Method of Experimental Evaluation of MOx Sensors for Real-Time Indoor VOCs Monitoring

Xin Guo[1], Bing Beverly Guo[1], Zhenlei Liu[1,2], Jialei Shen[1], Daniel Love[3], Peter J. McKinney[3], and Jianshun "Jensen" Zhang[1](✉)

[1] Syracuse University, Syracuse, NY 13244, USA
jszhang@syr.edu
[2] Oak Ridge National Laboratory, Oak Ridge, TN 37830, USA
[3] Carrier Corporation, Syracuse, NY 13057, USA

Abstract. This study is specifically aimed at evaluating commercially available metal oxide (MOx) sensors for real-time monitoring of volatile organic compounds (VOCs) in typical indoor environments. To evaluate MOx sensors' performance, we used a 50 L environmental chamber system to provide a well-controlled testing environment. The VOC types and test concentrations were based on relevant indoor air quality (IAQ) standards and guides in the literature. Test VOCs included toluene, formaldehyde, m-Xylene, phenol, benzene, naphthalene, acetaldehyde, acetone, dichloromethane, tetrachloroethylene, 1,1,1-trichloroethane. The evaluation tests are categorized into individual VOC tests, mixture VOCs tests, temperature and relative humidity dependence tests, short-term stability tests, and long-term drifting tests to investigate the sensitivity to specific VOC, mixture co-influence under realistic condition, moisture compensation, and reliability. This paper focuses on the procedures and results of the toluene test, identifying necessary improvements in the algorithm through comparisons between raw signals and TVOC readings. Results of this study will help provide guidance on the selection and utilization of MOx VOC sensors for VOC monitoring and IAQ control.

Keywords: VOC Sensors · Metal Oxide · Evaluation Approach

1 Introduction

There are two main approaches for evaluating volatile organic compound (VOC) sensor performance: field evaluations and laboratory evaluations [1]. In order to provide a well-controlled environment for assessment, this paper focuses on evaluating metal oxide (MOx) sensors' performance based on the laboratory evaluation method, which is crucial for clearly understanding. In laboratory evaluations, ISO 16000-29 [2] defines two categories: one for specific VOC detection and the other for VOC mixtures. The standard covers various detection types, including semiconducting (MOx sensor included), PID, and interference-enhanced reflection-type detectors. Considering the diverse in operating principles of VOC sensors, the variation in VOC types and concentrations across different indoor environments, as well as the intricate response relationships during

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monitoring, it becomes important to devise evaluation methods tailored to these distinct principles and applications. Such an approach is pivotal for advancing the enhancement and development of low-cost VOC sensors. This study zeroes in on the laboratory evaluation method for MOx sensors in real-time indoor VOC monitoring, with particular emphasis on test types, procedures, and evaluation parameters.

2 Unique Aspects

Metal oxide semiconductor (MOx) sensors are conductometric (resistive) type devices where changes in the electrical conductivity of the sensitive element correspond to VOC concentrations [3]. When evaluating MOx sensors for indoor VOC monitoring, several unique aspects merit attention.

Firstly, the effect of relative humidity (RH) on MOx sensors is crucial as water vapor significantly affects the MOx sensor's response. Water molecules are absorbed at the surface and abruptly change the properties of the gas-sensitive material. The adsorption of water at temperatures below 150 °C is attributed to physisorption or hydrogen bonding. At high temperatures (150–500 °C) the literature proposes various possible mechanisms behind the surface conductivity changes in the presence of water vapor. One such mechanisms suggests that the OH^- side of water molecule can react with the lattice oxygen from the Lewis base or with oxygen adsorbed on surface. This mechanism involves the release of electrons (e^-). As a result, the changes of conductivity produced by the sensor are affected [4, 5]. ISO 16000-29 [2] suggests maintaining RH within 10% during each test.

Secondly, in individual VOC tests, evaluating the common types and concentrations of VOCs is vital. The concentration levels should reflect those typically encountered in real indoor environments and should not be excessively high. Additionally, there should be an increased emphasis on monitoring harmful VOCs.

Thirdly, regarding the mixture test, ISO 16000-29 [2] categorizes it into two types: one involving a mixture of n-octane and xylene and another comprising a six-VOC mixture test (from different categories). From an application perspective, the evaluation performance tests should add additional mixed VOC tests. The two-VOC test should assess responses to VOCs from both different and the same categories to test if the sensor responses are simple additive. For tests involving more VOC types, consideration should be given to common VOCs in real indoor air environments, such as BTEX compounds (benzene, toluene, ethylbenzene, and xylenes) [6, 7]. The next step involves evaluating various types, concentrations, and percentages of VOCs specific to different indoor environments.

Fourth, ISO 16000-29 [2] mentions using gas cylinders to generate VOCs, which is an effective method. Alternatively, employing a Dynacalibrator with calibrated permeation tubes for VOC emission is viable. This approach will be detailed later in this paper.

3 Sensor Test Methods

3.1 Sensor Test Environments

The 50L chamber used for testing maintained well-controlled conditions of temperature, humidity, and tested VOC concentration by regulating the flow rate of clean air. As shown in Fig. 1, the air flows from a compressed air source, passes through the pressure regulator and various air filters, which can filter organic particles, organic chemical compositions, and other pollutants. The Dynacalibrator, produced by VICI metronics, Inc., served as a stable VOC injection source for chamber [8], with the emission rate adjustable through temperature and flow rate control.

All the individual and mixing tests were conducted at a temperature of 23 ± 1 °C and a RH of 30% ± 5% which are within the recommended range of ISO 7267 (±5 °C and ±10% respectively) [2].

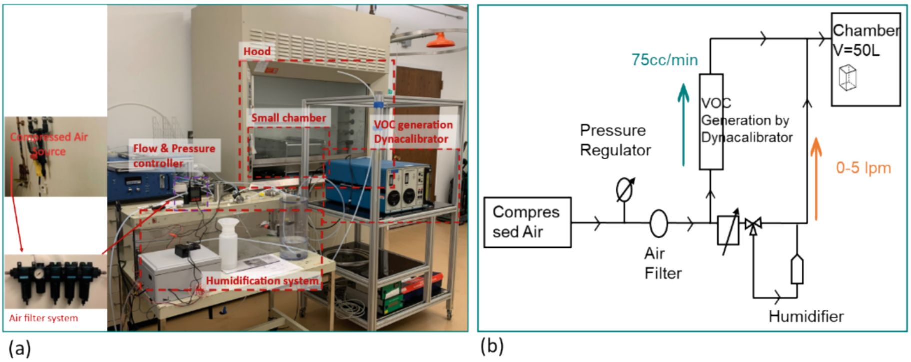

Fig. 1. (a) the scheme of test system. (b) the photo of the test system.

3.2 VOCs Selection and Their Target Concentrations for Testing

To better assess sensor performance, 11 selected VOCs were chosen for evaluating the performance of MOx sensors, and the properties of these 11 VOCs are detailed in Table 1 [9–12]. The selection of these 11 VOCs is based on their potential impact on human exposure and health impact. For example, formaldehyde is emitted from building materials and furniture and most clearly associated with asthma; benzene is another common VOC from office equipment associated with adult asthma. The design target concentrations (DTCs) were determined based on threshold values from World Health Organization (WHO), Office of Environmental Health Hazard Assessment (OEHHA), ANNEX 68 ELV, BIFMA M7.1-2010, and Agency for Toxic Substances and Disease Registry (ATSDR). Based on their molecular weight (MW), these VOCs can be roughly divided into three groups: light compounds (acetaldehyde with a MW of 44.05 g/mol, and formaldehyde with a MW of 30.03 g/mol), medium weight compounds (acetone, benzene, dichloromethane, phenol, toluene, m-Xylene), and heavy compounds (naphthalene with a MW of 128.17 g/mol, tetrachloroethylene with a MW of 165.82 g/mol, and 1,1,1-trichloroethane with a MW of 133.4 g/mol).

Table 1. Eleven selected VOCs for evaluating performance of MOx sensors.

VOC compound	CAS No.	MW g/mol	BP °C	TV μg/m3	DTC μg/m3	Source
Acetaldehyde	75-70-0	44.05	20.2	140	140	C
Acetone	67-64-1	58.08	56.1	70,000[a]	1200	CP, HB
Benzene	71-43-2	78.11	80.1	3	3	OE
Dichloromethane	75-09-2	84.93	39.6	400	400	OA
Formaldehyde	50-00-0	30.03	−19	9	33	BM, F
Naphthalene	91-20-3	128.17	217.9	9	9	BM, F, CWC
Phenol	108-95-2	94.11	181.7	200	10	OE
Tetrachloroethylene	127-18-4	165.82	121.1	35	35	CP
Toluene	108-88-3	92.14	110.6	300	300	F
1,1,1-trichloroethane	71-55-6	133.4	74	1,000	1000	CP
m-Xylene	108-83-3	106.16	138.5	700	500	F

Note: (1) a, acute; (2) molecular weight (MW), boiling point (BP), threshold values (TV); (3) combustion (C), building materials (BM), furniture (F), cleaning products (CP), human being (HB), office equipment (OE), outdoor air (OA), combustion of wood and coals (CWC)

3.3 Test Conditions and Procedures

For a thorough evaluation, the testing protocol should encompass individual VOC tests, mixed VOCs tests, assessments of temperature and relative humidity dependence, short-term stability tests, and long-term drift tests. Taking the individual toluene test as an example, this assessment includes both steady-state and transient tests. The transient test further encompasses both the increasing and decreasing phases.

Individual VOC Test. As shown in Fig. 2, in the individual VOC test, background was monitored prior to injection and after sensor has been exposure to high VOC concentration for checking the cleanness of chamber before and after VOC injection and investigate the impact on sensors' performance after exposure to high VOC concentration. A high concentration condition, low concentration condition, and background condition were tested for the sensors' performance to specific VOCs and concentrations. A second low concentration test was conducted after the second background monitoring to investigate the repeatability after exposure to high concentration. The results from one sensor are shown in Fig. 3, suggesting that the algorithm needs improvement, and a nonlinear relationship between the raw signal and toluene concentration. Each test included the following steps.

1) Warm up: Power on the sensors. Mark the time as Time Zero (t = 0) when VOC readings of all the sensors are stable under the background condition.
2) Start the test at t = 0.
3) Background monitoring: Record data for 3 h under background condition.

4) Low concentration test: Start toluene injection at t = 3 h. Wait 3 h for it to reach a steady state.
5) High concentration test: Change the air flow rate of mixing air branch where the humidifier is located, from 0.25ACH to 1ACH. Then wait 12 h. Record data for 3 h (t = 21 to 24 h) under high concentration.
6) Residual monitoring: Stop VOC injection at t = 24 h. And use 3 ACH flow rate to flush the chamber. Keep sensors under the background VOC condition for 3 h (t = 25 to 28 h).

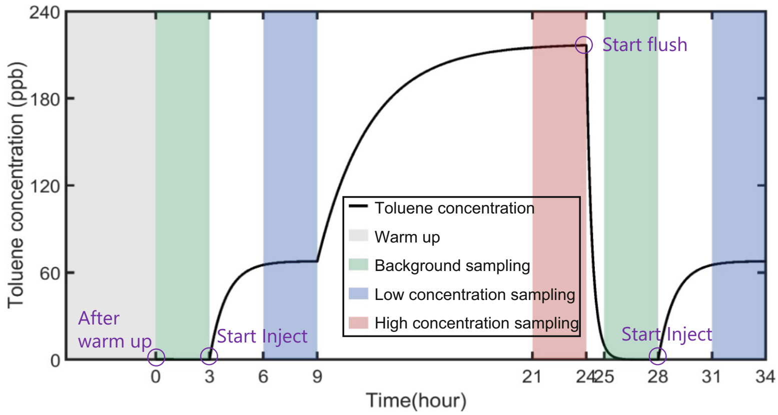

Fig. 2. Test procedure and the target Toluene concentrations in the chamber.

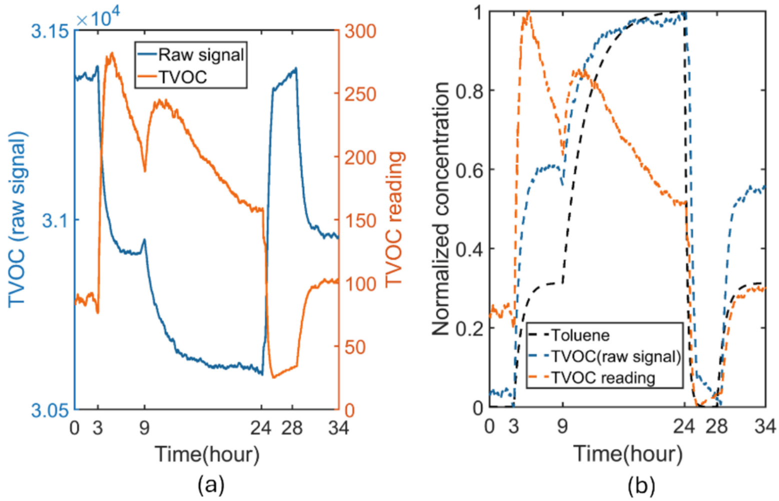

Fig. 3. (a) TVOC raw data with a 5-min moving average and TVOC reading from a sensor in toluene test. (b) Normalized toluene concentration in the chamber, with raw signal and TVOC readings. Normalized TVOC readings are calculated by (reading – min)/(max – min). Normalized TVOC raw signals are calculated as 1 - (reading – min)/(max – min).

7) Repeatability check: Repeat test of low VOC concentration.

4 Conclusions

The current evaluation methods for MOx sensor monitoring of indoor VOCs require enhancements, including the measurement of specific VOC types, concentration levels, and testing conditions. This paper has proposed a comprehensive testing methodology tailored to the sensor's operational mechanism and the VOC types and concentrations typical of indoor environments, exemplified through an individual VOC test. By analyzing both raw signals and TVOC readings, we have identified areas where the algorithm could be improved. Further discussions will continue to refine the test method to help develop more reliable low-cost VOC sensors.

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References

1. Duvall, R., Clements, A., Green, D., Dye, T.: Enhanced air sensor guidebook, pp. 1–195 (2022)
2. ISO. International Standard International Standard. 61010-1 © Iec2001 2003, vol. 13 (2003)
3. Pathak, A.K., Viphavakit, C.: A review on all-optical fiber-based VOC sensors: heading towards the development of promising technology. Sens. Actuat. A Phys. **338**, 113455 (2022)
4. Tomić, M., Šetka, M., Vojkůvka, L., Vallejos, S.: Vocs sensing by metal oxides, conductive polymers, and carbon-based materials. Nanomaterials **11**, 1–34 (2021)
5. Barsan, N., Weimar, U.: Conduction model of metal oxide gas sensors. J. Electroceramics **7**, 143–167 (2001)
6. Bhoonah, R., Maury-Micolier, A., Jolliet, O.: Integrated empirical and modelled determination of the human health impacts of building material VOCs. Build. Environ. **242**, 110523 (2023)
7. Felgueiras, F., Mourão, Z., Moreira, A., Gabriel, M.F.: Indoor environmental quality in offices and risk of health and productivity complaints at work: a literature review. J. Hazard. Mater. Adv. **10**, 100314 (2023)
8. Xu, J., Zhang, J.S.: An experimental study of relative humidity effect on VOCs' effective diffusion coefficient and partition coefficient in a porous medium. Build. Environ. **46**, 1785–1796 (2011)
9. Norwood Brown. New small, low-power MOX VOC sensors: how might they be used for indoor air quality monitoring? https://cdn-learn.adafruit.com/assets/assets/000/047/742/original/ATA1701_VOCs_and_IAQ_FINAL_ENG-wp.pdf?1509307332. Accessed 11 Aug 2024
10. Jia, C., Batterman, S.: A critical review of naphthalene sources and exposures relevant to indoor and outdoor air. Int. J. Environ. Res. Public Health **7**, 2903–2939 (2010)

11. Nicole, N., Loh, M., Harrison, P.: Tetrachloroethylene. WHO Guidel. Indoor Air Qual. Sel. Pollut. (2010)
12. Zhang, J.J., Chen, W., Liu, N., Guo, B.B., Zhang, Y.: Testing and reducing VOC emissions from building materials and furniture. Handbook of Indoor Air Quality (2021). https://doi.org/10.1007/978-981-16-7680-2_53