Proceedings

In Field Nitrogen Dioxide and Ozone Monitoring Using Electrochemical Sensors With Partial Least Squares Regression [†]

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Abstract: Low-cost gas sensors detect pollutants gas at part per billion level and may be installed in small devices to densify air quality monitoring networks for the spread analysis of pollutants around an emissive source. However, these sensors suffer from several issues such as environmental factors impact and cross-interfering gases. For instance, ozone (O_3) electrochemical sensor senses nitrogen dioxide (NO_2) and O_3 simultaneously without discrimination. Alphasense proposes the use of pair of sensors, the first one is equipped with filter dedicated to measure NO_2. The second one is sensitive to both NO_2 and O_3. Thus, O_3 concentration can be obtained by subtracting the concentration of NO_2 from the sum of the two concentrations. This technique is not practical and requires calibrating each sensor individually leading to biased concentration estimation. In this paper, we propose Partial Least Square regression (PLS) to build a calibration model including both of sensors responses and also temperature and humidity variations. The results obtained from data collected on field for two months show that PLS regression provides better gases concentrations estimation in terms of accuracy than calibrating each sensor individually.

Keywords: partial least square regression; gas sensors; electrochemical sensors; air pollution monitoring

1. Introduction

Urban air pollution is a major preoccupation [1]. Government organizations encourage researches on low cost gas sensors to improve their performances in order to complement the actual air pollution monitoring networks providing better spatiotemporal resolution of the pollutants spread [2]. Today low cost sensors such as electrochemical sensors can sense most of pollutants gas at the magnitude of part per billion (ppb) [3]. However, several limitations inhibit systems based on these sensors to reach high performance similar to the regular instruments [4]. Among these limitations, the influence of environmental factors, essentially the temperature and humidity and the interfering gases present in the ambient air, particularly in case of measuring O_3 and NO_2 [5]. The existing commercial electrochemical sensors for measuring O_3 respond simultaneously to O_3 and NO_2, without discrimination, because NO_2 and O_3 are reducible at similar potentials on carbon or gold electrodes [6]. Therefore, the responses of these sensors are proportional to the combined concentration of O_3 and NO_2. This non-selectivity of sensors becomes an obstacle for air monitoring applications where NO_2 and O_3 are present simultaneously with the same order of concentration magnitude. In this paper, we evaluate electrochemical sensors for O_3 and NO_2 for in field and in real conditions application. So, we propose to calibrate simultaneously the two sensors using Partial Least Square regression (PLS) with considering also the temperature and humidity variations. The remainder of this paper is organized

as follow: we present first experiment set up and data collection, then calibration procedure with results and finally a conclusion.

2. Experiment Set Up and Data Collection

In this work, we focused on measuring the concentration of O_3 and NO_2 in ambient air because they are the principal pollutant gases in French cities that still exceeding the limited values defined by the European directives [7]. Therefore, we designed a device constituted of two electrochemical sensors provided by Alphasense LTD: NO2-B41F and OX-B431 dedicated to measure NO_2 and oxidizing gases respectively. The device contains also, the sensors conditioning circuits, the gas exposure chamber and the data acquisition unit. The conditioning circuits consist essentially of potentiostat circuits allow amplifying and converting the sensor electrodes currents to voltages. The device is placed inside the air monitoring station managed by ATMO Grand Est agency. This station is located beside a highway, crossing Metz city, France. Our device works in dynamic mode for air sampling, thus, a pump and a mass flow controller are placed on the exposure chamber exit, to generate a constant and continuous airflow by suction (Figure 1). We set the airflow rate to 500ml/min, in order to obtain the same airflow rate as the ATMO Grand Est O_3 and NO_2 analyzers. The collected data represent the voltages of the sensor responses with a data sampling frequency of 200Hz. Sensor responses are then averaged over a period of 10s and recorded on a computer using Matlab software. Finally, recorded data are averaged again each 15 min in order to comply with the reference data provided by ATMO Grand Est. Data are collected continuously from the 22nd February 2019 to the 14th April 2019.
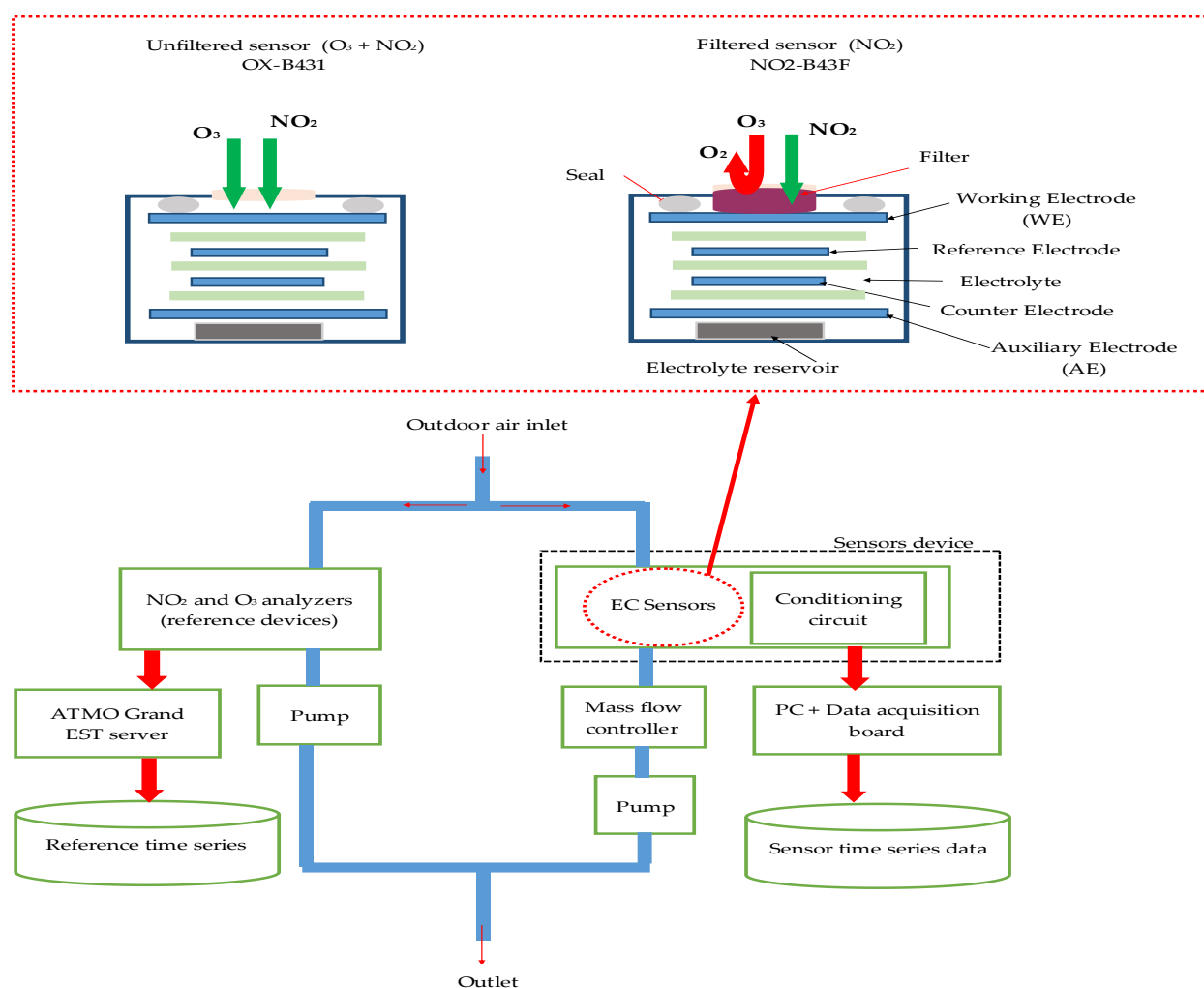
Figure 1. Experiment setup diagram and the schematic of filtered and unfiltered electrochemical sensors.

3. Sensors Calibration

To quantify O_3 and NO_2 concentrations, the manufacturer Alphasense recommends the use of a pair of electrochemical sensors: a model OX-B431 which responds to both of gases (O_3 + NO_2) and a model NO2-B43F which responds only to NO_2. The NO2-B43F sensor is equipped with a manganese dioxide filter, which catalyzes O_3 into oxygen, thus preventing the sensor to response to O_3 present in the environment (Figure 1). To determine the O_3 concentration, the contribution of NO_2 to the response of the OX-B431 sensor must be removed. Therefore, we first need to calculate the NO_2 concentration with the NO2-B43F sensor and then subtract it from the concentration provided by the OX-B431 sensor. The calibration procedure of this pair of sensors is done as follows:

• Calibrate the NO2-B43F sensor for measuring NO_2 according to Equation 1:

$$[NO_2] = (WE_{NO2\text{-}B43F} - AE_{NO2\text{-}B43F})\, \alpha_1 + \alpha_2, \tag{1}$$

where $[NO_2]$ is the concentration of the NO_2; $WE_{NO2\text{-}B43F}$, $AE_{NO2\text{-}B43F}$ are signals of the working and the auxiliary electrodes of NO2-B43F sensor, respectively; α_1, α_2 are regression coefficients that can be determined by a simple linear regression.

• Calibrate the OX-B431 sensor to measure of the mixture (NO_2 + O_3) also according to Equation 2:

$$[NO_2+O_3] = (WE_{OX\text{-}B431}) - AE_{OX\text{-}B431})\, b_1 + b_2, \tag{2}$$

where $WE_{OX\text{-}B431}$, $AE_{OX\text{-}B431}$ are signals of the working and the auxiliary electrodes of OX-B431 sensor, respectively; b1, b2 are regression coefficients determined by a simple linear regression.

The concentration of O_3 will be the difference between the concentration obtained by the OX-B431 sensor and the concentration obtained by the NO2-B43F sensor:

$$[O_3] = [NO_2+O_3] - [NO_2], \tag{3}$$

The concentrations of both O_3 and NO_2 are typically 5 to 120 µg/m³ at the roadside, so intelligent data analysis is required to differentiate each gas concentration. Our proposition is to combine both sensors signals in the same equation plus the temperature and humidity variations:

$$[NO_2] = c_0 + c_1\ WE_{NO2\text{-}B43F} + c_2\ AE_{NO2\text{-}B43F} + c_3\ WE_{OX\text{-}B431} + c_4\ AE_{OX\text{-}B431} + c_5\ T + c_6\ H, \tag{4}$$

$$[O_3] = d_0 + d_1\ WE_{NO2\text{-}B43F} + d_2\ AE_{NO2\text{-}B43F} + d_3\ WE_{OX\text{-}B431} + d_4\ AE_{OX\text{-}B431} + d_5\ T + d_6\ H, \tag{5}$$

Where c_0, c_1….c_6 and d_0, d_1….d_6 are regression coefficients determined by using PLS [8];T and H are the temperature and humidity respectively.

The comparison between calibration of each sensor individually and the combination of the two sensor signals with temperature and humidity variation using PLS regression shows that the concentration estimation is better in case of using PLS regression than the case of calibrate each sensor individually. Figure 2 illustrates that in case of using PLS regression, the root mean square errors RMSE are 4.71µg/m³ and 6.89 µg/m³ for NO_2 and O_3 respectively whereas in case of using each sensor individually, the RMSE were 6,34 µg/m³ and 8,76 µg/m³ respectively. We note also that the estimation of NO_2 is better than the estimation of O_3 in both cases of calibration. The reason behind this, is that NO_2 estimation depends essentially on one sensor, whereas of the estimation of O_3 depends on the sensors.
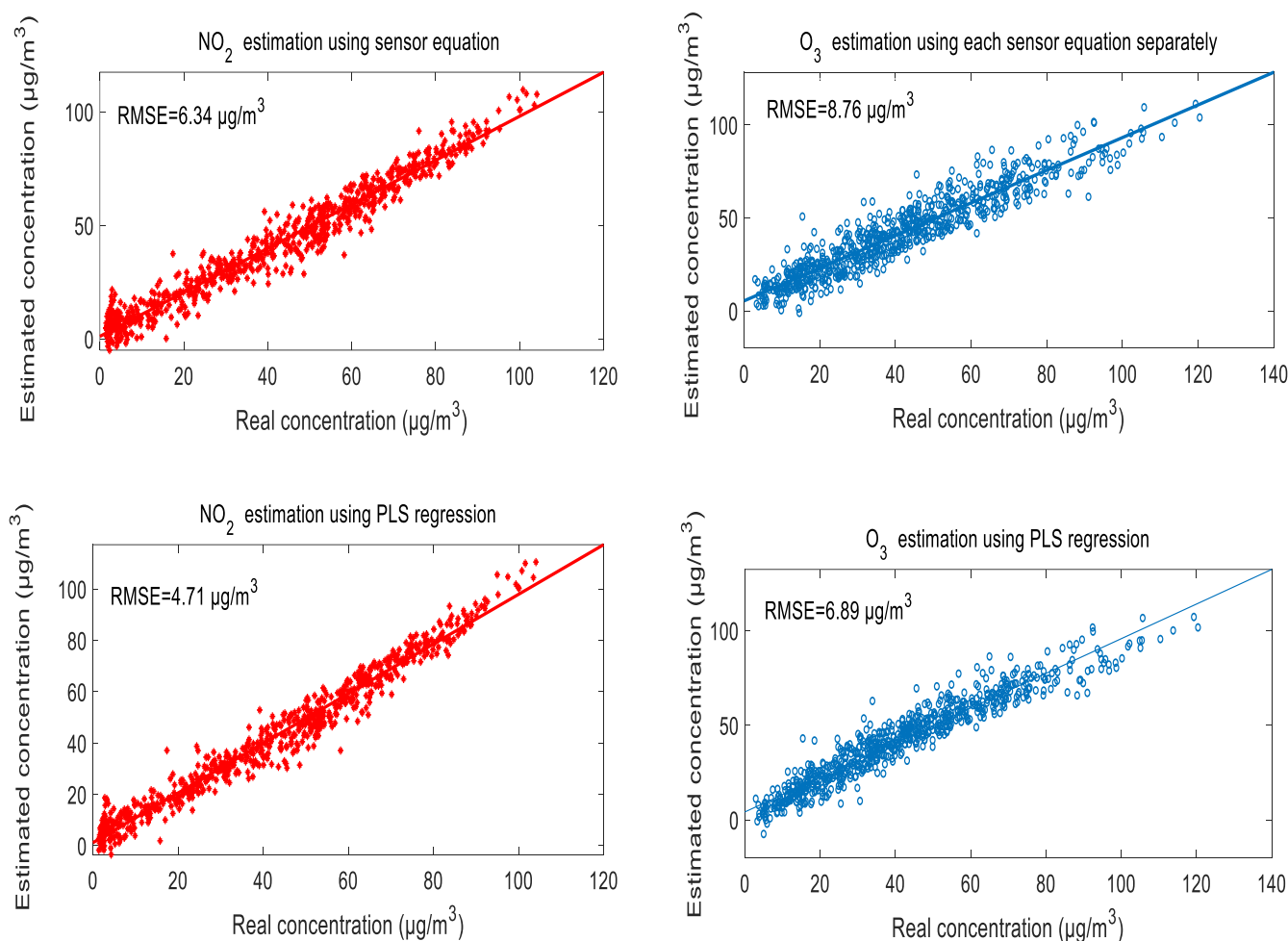
Figure 2. Correlation between reference concentration and estimated concentration of NO₂ and O₃.

4. Conclusions

In this work, electrochemical sensors calibration is proposed using PLS regression. Fist we deployed a device to collect data in real outdoor conditions, then we proposed multiple linear regression to estimate simultaneously nitrogen dioxide and ozone concentration. We find that the use of a pair with PLS regression is better than calibrate each sensor individually, the RMSE is reduced $8.76 \mu g/m^3$ to $6.89 \mu g/m^3$ for ozone concentration estimation.

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