Quantifying nitrogen oxides and ammonia via frequency modulation in gas sensors

Master thesis - Progress report

Marcos F Mourão

March 21, 2021

Most of the progress so far was on the writing of the thesis report: introduction, theory and data (partially) sections are fairly advanced. I also participate in regular meetings with Annika and other students (Erik and Mudith) to discuss writing and the content of our thesis. I have been also meeting with my external supervisor, Mike Andersson, for lab visits and discussions on the experiments.

As far as implementations of the methods goes, progress was hindered by a considerable delay on the data acquisition experiments. Delays were due to equipment fault, power cuts and other problems with the measurement system. As of now (March 21, 2021), the experiments are being run (during the weekend) and should be available this week. This new data is expected to be more complete, with a well defined measurement layout: more samples, more levels (possible concentrations), and the shape features (slope and average) are being directly measured in the lab, i.e. the raw sensor response will not be available.

Nonetheless, a few weeks ago some preliminary experiments were run and I managed to use the data from it to create a dummy dataset. The data, however, is significantly different from the real one, with very few data points. Additionally, the low sample rate from the lab equipment made the shape features extraction difficult. I go in a bit more detail as of why this data is different in my presentation.

I tried some basic regression methods, namely linear, principal components, partial least squares and ridge regression. Hyperparameters were chosen via cross-validation with root mean squared error (RMSE) scoring. In my presentation I display some very crude results of the regression predictions. The results are poor. I did not look deeper into it given the aforementioned limitations. The most promising method is Partial Least Squares Regression, as it is wildly used for this kind of data/field.

Regardless, code is (mostly) ready when the real data comes for these initial models. I also want to look into some non parametric regression techniques and compare. I have been thinking on support vector regression or a deep learning alternative.

I am aware that I am at risk of being late with my thesis, but I am trying / will try my best to meet the first submission. I am in regular contact with both Annika and Mike. Meanwhile, I am focused on other parts of the thesis work, namely reading literature and writing my report. I deeply believe I will make significant progress in the following weeks.

As soon as I have the real data, in addition to applying the methods, I intend to do a more thorough analysis, specially on linearity, possible outliers and collinearity of the predictors.

APPENDIX: SAMPLE TEXT

1 Introduction

1.1 Motivation

Nitric Oxide (NO) and Nitrogen Dioxide (NO_2), commonly referred together as NO_x, are hazardous gases to the environment and to humans. Its main sources are combustion processes in transportation, and industrial processes such as (but not limited to) auto mobiles, trucks, boats, industrial boilers, turbines, etc. [12].

NO_x exposure to humans can cause respiratory illnesses such bronchitis, emphysema and can worsen heart disease [4]. Environmentally, NO_x are deemed precursors of adverse phenomena such as smog, acid rain, and the depletion of ozone (O_3) [1]. It is of high interest, therefore, to reduce NO_x emissions.

One well studied and successful method of reducing emissions is Selective Catalytic Reduction (SCR), which consists in the reduction of NO_x by ammonia (NH_3) into nitrogen gas (N_2) and water (H_2O) [6], both harmless components. The process is based in the following reactions [6]:

- $4\,NH_3 + 4\,NO + O_2 \longrightarrow 4\,N_2 + 6\,H_2O$
- $2\,NH_3 + NO + NO_2 \longrightarrow 2\,N_2 + 3\,H_2O$
- $8\,NH_3 + 6\,NO_2 \longrightarrow 7\,N_2 + 12\,H_2O$

One key element in these reactions, however, is the amount of ammonia dosed into the SCR systems. Ammonia itself is hazardous to humans, causing skin and respiratory irritation, among other illnesses [2]. More importantly, ammonia is one of the main sources of nitrogen pollution and it has direct negative impact on biodiversity via nitrogen deposition in soil and water [8]. Hence it is also desired to keep ammonia emissions to a minimum. Too much ammonia in the SCR catalyst will guarantee NO_x reduction at the expense of undesired ammonia emissions. Concurrently, too little ammonia will impede SCR to occur properly, beating the purpose of the catalyst and as a consequence, undesired NO_x emissions.

To monitor gasses concentrations, chemical sensors are deployed, one of which is the Silicon Carbide Field Effect Transistor (SiC-FET). The identification and quantification of gasses is normally achieved through multiple sensor in so called sensor arrays. Ideally each sensor in the array needs to have different responses to different compounds [3]. The deployment of multiple sensors, on the other hand, proves itself cumbersome due to the increased chances of failure, and decalibration of the system should one or multiple sensors be replaced [3].

One solution to this problem is the cycled operation of one single sensor, referred as virtual multi-sensor [3]. By cycling the working point parameters of the sensor, different substances react differently in the sensor surface, which in turn produces different responses. Temperature Cycled Operation (TCO), Gate Bias Cycled Operation (GBCO), and the combination of the two have been proven to increase selectivity of SiC-FET sensors [3].

TCO, in contrast with a constant temperature evaluation, produces unique transient sensor responses, i.e. each gas mixture yields a slightly different sensor output. This unique gas signature increases selectivity [5]. Additionally, the high temperatures reached in these cycles help in the cleansing of the sensor surface, preparing it for the new mixtures to come.

Frequency modulation tries to achieve the same goal: avoid steady state responses in exchange of unique signatures that could help identify/quantify the gasses at hand. It consists on operating the sensor in Alternating Current (AC). One then can regulate the frequency of this operation and create cycles of different frequencies, similar to what is done in TCO. This is equivalent to GBCO, but with more frequency changes and achieving overall higher frequencies.

The main question is: given these set of unique sensor responses, how one can quantify the gasses that produced them? The answer lies in multivariate regression techniques. Partial Least Squares Regression (PLSR) has been used in chemometrics extensively and it has been proven to be good at this task [3] [13]. Other multivariate regression methods, naturally, can also be used. This is the aim of this thesis work, which is shown in the following section.

1.2 Aim

The aim of this thesis is to investigate different regression methods, namely: PLSR, Ridge Regression and (neural nets XXXX - TENTATIVE), and their fit to correctly quantify gas mixtures such NO_x and Ammonia subjected to sensor frequency modulation.

1.3 Research questions

1. Is it possible to achieve acceptable prediction levels for NO_x and Ammonia using frequency modulation?
2. Which method yields best predictions of gas concentrations?

Bibliography

[1] R. Alberto Bernabeo, K. Webster, and M. Onofri. "Health and Environmental Impacts of Nox: An Ultra- Low Level of Nox (Oxides of Nitrogen) Achievable with A New Technology." In: *Global Journal of Engineering Sciences* 3 (), pp. 2–7. DOI: 10.33552/gjes.2019.02.000540.

[2] ASTDR. "Sheet for ammonia published by the Agency for Toxic Substance and Disease Registry (ASTDR)." In: 2672 (2004), pp. 1–18. URL: https://www.atsdr.cdc.gov/MHMI/mmg126.pdf%5C%0Ahttps://www.atsdr.cdc.gov/mmg/mmg.asp?id=7&tid=2#bookmark02.

[3] Manuel Bastuck. "Improving the performance of gas sensor systems with advanced data evaluation, operation, and calibration methods." PhD thesis. Jan. 2019, p. 267.

[4] Thirupathi Boningari and Panagiotis G. Smirniotis. "Impact of nitrogen oxides on the environment and human health: Mn-based materials for the NOx abatement." In: *Current Opinion in Chemical Engineering* 13.x (2016), pp. 133–141. ISSN: 22113398. DOI: 10.1016/j.coche.2016.09.004. URL: http://dx.doi.org/10.1016/j.coche.2016.09.004.

[5] Christian Bur, Manuel Bastuck, Anita Lloyd Spetz, Mike Andersson, and Andreas Schütze. "Selectivity enhancement of SiC-FET gas sensors by combining temperature and gate bias cycled operation using multivariate statistics." In: *Sensors and Actuators B: Chemical* 193 (2014), pp. 931–940. ISSN: 0925-4005. DOI: https://doi.org/10.1016/j.snb.2013.12.030. URL: https://www.sciencedirect.com/science/article/pii/S0925400513015037.

[6] Pio Forzatti. "Present status and perspectives in de-NOx SCR catalysis." In: *Applied Catalysis A: General* 222.1 (2001). Celebration Issue, pp. 221–236. ISSN: 0926-860X. DOI: https://doi.org/10.1016/S0926-860X(01)00832-8. URL: https://www.sciencedirect.com/science/article/pii/S0926860X01008328.

[7] Jerome Friedman, Trevor Hastie, Robert Tibshirani, et al. *The elements of statistical learning*. Vol. 1. 10. Springer series in statistics New York, 2001.

[8] Susan Guthrie, Sarah Giles, Fay Dunkerley, Hadeel Tabaqchali, Amelia Harshfield, Becky Ioppolo, and Catriona Manville. *Impact of ammonia emissions from agriculture on biodiversity: An evidence synthesis*. Santa Monica, CA: RAND Corporation, 2018. DOI: `10.7249/RR2695`.

[9] Richard Arnold Johnson, Dean W Wichern, et al. *Applied multivariate statistical analysis*. Vol. 5. 8. Prentice hall Upper Saddle River, NJ, 2002.

[10] Kee Siong Ng. "A simple explanation of partial least squares." In: *The Australian National University, Canberra* (2013).

[11] Jonathon Shlens. "A tutorial on principal component analysis." In: *arXiv preprint arXiv:1404.1100* (2014).

[12] USEPA. *Nitrogen Oxides Control Regulations*. `https://www3.epa.gov/region1/airquality/nox.html`. Accessed 2021-02-09. 2019.

[13] Svante Wold, Michael Sjöström, and Lennart Eriksson. "PLS-regression: a basic tool of chemometrics." In: *Chemometrics and Intelligent Laboratory Systems* 58.2 (2001). PLS Methods, pp. 109–130. ISSN: 0169-7439. DOI: `https://doi.org/10.1016/S0169-7439(01)00155-1`. URL: `https://www.sciencedirect.com/science/article/pii/S0169743901001551`.

[14] Kevin Wright. *The NIPALS algorithm*. `https://cran.r-project.org/web/packages/nipals/vignettes/nipals_algorithm.html`. Accessed: 2021-03-12.