanol and 2-Propanol. The output of the classifier for a given experiment \( i \) is denoted by:

\[
D_i = [1, 0, 0]^T \quad \forall i \in C_1 \quad (4.13a)
\]

\[
D_i = [0, 1, 0]^T \quad \forall i \in C_2 \quad (4.13b)
\]

\[
D_i = [0, 0, 1]^T \quad \forall i \in C_3 \quad (4.13c)
\]

where \( D_i \) denotes the class decision vector for an experiment \( i \).

A Support Vector Machine (SVM) with a linear kernel is used as a classifier. SVM is a maximum margin classifier [85]. One of its most important properties is that the estimation of the model parameters is a convex optimization problem, and therefore any local solution is a global maximum. Since SVM is by definition a binary classifier, a multi class extension of the original algorithm named “one-versus-rest” was used. In this approach, an individual SVM is trained for each class \( C_k \) in the discrimination problem where all the elements that belong to the \( C_k \) are considered as positive examples while the rest of the elements in the training set are considered as negative examples.

### 4.10 Validation

In order to estimate the generalization performance of the pattern recognition block of the PTM e-nose, validation is performed to measure its accuracy on
previously unseen data samples. In this work, we used \( K\text{-Fold} \) validation, which can be seen as a generalization of \textit{Cross-Validation}.

\subsection*{4.10.1 \textbf{Cross-Validation}}

\textit{Cross-Validation} is a common technique to evaluate a classifier performance. It estimates how the results of a statistical analysis generalize to an independent data set [86--88] by partitioning the data base in two subsets. The first subset is used to train the classifier (i.e. training set) and the validation is carried out with the remaining subset (i.e. testing set).

However, \textit{Cross-Validation} can lead to a suboptimal performance of the classifier. There is a trade-off between the size of the training and the validation set. If a small portion of the data set is using for testing, then the estimate of the generalization performance may be unreliable. On the other hand when a considerable amount of data is used for validation, the classifier training may be suboptimal. And regardless of the size of the training and datasets, there is no way to recognize whether the data that is set aside for testing; regardless of its size, is a representative of the data that the classifier might see on field performance.

\subsection*{4.10.2 \textbf{K-Fold Validation}}

\( K\text{-Fold} \) validation provides an estimate of the true generalization performance of a classifier. In \( K\text{-Fold} \) validation (Figure 4.13), the full data set of \( M \) elements is partitioned into \( K \) subsets. Of the \( K \) subsets, one is retained as a testing set and the remaining data are used for training the classifier. The cross-validation process is then repeated \( K \) times, with each of the \( K \) subsets used exactly once as a testing set.

The classifier performance is then given by the average of the performance from each one of the folds \( (P_i) \) as shown below:

\[
P = \frac{1}{k} \sum_{i=1}^{k} P_i
\]

\text{(4.14)}

The advantage of this method over repeated random sub-sampling is that all observations are used for both training and validation, and each observation is used for validation once [89].

The choice of \( K \) is data dependent. For sufficiently large datasets, \( K \) is typically taken as 5 or 10; however, for smaller datasets, \( k \) may be chosen larger to allow for a larger size of the training set [44].
Figure 4.13: K-Fold cross validation.
Chapter 5
Experimental Results

In this chapter, we present the results obtained in controlled and natural environments for a classification problem of three analytes using a four sensor PTM e-nose.

As mentioned above, the PTM e-nose has three working parameters that define the modulation sinusoids: DC level \( (V_a) \), amplitude \( (V_b) \) and frequency \( f \). Selecting these parameters introduces a trade-off between class separability and exposure time as detailed below.

For controlled environments, the results obtained in dynamic equilibrium as well as in transient response are presented. The chapter closes with the results in natural environments where classification can only be performed using the transient response of the sensors.

5.1 Test Setup

5.1.1 Gas Sources

The classification experiments were based on three analytes namely Ethanol \((C_2H_5OH)\), 2-Propanol \((C_3H_8O)\) and Acetone \((C_3H_6O)\). These analytes are invisible in air and, in small quantities, harmless for humans.

With boiling points of 78.4\(^\circ\)C, 82.5\(^\circ\)C and 56.53\(^\circ\)C respectively, the three analytes evaporate quite quickly at room temperature. Furthermore, Ethanol and 2-Propanol have a comparable vapour pressure at room temperature \((23\(^\circ\)C)\). In order to perform discrimination with gases at comparable vapour pressure levels and hence, similar concentrations, some experiments were carried out with samples of Acetone cooled down to \(-10\(^\circ\)C\).

5.1.2 Sampling in Controlled Environments

The setup for the gas discrimination experiments in controlled environment is shown in Figure 5.1. The measurement process comprises a three phase sampling inside a Plexiglas chamber of 7.9 l. The baseline is recorded by opening
the top cover of the chamber and exposing the PTM e-nose to the reference gas (ambient air at room temperature) for 800s (Figure 5.1.A). Then, a cup filled with one of the three target analytes is placed inside the chamber and the top cover is closed (Figure 5.1.B). The chamber then remains closed long enough for the sensors of the PTM e-nose to sample an odour signature in dynamic equilibrium state. To recover the sensors, the chamber is again opened and the PTM e-nose is exposed to the reference gas until the baseline level is reached.

![Diagram](image1)

Figure 5.1: Setup and measurement process for the controlled environment scenario. A) The electronic nose is exposed to the reference gas (ambient air at room temperature). B) The electronic nose is exposed to one of the target analytes.

The process was manually repeated $M$ times randomly alternating between the three analytes with the chamber placed in an enclosed area where the temperature and humidity values are approximately constant.
5.1.3 Sampling in Natural Environments

The setup for the measurements conducted in natural environments is shown in figure 5.2. A bottle with a few decilitres of one of the target analytes is connected to a pump with a plastic tube. The analyte inside the bottle evaporates and mixes with the overhead air. In addition, incoming fresh air is led with another plastic tube to the bottom of the bottle. The PTM e-nose is placed at 0.2m from the outlet of the pump and the whole system is then located in an outdoor area and experiments were conducted for two consecutive days where the temperature fluctuated between 20°C to 25°C.

In the measurement process, the PTM e-nose is exposed to fresh air for a 800s to sample the baseline level. Then, the pump is switched on to allow the gas mixture to reach the PTM e-nose. However, the dynamic equilibrium is never reached in this setup and hence, only the transient response can be recorded. Finally, the pump is switched off and the sensors recover the baseline level.

In a similar way as in the controlled environment setup, M samples were taken, randomly alternating between the analytes.
5.2 Parameter Selection

As previously explained, the implemented PTM e-nose has three adjustable working parameters (DC voltage, Amplitude and frequency) that regulates the modulation sinusoids. The parameter combination was selected based on three criteria: exposure time, class separability and the minimum temperature level needed for the sensors to respond when exposed to the target analytes.

5.2.1 DC Level and Amplitude

The response of a MOX sensor is dependent on its surface temperature. If the sensors are not sufficiently warm, no significant conductance change will be produced when the sensors are exposed to a target analyte. Consider Figure 5.3.A, where the DC level of the modulation sinusoid for a TGS2620 was set to 0V. As can be seen in Figure 5.3.B, the sensor response shows no change in its conductance during a period of time $e$, even when the sensor is exposed to one of the target analytes (Ethanol). It is only until the sinusoid voltage surpasses $V_{a, min}$ when a rising edge in the sensor response is detected. In Figure 5.3.D, is shown the sensor response when the DC level of the modulation sinusoid is set to 3.75V (Figure 5.3.C) and the sensor is exposed to Ethanol. It can be noticed that there is no delay $e$ since the sinusoid voltage is always above $V_{a, min}$.

Figure 5.3: TGS2620 response with different DC levels. A) and B) DC level = 0V and the corresponding sensor response. C) and D) DC level = 3.75V and the corresponding sensor response
In a systematic way, we determined the minimum DC level needed to pro-
duce a conductance change in the sensors when exposed to the target analytes.
The four sensors of the PTM e-nose were exposed to a sample of Ethanol in-
side the Plexiglas chamber and the sensors heater elements were connected to a
constant DC level that was gradually incremented (starting from 0V) until a sig-
nificant change in the four conductances were detected. With this method and
considering the voltage limit for the heater element is 5V, the DC and amplitude
values selected were $V_a = 1.3$V and $V_b = 3.7$V respectively.

\subsection*{5.2.2 Modulation Frequency}
We based the frequency selection on the class separability between the three
analytes. As a measurement of separability, we used the Mahalanobis Distance
(MD) as suggested in the work of Muezzinoglu et al. [90]. The MD is directly
proportional to the distance between the class centres and inversely propor-
tional to the individual covariances of each class. The MD distance for two
classes $C_1$ and $C_2$ is given by:

$$D(C_1, C_2) = \sqrt{(\mu_1 - \mu_2)^T S^{-1}_{12} (\mu_1 - \mu_2)} \quad (5.1)$$

where $\mu_1$ and $\mu_2$ are the class centers and $S_{12}$ is the average of the two
covariance matrices $S_1$ and $S_2$.

For more than two classes, the authors propose a generalization of the MD
given by:

$$MD_K = \sqrt{\sum_{i,j=1}^{K} D^2(C_i, C_j)} \quad (5.2)$$

where $K$ is the number of classes. In this work, $K=3$.

The MD distances were computed with the features extracted in dynamic
equilibrium (projected in a two dimensional space using LDA) for the eight pos-
sible frequencies of the PTM e-nose. The results are shown in table 5.1. $t_e$ repre-
ts the exposure time needed to collect an odour signature in dynamic equi-
librium. $D_{ae}$, $D_{ep}$ and $D_{ap}$ represent the binary MD between Acetone/Ethanol,
Ethanol/2-Propanol and Acetone/2-Propanol. $MD_3$ represents the three-class
MD.

As can be seen in table 5.1, and in Figure 5.4, the general tendency is that
$MD_3$ decreases at higher modulation frequencies. In Figure 5.5.A to Figure
5.5.H the LDA plots obtained in dynamic equilibrium for the eight possible fre-
quencies are shown. Clearly, $MD_3$ is negatively affected when the within class
variance increases (i.e. when the data is less clustered). It can also be noticed
that the lowest $MD_3$ value corresponds to $f=1.00$Hz, when the classes start to
overlap. The best frequency possible, according to $MD_3$, is 0.10Hz. However,
the exposure time to collect an odour signature is 2.5s. Therefore, we selected
the frequency that gives a reasonable trade-off between class separability and exposure time. Hence, we selected $f=0.50\text{Hz}$ as the modulation frequency for all the classification experiments.

<table>
<thead>
<tr>
<th>Frequency</th>
<th>$t_e$</th>
<th>$D_{ae}$</th>
<th>$D_{ep}$</th>
<th>$D_{ap}$</th>
<th>$MD_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05Hz</td>
<td>5.00s</td>
<td>16.47</td>
<td>20.84</td>
<td>33.09</td>
<td>42.43</td>
</tr>
<tr>
<td>0.10Hz</td>
<td>2.50s</td>
<td>49.88</td>
<td>37.14</td>
<td>58.32</td>
<td>85.26</td>
</tr>
<tr>
<td>0.20Hz</td>
<td>1.25s</td>
<td>22.68</td>
<td>30.72</td>
<td>40.42</td>
<td>55.61</td>
</tr>
<tr>
<td>0.25Hz</td>
<td>1.00s</td>
<td>23.56</td>
<td>15.16</td>
<td>26.90</td>
<td>38.84</td>
</tr>
<tr>
<td>0.33Hz</td>
<td>0.75s</td>
<td>11.09</td>
<td>16.98</td>
<td>36.70</td>
<td>41.93</td>
</tr>
<tr>
<td>0.50Hz</td>
<td>0.50s</td>
<td>12.74</td>
<td>8.39</td>
<td>17.49</td>
<td>23.22</td>
</tr>
<tr>
<td>0.66Hz</td>
<td>0.38s</td>
<td>3.25</td>
<td>3.83</td>
<td>7.00</td>
<td>8.62</td>
</tr>
<tr>
<td>1.00Hz</td>
<td>0.25s</td>
<td>4.60</td>
<td>1.79</td>
<td>3.97</td>
<td>6.34</td>
</tr>
</tbody>
</table>

Table 5.1: Pairwise MD between Acetone, Ethanol and Propanol and its corresponding $MD_3$.

Figure 5.4: Modulation Frequency vs. $MD_3$ chart.
5.2. PARAMETER SELECTION

Figure 5.5: Obtained LDA plots in dynamic equilibrium with working parameters $V_a = 1.3V$, $V_b = 3.7V$ and A) $f=0.05Hz$, B) $f=0.1Hz$, C) $f=0.2Hz$, D) $f=0.25Hz$, E) $f=0.33Hz$ F) $f=0.5Hz$, G) $f=0.66Hz$, H) $f=1.00Hz$. 
5.3 Results and Discussion

5.3.1 Controlled Environments

Using the selected parameters ($V_a = 1.3\text{V}$, $V_b = 3.7\text{V}$ and $f=0.50\text{Hz}$), a total of 48 experiments were made (16 for each analyte). Classification was evaluated in both, the transient response and the dynamic equilibrium states.

5.3.1.1 Classification in Dynamic Equilibrium State

Figure 5.6.A and Figure 5.6.B show a comparison between the LDA plot obtained with data collected by a single sensor during a full modulation cycle and the LDA plot from data collected with the PTM e-nose in one fourth of the modulation cycle, both in dynamic equilibrium. As shown in the figures, in both cases well defined and separable clusters were obtained. With the linear SVM classifier and an 8-fold cross validation, the success rate obtained with both methods was 100%. However, the exposure time in dynamic equilibrium with the PTM e-nose was reduced to 0.5s compared to 2s with the standard e-nose approach.

![Figure 5.6: LDA plots obtained in dynamic equilibrium (f=0.50Hz, $V_a=1.3\text{V}$, $V_b=3.7\text{V}$): A) Classical method, one sensor collecting data during T. B) Proposed PTM e-nose operating under the same working parameters collecting data during T/4.](image)

5.3.1.2 Classification in Transient Response

The analysis for the transient response was performed by applying the DWT over the rising edge of the sensors readings (Figure 5.7) in order to extract the coefficients located in the frequency band of the modulation signal (for the
selected frequency, the detailed coefficients at the 5th level of decomposition) and LDA as dimensionality reduction before using a linear SVM classifier.

Figure 5.7: Transient response obtained with a modulation frequency equal to 0.5Hz. Labels “0”, “1” and “2” are explained in the text.

With the same dataset of 48 experiments, classification success rates were investigated at different exposure times ($t_e$). In Figure 5.7, label “0” denotes the rising edge detection. As a first attempt, data were collected during the first 0.5s of the transient (enough to reconstruct one odour signature with the PTM e-nose). However, the reconstructed signature is not informative enough for a robust classification. The success rate obtained with an 8-Fold cross validation was 54% ± 18%.

In order to improve the performance, the odour signature is reconstructed from the response collected starting at a tolerance time ($t_t$) after the rising edge was detected. As shown in Figure 5.7, $t_t$ is delimited by labels “0” and “1” and the information used to reconstruct the odour signature is collected in the time span between “1” and “2”. Hence, the total exposure time in transient response is given by:

$$t_e = t_t + T/4$$

(5.3)

where, for the selected frequency ($f = 0.50$Hz), $T/4 = 0.5s$. Table 5.2 and Figure 5.8 summarizes the results obtained at different exposure times where $t_t$ was incremented from 0s to 4s with steps of 0.5s. From the obtained results, it can be noticed that the classification performance improves as the transient response progresses, having good classification performance from $t_e = 2s$ (89% ± 10%). The best performance is obtained at $t_e = 4.5s$ (100%). In Figure 5.9.A to Figure 5.9.D the LDA plots and the decision boundaries obtained for $t_e = 0.5s$, $t_e = 2.5s$, $t_e = 3.5s$ and $t_e = 4.5s$ are shown.
Table 5.2: Classification performances obtained in controlled environments at different exposure times $t_e$ with a PTM nose with configuration parameters $V_a = 1.3V, V_b = 3.7V$ and $f=0.5Hz$.

<table>
<thead>
<tr>
<th>$t_e$ (s)</th>
<th>Performance</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>54% ± 18%</td>
</tr>
<tr>
<td>1.0</td>
<td>50% ± 16%</td>
</tr>
<tr>
<td>1.5</td>
<td>54% ± 26%</td>
</tr>
<tr>
<td>2.0</td>
<td>89% ± 10%</td>
</tr>
<tr>
<td>2.5</td>
<td>93% ± 7%</td>
</tr>
<tr>
<td>3.0</td>
<td>95% ± 5%</td>
</tr>
<tr>
<td>3.5</td>
<td>93% ± 7%</td>
</tr>
<tr>
<td>4.0</td>
<td>97% ± 3%</td>
</tr>
<tr>
<td>4.5</td>
<td>100%</td>
</tr>
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</table>

Figure 5.8: Error bar chart at different exposure times $t_e$ in controlled environments with a PTM nose with configuration parameters $V_a = 1.3V, V_b = 3.7V$ and $f=0.5Hz$. 
5.3. RESULTS AND DISCUSSION

Figure 5.9: LDA plots obtained with a PTM nose in controlled environments with configuration parameters $V_a = 1.3V, V_b = 3.7V$ and $f=0.5Hz$ at different $t_e$. A) $t_e = 0.5s$. B) $t_e = 2.5s$. C) $t_e = 3.5s$. D) $t_e = 4.5s$. 
5.3.2 Natural Environments

In natural uncontrolled environments, 63 experiments were recorded (21 for each of the target analytes) during two consecutive days where the ambient temperature fluctuated between 20°C to 25°C. As shown in Figure 5.10.A, the equilibrium state in the sensor readings was never reached, therefore the classification was performed only in the early stages of the transient response, where the PTM e-nose is supposed to be in the plume of the analytes.

Figure 5.10: A) Sensor response when exposed to an Ethanol patch of gas in natural environments. B) Transient response segment where “0” denotes the detected rising edge, “0” to “1” delimits $t_1$ and the exposure time is given from “0” to “2”.

Similarly to the case of controlled environments, classification was performed and evaluated with 8-fold cross validation at different exposure times ($t_e$) as shown in Table 5.3 and in Figure 5.11. It can be noticed that acceptable results are obtained from $t_e = 2.0s$ ($83\% \pm 14\%$). However, the performance is lower compared with the transient classification in closed environments. This result can be expected because the interaction with the airflows present in natural environments produces irregular concentration patterns (Figure 5.10.A and 5.10.B) while the volatiles travel from the pump outlet to the PTM e-nose. In Figure 5.12.A to Figure 5.12.D the LDA plots and the decision boundaries obtained for $t_e = 0.5s$, $t_e = 2.5s$, $t_e = 3.5s$ and $t_e = 4.5s$ in natural environments are shown.
5.3. RESULTS AND DISCUSSION

<table>
<thead>
<tr>
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<tr>
<td>0.5s</td>
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<tr>
<td>1.0s</td>
<td>48% ± 24%</td>
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<td>3.0s</td>
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<td>92% ± 7%</td>
</tr>
<tr>
<td>4.5s</td>
<td>92% ± 7%</td>
</tr>
</tbody>
</table>

Table 5.3: Classification performances obtained at different exposure times $t_e$ in natural environments with a PTM nose with configuration parameters $V_a = 1.3\, \text{V}, V_b = 3.7\, \text{V}$ and $f=0.5\, \text{Hz}$.

Figure 5.11: Error bar chart at different exposure times $t_e$ in natural environments with a PTM nose with configuration parameters $V_a = 1.3\, \text{V}, V_b = 3.7\, \text{V}$ and $f=0.5\, \text{Hz}$.
Figure 5.12: LDA plots obtained with a PTM nose in natural environments with configuration parameters $V_a = 1.3V, V_b = 3.7V$ and $f=0.5Hz$ at different $t_e$. A) $t_e = 0.5s$. B) $t_e = 2.5s$. C) $t_e = 3.5s$. D) $t_e = 4.5s$. 

<table>
<thead>
<tr>
<th>Color</th>
<th>Description</th>
<th>2nd LDA Component</th>
<th>1st LDA Component</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red</td>
<td>Acetone</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Green</td>
<td>Ethanol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blue</td>
<td>2-Propanol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gray</td>
<td>Missclassified</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Chapter 6
Conclusions and Future Work

A fast, selective and low cost device is a key component for gas sensing applications in natural uncontrolled environments. The main contribution of this thesis work was the introduction of the PTM e-nose concept, which is an effective means to reduce the exposure time to a target analyte by replicating a base sensor \( n \) times and using phase shifted modulation sinusoid signals in to order to measure the response to a target analyte in parallel. In this way, the exposure time can be reduced to an \( nth \) of the modulation sinusoid period.

The proposed operational principle was tested with a gas discrimination problem of three organic solvents (namely Acetone, ethanol and 2-Propanol) in controlled and natural environments. These tests were performed with an instance of a PTM e-nose that comprised four TGS2620 MOX gas sensors.

The implemented PTM e-nose has three parameters that regulate the modulation sinusoids: DC level \( (V_a) \), amplitude \( (V_b) \), and frequency \( f \). Considering that in order to operate, the surface of the MOX sensors needs to be heated, \( V_a \) was set to the minimum voltage level that produces a response when the sensors are exposed to the target analyte. The value of \( V_b \) was selected considering the maximum voltage level that can be applied to the heater element according to the manufacturer. \( f \) was selected by considering class separability using the Mahalanobis distance as a measurement index.

The results obtained show that under laboratory conditions and when discrimination is carried out in the equilibrium state of the sensors response, the performance is similar to the results obtained with a single gas sensor but with a considerably reduced exposure time (i.e. the exposure time was reduced by a factor of 4).

In the case of transient classification, experiments were carried out in both, laboratory conditions and natural environments and classification was attempted at different exposure times. It was observed that in both conditions, successful classification can be obtained from 2.0s of exposure time, with a slight performance decrease in natural environments.
Compared to related works, the PTM e-nose can provide a similar classification performance at a reduced exposure time. In the approach of Vergara et al. [81], a success classification rate of 100% was obtained by using a segment of 1s of the dynamic equilibrium response, while in the PTM e-nose approach, a success rate of 100% was obtained with a segment of 0.5s and the principle of the PTM e-nose allow for even shorter times with a higher degree of parallelization.

Regarding classification in transient response, Muezzinoglu et al. [47] obtained a successful classification rate of 82.9% at 10.0s exposure time, while Marques et al. [48] obtained a success rate of 83.0% with the first four seconds of exposure time. Comparable performance rates can be obtained with the PTM e-nose at exposure times of 2.0s in both, laboratory conditions and natural environments. Furthermore, at 4.0s of exposure time, the measured performance of the PTM e-nose with an 8-fold cross validation was 97% ± 3% and 92% ± 7% under laboratory conditions and in natural environments respectively.

Suggested future work directions are:

- Explore the feasibility of adding more than four sensors to a PTM e-nose array.
- Selection of working parameters $V_a$ and $V_b$ based also on the class separability index.
- So far, the parameter selection was performed considering only the dynamic equilibrium response. Classification in transient analysis might be improved if a set of working parameters is selected considering the transient response.
- For transient classification, a rejection criterion could be added to discard those samples that show a poor or irregular response.
- Explore the use of a PTM e-nose along with a mobile robotic platform for gas discrimination experiments and gas distribution mapping.
Bibliography


