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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.

Acknowledgments

Acknowledgments.tex

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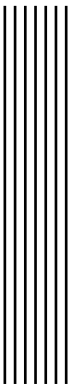

Acronyms

AC Alternating Current. 3

GBCO Gate Bias Cycled Operation. 3

Hz Hertz. 6

mA miliamperes. 5

PLSR Partial Least Squares Regression. 3

ppm parts per million. 5

SAS Sensor and Actuator Systems. 5

SCR Selective Catalytic Reduction. 2, 3

SiC-FET Silicon Carbide Field Effect Transistor. 3, 5

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

2.1 Principal Component Regression

It is often the case that the number of inputs is large and highly correlated. This often leads to obstacles in analysis and interpretation. A

2.2 Partial Least Squares Regression

2.3 Ridge Regression

3 Data

The data was acquire at the Sensor and Actuator Systems (SAS) laboratory at Linköping University. The experiment — as shown on Figure 3 — consisted of exposing different gas combinations to the SiC-FET sensor under a certain frequency cycle and recording its response, measured in miliamperes (mA). The is then used to extract secondary features, namely average and slope values from certain regions of the frequency cycle.

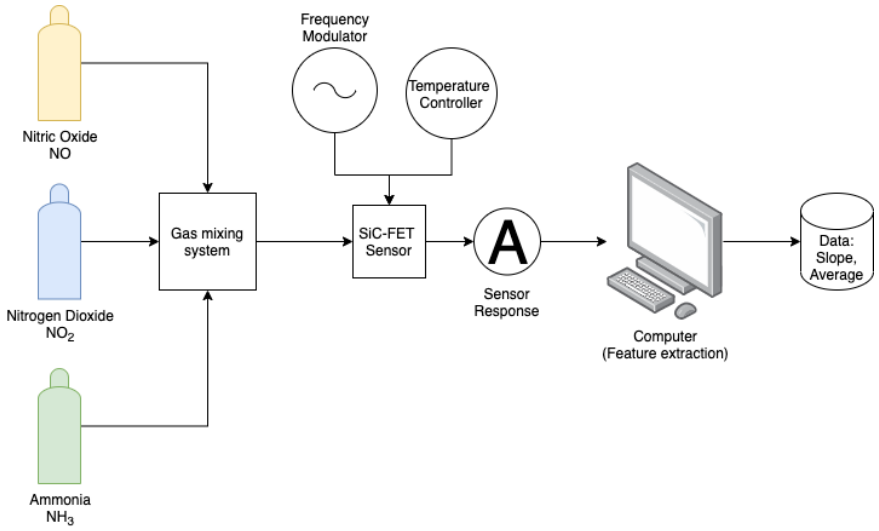

Figure 3.1: Schema of the data acquisition process.

In more detail, NO, NO_2 and NH_3 had five possible concentration values each: 10, 20, 40, 80 and 160 parts per million (ppm). The experiment was designed to encompass all possible combinations of these gasses, which totals to 125 different gas mixtures. Each feature was submitted to the same frequency cycle five times. The cycle consists of 16 unique frequencies: 0.05, 0.1, 0.25, 0.5, 1, 2, 5,

10, 25, 50, 100, 200, 500, 1000, 2500 and 5000 Hertz (Hz). A typical raw sensor response is shown on Figure 3 .

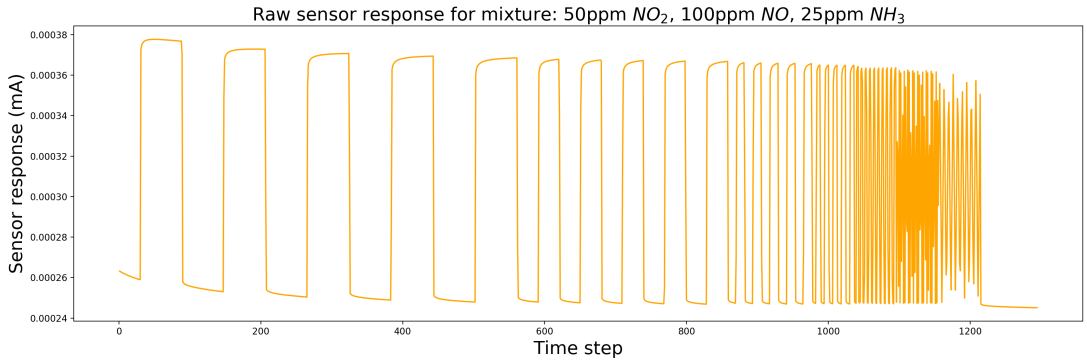

Figure 3.2: An example of row sensor response

For each frequency in each cycle, two slope and two average features were extracted. Finally, all 125 gas mixtures were subjected to the experiment three times, each time at a different temperature. Table 3.1 summarizes the data acquisition details.

Parameter	**Value**
Factors (gases)	3
Levels (concentrations)	5
Frequencies	16
Features per frequency	4 (2 slopes and 2 averages)
Features per cycle	64
Number of cycles	5
Data points per mixture	320
Number of mixtures	125
Datapoints per experiment	40.000
Number of experiments	3
Total data points	120.000

Table 3.1: Data acquisition details

TODO: add data itself. (Fingers crossed it will be this week.)

4 Method

5 Results

6 Discussion

6.1 Results

6.2 Method

6.3 The work in a wider context

7 Conclusion

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