MULTI-FREQUENCY TEMPERATURE MODULATION FOR METAL-OXIDE GAS SENSORS

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Outline

■ Introduction

■ Experimental setup
  • Analyte selection and exposure
  • Temperature modulation profiles

■ Data analysis
  • Selectivity improvements
  • Pattern stability

■ Discussion
  • Conclusions
  • Future work
INTRODUCTION
Introduction

- Approaches to improving the selectivity of commercial MOS sensors
  - Computational
    - Transient response analysis
  - Analytical
    - Thermal desorption, chromatography, filters
  - Instrumentation
    - Temperature modulation, AC impedance

- Goals of this study
  - Study the effect of modulation frequency
  - Analyze the stability of temperature-modulated patterns
MOS transduction principle

In clean air
- Atmospheric oxygen chemisorbed on the surface
- Electronic carriers are tied, creating a potential barrier $\phi_b$
- As a result, the conductivity of the MOS decreases

In the presence of reactive gases
- Oxygen reacts and is removed from the surface
- Electrons are freed
- The conductivity of the MOS increases

Why temperature modulation?
- The stability of oxygen species ($O_{2-}$, $O^-$, $O^{2-}$) will depend on temperature
- Different gases have different optimal reaction temperatures
Temperature modulation ()

- Isothermal operation
  - Constant heater resistance
  - Constant heater voltage
- Temperature modulation
  - Operating temperature is cycled during exposure to analytes
Physical structure of the sensors

TGS 2610

FIS SB11A

Gas sensitive material

Electrodes

Heater

(Reverse side)

Substrate

Heater coil

Gas sensitive material

Lead wire

0.5 mm

0.3 mm
EXPERIMENTAL
Exposure to analytes

- **Static headspace analysis**
  - 30ml glass vial with 10 ml analytes
  - Sensor inserted through a tight aperture on the cap
  - This setup eliminates cooling effects by effluent flow

- **Analyte database**
  - Blank (air)
  - Vinegar (5% acetic acid)
  - Ammonia
  - Isopropyl Alcohol
  - Acetone

- **Data collection**
  - 10 days, 30 samples/analyte
How to test for selectivity enhancements if analytes can be discriminated isothermally?

- Each analyte is serially diluted in water until the sensor response is the same for all the analytes.
- Therefore, the concentration range is at or below the isothermal discrimination threshold at nominal temperature.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Dilution (v/v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>-</td>
</tr>
<tr>
<td>Vinegar</td>
<td>100%</td>
</tr>
<tr>
<td>Ammonia</td>
<td>28%</td>
</tr>
<tr>
<td>IPA</td>
<td>0.8%</td>
</tr>
<tr>
<td>Acetone</td>
<td>0.08%</td>
</tr>
</tbody>
</table>
**Instrumentation**

- **Data acquisition**
  - Personal computer with a data-acquisition card
  - Data generation and acquisition at 100Hz

- **Measurement**
  - Sensitive element placed in a voltage divider

- **Heater excitation**
  - Analog output generates heater voltage
  - Current-boosting with a Darlington pair
**Heater profile**

- **Isothermally**
  - Heater voltage maintained at manufacturer’s nominal value

- **Temperature-modulation**
  - SIX segments at 0.125Hz, 0.25Hz, 0.5Hz, 1Hz, 2Hz and 4Hz
  - TEN cycles per frequency

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![Heater profile graph](image-url)

The graph shows the evolution of $V_H$, $V_{TGS}$, and $V_{FIS}$ over time for different frequency segments.
ANALYSIS
Sensor response

**ISOTHERMAL**

**TEMPERATURE-MODULATION**

![Graphs showing sensor response under isothermal and temperature-modulation conditions for TGS2610 and SB11A sensors with varying output (V) for different gases (AIR, ACET, AMM, IPA, VIN) at 0.125Hz and 0.500Hz.](image-url)
Pattern analysis

- **Feature selection**
  - Sub-sampling (down to 25 features per TM pattern)

- **Dimensionality reduction**
  - Linear Discriminants Analysis (down to 4 dimensions)

- **Classification**
  - K Nearest Neighbors (k=N/Nc/2)

- **Validation**
  - 10-fold cross-validation (1 fold = 1 day)

<table>
<thead>
<tr>
<th>Freq (Hz)</th>
<th>DC</th>
<th>0.125</th>
<th>0.25</th>
<th>0.5</th>
<th>1</th>
<th>2</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>TGS2610</td>
<td>51</td>
<td>100</td>
<td>97</td>
<td>85</td>
<td>85</td>
<td>75</td>
<td>67</td>
</tr>
<tr>
<td>SB11A</td>
<td>47</td>
<td>99</td>
<td>99</td>
<td>97</td>
<td>96</td>
<td>87</td>
<td>73</td>
</tr>
</tbody>
</table>
Pattern stability

- How to measure the stability of sensor patterns over time?
  - Increasing training data (N) allows the pattern-classifier to filter out the drift
  - Larger time-stamp differences (D) between training and test data are likely to reduce pattern-classification rate

- Worst-case scenario
  - Set N=1 ⇒ pattern-classifier is trained on data from a single day

![Diagram showing training and test sets with labels N and D]
Predictive accuracy over time

(a) Raw TGS

(b) Raw FIS

A 0.125 Hz
B 0.250 Hz
C 0.500 Hz
D 1.000 Hz
E 2.000 Hz
F 4.000 Hz
Drift compensation

- Drift behavior
  - Mostly multiplicative (gain)
  - Also additive (offset)
- Compensation by normalization

\[ G_T = \frac{G_T - \min(G_T)}{\max(G_T) - \min(G_T)} \]

\[ x \times 10^{-4} \]

\[ x \times 10^4 \]
Normalized patterns

Raw TGS-vinegar

Norm TGS-vinegar

Raw FIS-ammonia

Norm FIS-ammonia
Predictive accuracy over time
DISCUSSION
Conclusions

- **Selectivity**
  - Temperature modulation increases the selectivity below the isothermal discrimination threshold

- **Information content**
  - At low frequencies: in the shape
  - At high frequencies: in the DC offset

- **Speed**
  - FIS allows for faster frequencies than TGS due to physical dimensions

- **Stability**
  - Both sensors are, unfortunately, also affected by drift
  - TGS appears to be more stable than FIS
Future work

- Study pattern stability over longer periods of time (weeks, months)
- Study pattern repeatability across nominally identical sensors
- Drift compensation by normalization with respect to a reference gas
- Merging information from multiple frequencies
- Heater resistance control as opposed to heater voltage control
- Discrimination performance with mixtures and complex odors