Atmospheric Measurement Techniques Discussions

Atmos. Meas. Tech. Discuss., author comment AC1
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Reply on RC1

Daniel Furuta et al.

Author comment on "Characterization of inexpensive metal oxide sensor performance for trace methane detection" by Daniel Furuta et al., Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2022-110-AC1, 2022

Thank you for your perceptive and thorough comments. For the most part, we agree with your notes and requests for clarification. We respond point-by-point.

- Why did the authors select a 10-kΩ voltage divider (resistor)? As shown in Figure 2, most MOx sensors had a resistance (Rs) far greater than 10 kΩ during the experiment. From a circuit standpoint, a voltage divider with resistance close to typical Rs values would make the measurement more sensitive or accurate. A relevant question is – why 10-kΩ for all sensors?

We agree that 10 kΩ may not be an optimal resistance. As Fig. 4 illustrates, we found Rs for TGS2600 and TGS2602 in the 10 to 30 kΩ; TGS2611-C00 in the 20 to 40 kΩ range, and TGS2611-E00 and MQ4 in the 40 to 125 kΩ range. We selected the voltage divider values as a best guess for a reasonable resistance from manufacturer datasheets and a quick initial test. Interestingly and, we believe, coincidentally, the measurements with the worst sensitivity (MQ4 and TGS2611-E00) showed the best performance.

Figures 2 and 4 provides enough information to pick better resistance values for future work, as they show the expected resistance ranges for the sensors in these conditions; we will add a note to this extent in the discussion.

- Figure 1: What was the inlet airflow rate? To my understanding, the LI-7810 analyzer has a sampling airflow rate of 0.25 LPM. Did this go back to the testing chamber?

As the reviewer notes, the reference instrument has a flow rate of 0.25 LPM. We had no other pump in the system, and so airflow into the test chamber was the same 0.25 LPM. The outlet of the LI-7810 was vented to the outside laboratory, causing the gradual decrease in methane concentration in the test chamber for each pulse.

- (Again) Figure 1: What was the response time of the LI-7810 analyzer, considering the length of tubing, averaging time, and so on? Did the authors synchronize the readings from MOx sensors and the LI-7810 by considering response time differences?

The reference analyzer was connected to the test chamber by a short length of small-diameter tubing. We found that the LI-7810 responded to the methane pulse injections into the test chamber within seconds. As we averaged all measurements to the minute and the pulse decay to background took place over a relatively long time scale, we

considered this error negligible and did not synchronize the readings beyond aligning system clocks for the various devices.

- (Again) Figure 1: I saw quite a few capacitors on the PCB. Please briefly explain their purpose (to avoid unnecessary confusion regarding the measurement circuit).

The capacitors in Fig. 1 (the small red and brown components seen on the PCB) were for power supply bypassing, to reduce the effect of power supply noise and to isolate the effects of any transients. As we were using a bench power supply for this experiment these components were likely unnecessary. As the reviewer suggests, the capacitors were not in the direct path of the measurement circuit.

- Please provide the ADC's bit info for LabJack T7. As per the company, a LabJack T7 may use an ADC from 12 to 24-bit. The number of bits can have a large influence on the resolution of acquired data, especially for high Rs

Our setup used the default T7 settings, which correspond to an effective bit depth of 19.1 bits, and an effective resolution of 37 μV as per the company (https://labjack.com/support/datasheets/t-series/appendix-a-3-2-2-t7-noise-and-resolution). The largest Rs we observed was less than 150 kΩ; at a 150 kΩ resistance, a 37 μV change corresponds to a resistance change of around 0.013%. We believe that errors due to ADC resolution are likely insignificant compared to the uncertainty of the sensor itself, and likely even compared to overall electrical system noise.

As our measurements were also averaged to a longer time scale for analysis (from approximately one reading every five seconds to the minute scale), the actual accuracy may be somewhat better than this simple calculation.

- Line 149: Vs is a bit misleading. It is the voltage drop across the 10-kΩ voltage divider instead of the sensor (Rs). I suggest the authors use a different subscript.

We agree; V_{OUT} would be more suitable.

- Equation 2: Even though the sensors are heated, they still suffer from temperature variation, which in turn would influence the sensors' resistance. That being said, why was temperature not included in the calibration equation?

Due to limitations of our experimental setup, temperature and absolute humidity were highly correlated (Pearson's r = 0.95, see Fig. 3). Accordingly, to avoid a non-generalizable improvement in R^2 we chose to only include one of the two in our calibration equation, selecting absolute humidity for the stated reasons. As you correctly note, ambient temperature will also have an effect on sensor response. As we mentioned in our manuscript, these effects will need to be untangled in future work, and this should be a priority for further calibration work using these sensors.

- Figure 2: A side note – The highest Rs we observed for TGS2600 at ~2 ppm was close to 800 kΩ. That was achieved by filtering out all VOCs and water vapors.

Thank you for the interesting note. This very high resistance likely emphasizes further the importance of environmental conditions in the sensor response (as compared to 10 to 30 kΩ we found in normal humidity levels).

- Line 187: As per Figure 2, the relative humidity decreased with an increase in temperature. To me, this is related to the temperature dependency of vapor pressure. I would suggest the authors remove "likely as the result of a condensation and evaporation cycle."

We agree that this effect is responsible for some of the change in relative humidity. However, we also saw a cycle in absolute humidity levels along with temperature. We believe this was the result of some moisture condensing on and evaporating from the walls of the test chamber as the temperature cycled.

- Line 195-196: I suggest the use of r instead of R for Pearson's correlation coefficients, to avoid unnecessary confusion (R versus R2).

We agree.

- Figure 4: Were all the three sensors of the same model coming from the same batch of products? Different batches of sensors could differ in response factors.

The Figaro sensors of each type were taken from the same batch. The MQ4 does not appear to have a batch code printed on it; the MQ4 sensors were ordered from the distributor at the same time, but they were individually packaged and so we are unsure whether they were from the same batch. This could be a possible influence on the greater variability for the MQ4 than for the Figaro sensors. We agree that evaluating the sensors for batch-to-batch consistency can be an important addition to future work.

- I would suggest the authors offer a discussion about the potential application scenarios of those CH4 sensors for ambient air and source measurement towards the end of the manuscript.

Thank you for this suggestion. Other reviewers mentioned the same issue. Prior to the preprint we revised the discussion section to emphasize this important question. In particular, we believe some of these sensors may be usable as-is for natural gas leak detection in urban areas or around fossil fuel infrastructure; it is also possible that more sophisticated algorithms or system design that reduces environmental influences may allow ambient air measurement around atmospheric levels.

- A final thought: As per the Figaro Company, the TGS26XX sensors' response is nearly linear (Rs/R0 versus gas concentration) on a log-log graph. I just feel there could be a calibration equation better fitting the experimental data than equation 2. Here comes a question – why was general linear regression used to build the calibration curve?

We did try fitting log-transformed data, and did not find meaningful performance improvement. The manufacturer curves for most of the sensors (excepting TGS2600) lack data in the methane concentration range we examined; possibly the sensor response in this very low range (relative to design parameters) is not linear.

We agree that Equation 2 is a crude calibration equation, and we do not propose it as necessarily the best option for a sensing system using these sensors. As our goal was to compare these devices and their sensitivity to environmental conditions, we thought a simple linear model was suited to roughly evaluating sensor response to methane and humidity/temperature, while being relatively robust with a low risk of overfitting. For real-world use, a more sophisticated model (whether non-linear regression, machine learning, or something else) might provide better performance, but we think it unlikely that a better algorithm will upend the relative performance of these sensors.

As we note in Section 4.1, our RMSE and R^2 values are similar to those found in some previous studies. Two previous studies found better error values for TGS2600. Riddick et al. (2020a) had uncertainty of 0.01 ppm, but only an R^2 of 0.23 for their best model, as compared to our R^2 of 0.16. Collier-Oxendale et al. (2018) also found good performance for TGS2600 in a field study with more sophisticated algorithms, but found different algorithms to perform better at their two sites - due to the complexities of real-world

deployments, there may be more influence from site-specific effects or overfitting than in our relatively controlled laboratory environment. Although we agree with the reviewer that more sophisticated algorithms could perform better, we feel that the general “ballpark” agreement of our results with previously published work supports our overall conclusions.