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Improving the identification of nitrogen oxides and ammonia via frequency modulation in gas sensors
– **DRAFT**

Förbättra identifieringen av kväveoxider och ammoniak med frekvensmodulering i gassensorer

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Abstract

The abstract resides in file `Abstract.tex`. Here you should write a short summary of your work.

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Acronyms

AC Alternating Current. 3

GBCO Gate Bias Cycled Operation. 3

PLSR Partial Least Squares Regression. 3, 4

SCR Selective Catalytic Reduction. 2, 3

SiC-FET Silicon Carbide Field Effect Transistor. 3

TCO Temperature Cycled Operation. 3

1 Introduction

1.1 Motivation

Nitric Oxide (NO) and Nitrogen Dioxide (NO_2), commonly referred together as NOx, 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. [8].

NOx exposure to humans can cause respiratory illnesses such bronchitis, emphysema and can worsen heart disease [4]. Environmentally, NOx 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 NOx emissions.

One well studied and successful method of reducing emissions is Selective Catalytic Reduction (SCR), which consists in the reduction of NOx by ammonia (NH3) into nitrogen gas (N2) and water (H2O) [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 [7]. Hence it is also desired to keep ammonia emissions to a minimum. Too much ammonia in the SCR catalyst will guarantee NOx 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 NOx 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] [9]. 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 NOx and Ammonia subjected to sensor frequency modulation.

1.3 Research questions

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

2 Theory

The main purpose of this chapter is to make it obvious for the reader that the report authors have made an effort to read up on related research and other information of relevance for the research questions. It is a question of trust. Can I as a reader rely on what the authors are saying? If it is obvious that the authors know the topic area well and clearly present their lessons learned, it raises the perceived quality of the entire report.

After having read the theory chapter it shall be obvious for the reader that the research questions are both well formulated and relevant.

The chapter must contain theory of use for the intended study, both in terms of technique and method. If a final thesis project is about the development of a new search engine for a certain application domain, the theory must bring up related work on search algorithms and related techniques, but also methods for evaluating search engines, including performance measures such as precision, accuracy and recall.

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Having found a relevant article one can use the function for viewing other articles that have cited this particular article, and also go through the article's own reference list. Among these articles on can often find other interesting articles and thus proceed further.

It can also be a good idea to consider which sources seem most relevant for the problem area at hand. Are there any special conference or journal that often occurs one can search in more detail in lists of published articles from these venues in particular. One can also search for the web sites of important authors and investigate what they have published in general.

This chapter is called either *Theory, Related Work*, or *Related Research*. Check with your supervisor.

3 Data

4 Method

5 Results

6 Discussion

6.1 Results

6.2 Method

6.3 The work in a wider context

7 Conclusion

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] 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.

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

[9] 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.