2021

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ABSTRACT

Owing to concerns about climate change, many jurisdictions are phasing out high global warming potential refrigerants in HVAC&R systems. Their near-term replacements are class A2L (mildly-flammable) refrigerants. Area monitoring detectors will be required for most future residential, commercial, and industrial HVAC systems that use these refrigerants. UL Standard 60335-2-40 requires these detectors to have a set-point of 25% of the lower flammability limit (LFL) and to detect the set-point within 10 s when exposed to a gas mixture at the LFL. Inexpensive detectors that meet these requirements do not exist, which has delayed the adoption of A2L refrigerants. A technology with good potential is based on metal-oxide semiconductors (MOS). MOS detectors are tested here, considering their response to leaks of R-32 and R-454B. They are characterized here for their sensitivity, response time, false alarms from contaminants, and poisoning. The sensors have good sensitivity with a steady-state output that is linear with respect to the logarithm of concentration. The sensors fail narrowly to meet the 10 s response time requirement for both R-32 and R-454B. The sensors do not alarm when exposed to the contaminants in the standard. However, several of the contaminants do poison the sensors, at least temporarily.

1. INTRODUCTION

To reduce global warming, several states and countries have passed laws requiring refrigerants with low global warming potential (GWP) in heating, ventilation, air conditioning, and refrigeration (HVAC&R) systems. For example, California will ban the use of refrigerants with GWP 750 and higher in new residential HVAC&R systems in 2025, while commercial and industrial systems will be limited to GWP 150 [1]. Currently hydrofluorocarbons (HFCs) are the most common refrigerants used in these systems and these typically have GWPs above 1000 [2]. The likely replacements are generally mildly flammable HFCs or hydrofluoroolefins (HFOs), both of which are class A2L refrigerants. These refrigerants have GWP values between 1 – 675 [2], but are mildly flammable [3-5].

For residential HVAC systems the adoption of A2L refrigerants will require area monitoring sensors that are able to quickly detect leaks without false alarms. Many sensors exist, but most are too slow or costly for residential applications [6,7]. Furthermore, it is unclear if existing sensors can meet the desired service interval of 5 years (15 years preferred). UL standard 60335-2-40 [8] requires these sensors to alarm at a set-point of 25% of the lower flammability limit (LFL) and to alarm within 10 s when exposed to a gas mixture at the LFL. The standard also requires sensors not to alarm when exposed to a prescribed list of possible contaminants, and that the sensor state-of-health be maintained.

A leading sensor technology for this application involves metal-oxide semiconductors (MOS). These sensors are widely used for other applications, have long lifetimes, and are relatively inexpensive [6,7]. However, they have not been fully characterized for A2L refrigerants.

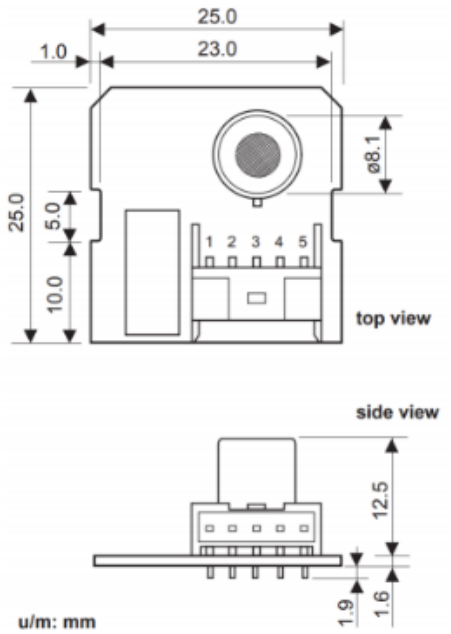
The objective of this research is to evaluate the suitability of MOS sensors for R-32 and R-454B in residential HVAC systems.

2. EXPERIMENTAL

2.1 Sensors

The Figaro FCM2630-C00 detector [9,10] was selected for this study because it has the widest detection range of any MOS sensor for refrigerants and a price of approximately US$ 50. Its dimensions are 25 × 25 × 17 mm and its mass is 4 g. Figure 1 shows its schematic and pinout. For this study the excitation, V_c, was maintained at 5.0 ± 0.5 VDC. The sensor output is V_{out} . The reference voltage, V_{REF}, is 3.8 VDC and is the default alarm set-point with the intention that an alarm is indicated when $V_{out} > V_{REF}$., i.e., when exposed to 5000 ppm or higher of R-32 [9]. This is lower than 25% of the LFL, which has become the standard alarm set-point. In steady state the refrigerant concentration correlates with the difference $\Delta V = V_{REF} - V_{out}$.

The sensors were connected to a power supply (for excitation and ground) and to the analog inputs of a data acquisition (DAQ) system (for V_{out} and V_{REF}). A manual switch connected a 5 VDC terminal on the power supply to an analog input on the DAQ and was toggled at the instant when the sensor was exposed to refrigerant or contaminant. Figure 2 shows the wiring schematic.



Pin No.	Name	Description
1	Vc	Circuit voltage
2	Vout	Output voltage
3	VREF	Reference voltage
4	-	-
5	GND	Common ground

Figure 1: Figaro FCM2630-C00 schematic and pinout [9].

2.2 Apparatus

An apparatus was constructed to expose the sensors to known gas compositions. Many of these tests involved a steady flow rate of a mixture of refrigerant and air at a known composition. The air and refrigerant flow rates were controlled with needle valves and measured with calibrated rotameters. They were fully mixed before entering the test vessel. The temperature of the refrigerant was monitored to ensure it remained at laboratory temperature. Downstream of the rotameters the two gas streams were merged before they flowed into the test vessel. The discharge from the test vessel was directed into a fume hood. The image and schematic of this apparatus is shown in Fig. 3.

The test vessel used was a 500 mL Nalgene bottle made of tritan copolyester. Holes drilled in the top and bottom and sealed to tubes allowed gas inflow and outflow. A 20 mm plunge hole was drilled into the side of the vessel to admit the sensors. Duct tape covered the plunge hole prior to each test. Additional details are provided in Wack [11].

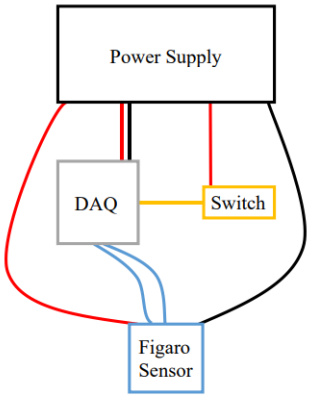


Figure 2: Wiring schematic.

2.3 Effects of Humidity

These sensors respond to changes in humidity. When a sensor was plunged from laboratory air (with a measured relative humidity of 50% RH) into dry air flowing from a compressor (with a relative humidity of 0% RH), V_{out} increased by 0.3 V as seen in Fig. 4a. When it was plunged from laboratory air into moist air (previously bubbled through water to obtain 95% RH), there was no such increase, see Fig. 4b. To avoid this spurious signal in subsequent tests, air at 95% RH was used throughout.

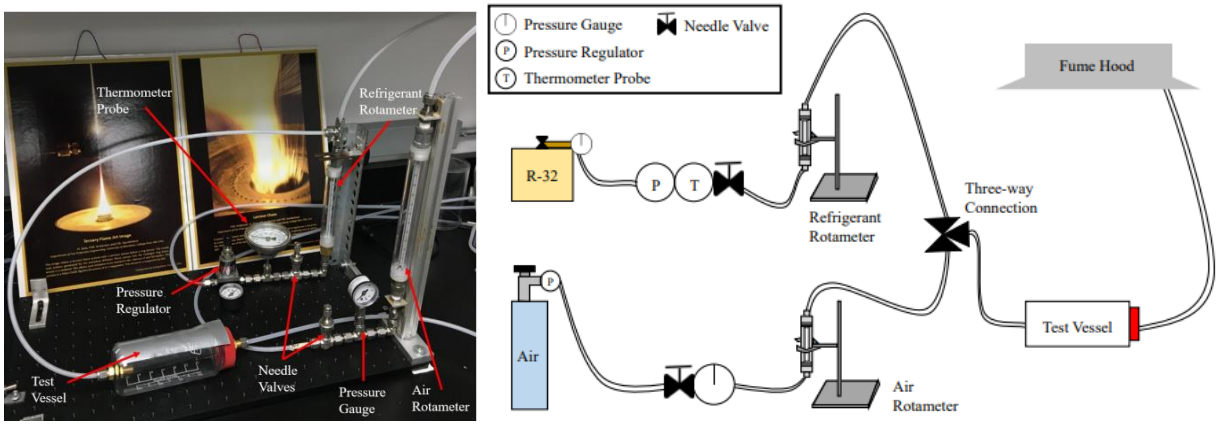


Figure 3: Test apparatus image and schematic.

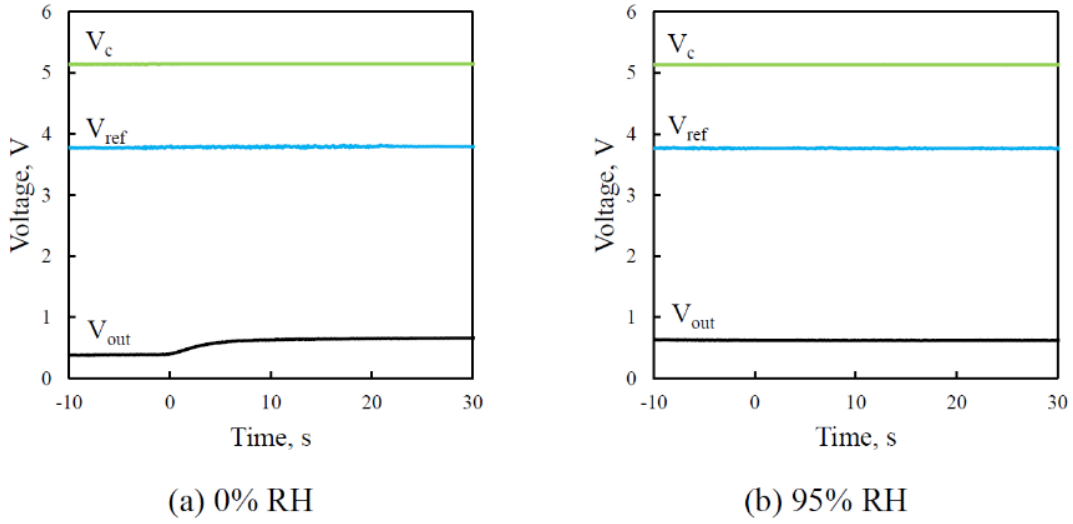


Figure 4 (a): 0% RH sensor response and **(b)**: 95% RH sensor response.

3. RESULTS

3.1 Refrigerant Plunge Tests

For refrigerant plunge tests the vessel was filled with mixtures of refrigerant and moist air. These were performed at various fractions of the LFLs, which are 14.4 vol % for R-32 [12] and 11.25 vol % for R-454B [13]. A sensor was plunged into the vessel and its output was recorded with the DAQ until V_{out} became steady. The sensor was then removed to laboratory air for at least 30 minutes for recovery.

Figure 5 shows the steady-state sensor output for R-32 and R-454B plunge tests at various refrigerant concentrations. The correlations are nearly identical for the two refrigerants. The measurements are reasonably fit with the logarithmic functions shown. The output sensitivity decreases with increasing

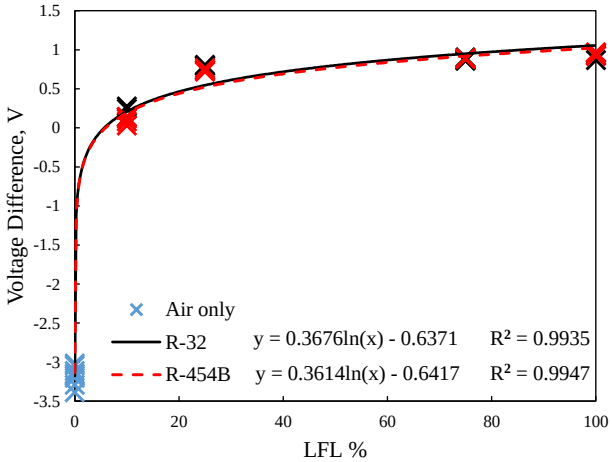


Figure 5: Voltage difference ΔV (i.e., $V_{REF} - V_{out}$) for various concentrations of R-32 and R-454B.

refrigerant concentration but is reasonable for the entire range of 0 – 100% LFL.

Figure 6 shows the sensor outputs versus time for representative plunge tests into mixtures at their LFLs. Horizontal lines show the steady-state outputs at 10% and 25% of LFL from Fig. 5.

The tests of Fig. 6 allow the sensor time constant, τ, to be found from fits to the measurements in the form of

$$\exp(-t/\tau) = (\Delta V - \Delta V_\infty)/(\Delta V_0 - \Delta V_\infty), \quad (1)$$

where t is time and subscripts 0 and ∞ denote times before the plunge and in steady state. These time constants, with their 95% confidence intervals (CI_{95}), are shown in Table 2. Although these time constants are short, as desired, quantity τ is not used by standards to qualify sensors for area monitoring.

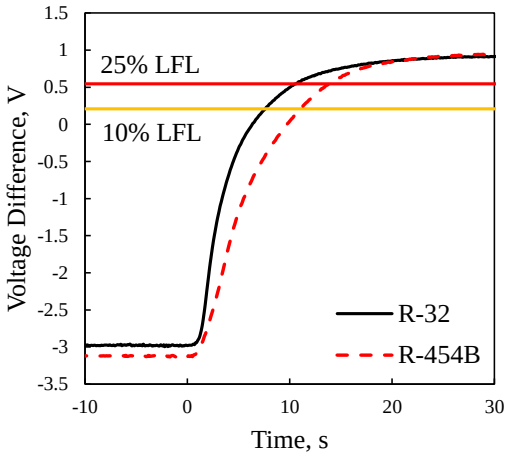


Figure 6: Voltage difference ($V_{REF} - V_{out}$) for R-32 and R-454B plunge tests at 100% LFL.

The leading standard for such qualifications is UL 60335-2-40 [8]. Annex LL of this standard requires that, when plunged into a mixture at the LFL, the sensor alarm within 10 s. This alarm is defined as producing an output equivalent to its steady output at 25% of the LFL, thus it is denoted t_{25} here. As shown in Table 2, these sensors fail to meet the t_{25} requirement of 10 s or less.

Table 2: Summary of plunge tests at 100% LFL.

Refrigerant	Number of trials	$\tau \pm CI_{95}$ s	$t_{25} \pm CI_{95}$ s	$t_{10} \pm CI_{95}$ s
R-32	3	4 ± 2	19 ± 10	8 ± 2
R-454B	4	5 ± 0.5	17 ± 2	10 ± 2

Owing to this, a different sensor response when plunged into a mixture at the LFL was considered. Denoted t_{10} here, this is the time for the sensor to produce an output equivalent to its steady output at 10% of the LFL. As shown in Table 2, the sensors do have t_{10} times of 10 s or less. This implies that setting their alarm threshold at 10% of the LFL would produce an alarm within 10 s when plunged at the LFL. Unfortunately this modification will not satisfy UL 60335-2-40, and it could lead to more common false alarms.

3.2 Contaminant Tests

UL 60335-2-40 Annex LL [8] contains a list of contaminants and their mole fractions in air, X, to which a sensor must be exposed. This list is reproduced in Table 3. The last row in the standard is Silicone at 100 ppm, for which the last two compounds in Table 3 were selected.

Table 3: Summary of the contaminants and their test results.

Contaminant	Formula	X ppm	t_e min	Deteriorated Health?
Methane	CH_4	500	17	Y
n-Butane	C_4H_{10}	300	10	Y
n-Heptane	C_7H_{16}	500	10	Y
Ethyl acetate	$C_4H_8O_2$	200	10	N
Isopropyl alcohol	C_3H_8O	200	10	Y
Carbon dioxide	CO_2	5000	10	Y
Ammonia	NH_3	100	10	N
Ethanol	C_2H_5OH	200	10	Y
Toluene	C_7H_8	200	55	Y
Trichloroethane	$C_2H_3Cl_3$	200	120	N
Acetone	C_3H_6O	200	10	Y
Octamethylcyclo-tetrasiloxane	$C_8H_{24}O_4Si_4$	100	10	N
Decamethylcyclo-pentasiloxane	$C_{10}H_{30}O_5Si_5$	100	17	Y

UL 60335-2-40 requires that upon exposure to the contaminants in Table 3 a sensor "shall not indicate presence of refrigerant concentration above the set-point." This set-point is 25% of the LFL.

For each test a sensor was powered up for at least 1 hour and then installed in the vessel with moist air flowing for at least 1 min. For each gas in Table 1 (methane, butane, carbon dioxide, and ammonia), the contaminant flow rate was measured with a rotameter and added to the air stream such that the gases were fully mixed before entering the test

vessel. The other contaminants were liquids. For these vapor was obtained by bubbling nitrogen through a 500 mL filtering flask on a load cell. The evaporation rate was measured with the load cell. The vapors were then fully mixed with air before entering the test vessel. The flow rate of the mixture of air and contaminant was 1.1 – 2.6 LPM [11].

For most tests ΔV became constant and the test was stopped after an exposure time, t_e, of 10 minutes. For some tests ΔV continued to rise after 10 min so the exposure time continued until a plateau was reached. The exposure times are shown in Table 3.

Figure 7 summarizes the contamination tests. The sensor had the strongest response to *n*-butane and the weakest response to isopropyl alcohol. Although ΔV increased upon exposure to each contaminant, it never approached the set-point of 25% of the LFL, i.e., 0.55 V. Therefore these sensors satisfy the requirements of UL 60335-2-40 for false alarms from contaminants.

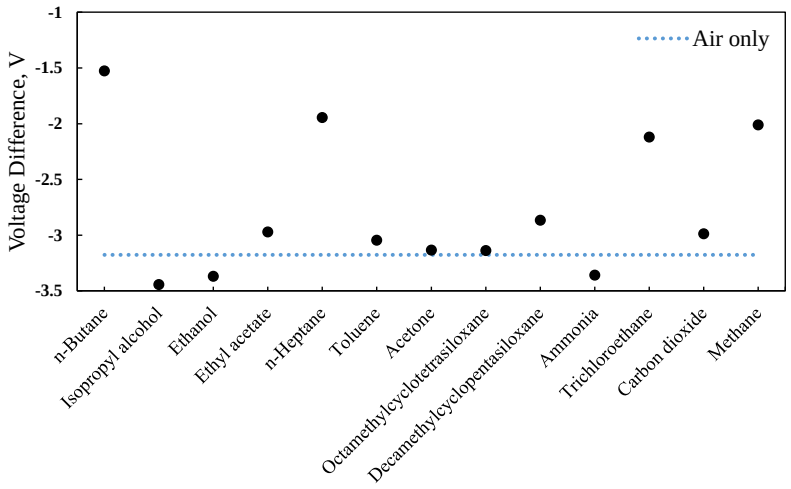


Figure 7: Steady-state ΔV for contaminants at the concentrations shown in Table 3 and in the order tested.

A state-of-health test was performed on each sensor soon after each contaminant test according to UL 60335-2-40 [8]. This involved a test like that of Fig. 6 to identify the t_{10} response time. The sensor health was considered to be deteriorated if and only if this time exceeded 10 s. These tests are summarized in Fig. 8. As shown in Fig. 8 and Table 3, only for four of the contaminants was the state-of-health maintained.

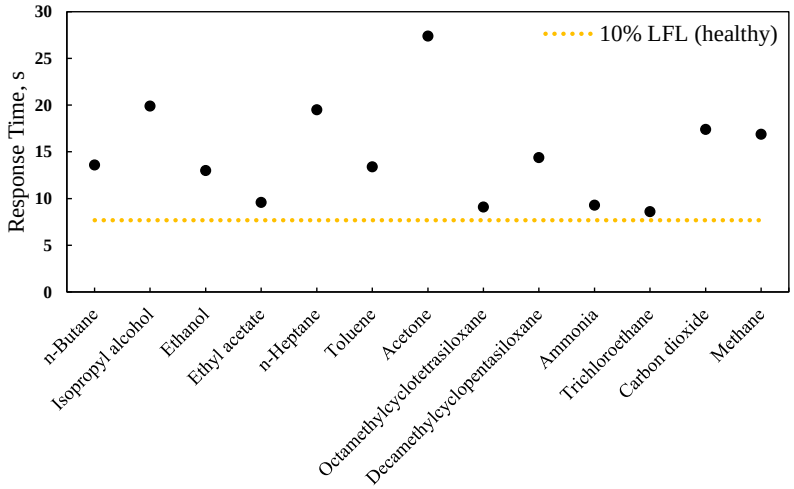


Figure 8: Sensor t_{10} response times following each contaminant test in the order tested.

Additional state-of-health tests were performed after 24 hours with the sensor in air. These tests indicated that in most cases the sensors recovered their initial state-of-health.

CONCLUSIONS

MOS sensors were tested to characterize their response times to R-32 and R-454B, and their response to contaminants, according to UL 60335-2-40. The main findings are as follows.

1. These sensors do not meet the requirement for alarming within 10 s that the set-point (25% of LFL) was reached when plunged into a refrigerant-air mixture at the LFL. Instead, the mean t_{25} response time was 18 s. However the sensors did satisfy this requirement for a set-point of 10%. This set-point does not satisfy the standard and would likely increase the incidence of false alarms.
2. The sensors did not return any false alarms when exposed to the contaminants prescribed by UL 60335-2-40.
3. The sensors did show deteriorated health shortly after being exposed to these contaminants. However in most cases this improved within 24 hours of removing the sensor to air.

Based on these findings, it is recommended that small improvements in MOS sensor performance should be made such that they meet the requirements of UL 60335-2-40.

REFERENCES

1. ACHR News, California Approves Rules To Phase Down HFCs, https://www.achrnews.com/articles/144212-california-approves-rules-to-phase-down-hfcs. Accessed Feb. 3, 2021.
2. S. Kujak, K. Schultz, Insights into the next generation HVAC&R refrigerant future, Science and Technology for the Built Environment 22 (2016) 1226–1237.
3. S.G. Davis, J.L. Pagliaro, T.F. DeBold, M. van Wingerden, K. van Wingerden, Flammability and explosion characteristics of mildly flammable refrigerants, J. Loss Prevention in the Process Industries 49 (2017).
4. P. Papas, P. Verma, R. Lord, L. Burns, Turbulent deflagrations of mildly flammable refrigerant-air mixtures, J. Loss Prevention in the Process Industries, 61 (2019) 255-261.
5. D.K. Kim, P.B. Sunderland, Viability of various sources to ignite A2L refrigerants, Energies 14 (2021) 121.
6. R.E. Tapscott and C.W. Sohn, Halocarbon Refrigerant Detection Methods, USACERL Technical Report 96/22, U.S Army (1996).
7. M. Wagner and R. Ferenchiak, Leak detection of A2L refrigerants in HVACR equipment AHRTI Report No. 9009 (2017).
8. UL 60335-2-40, Standard for Household And Similar Electrical Appliances - Safety - Part 2-40: Particular Requirements for Electrical Heat Pumps, Air-Conditioners and Dehumidifiers (2020).
9. Figaro, A2L Refrigerant Gas Sensor Module FCM2630, https://www.figarosensor.com/product/feature/fcm2630.html, accessed Feb. 3, 2021.
10 K. Izawa, SnO_2-based gas sensor for detection of refrigerant gases, MDPI Proceedings 14 (2019) 32.
11. Wack, Garrett, Characterization of metal-oxide semiconductor sensors for R-32 and R-454B leaks, M.S. Thesis, University of Maryland, 71, pp., Aug., 2020.
12. D.K. Kim, A.E. Klieger, P.Q. Lomax, C.G. McCoy, J.Y. Reymann, P.B. Sunderland, An improved test method for refrigerant flammability limits in a 12 L vessel, Science and Technology for the Built Environment 24 (2018) 861-866.
13. Opteon™ XL41 (R-454B) Refrigerant, https://www.opteon.com/en/products/refrigerants/xl41, accessed Feb. 3, 2021.