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Characterizing Commercially Available Formaldehyde Sensors

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SUMMARY

Five commercial off-the-shelf (COTS) formaldehyde sensors aimed to monitor indoor concentrations below 10 ppm were tested for their performances, including linearity, hysteresis, repeatability, stability and selectivity. The effects of humidity (9 to 95%) and temperature (10 to 39 ^{o}C) were also tested. Three of the COTS sensors (COTS_1, 2 and 3) are electrochemical sensors, while two of them (COTS_4 and 5) are photoelectrical photometry based sensors. COTS_1 performed best in linearity, hysteresis, repeatability, stability and environmental effect tests. However, COTS_1 showed cross-sensitivity to organic gases including aldehydes (acetaldehyde and hexanal), alcohols (ethanol, 2-propanol and 1-butanol) and limonene. COTS_4 showed good performance in linearity, repeatability, stability and sensitivity, but they responded linearly to temperature and relative humidity changes.

IMPLICATIONS

This study shows that commercial sensors responded linearly between 0 and 0.6 ppm and were sensitive enough to detect 0.05 ppm of formaldehyde. However, it also demonstrates that electro-chemical sensors need to improve selectivity. Photoelectric photometry needs improvements in practicality for continuous monitoring and compensation for environmental effects.

KEYWORDS

Indoor air, linearity, selectivity, cross-sensitivity, environmental variables

INTRODUCTION

Formaldehyde is one of the most recognized indoor air pollutants partly due to its carcinogenicity and ubiquitous presence indoors. It is also suspected to be linked to asthma, specially, for children (McGwin, 2009). Health Canada recommends an exposure limit of 40 ppb (8 hour average) and 100 ppb (1 hour average) as residential indoor air quality guidelines (Health Canada, 2006). The demand of continuous monitoring of formaldehyde indoors is growing. If an accurate and reliable sensor is available for continuous monitoring, it can be realized to assess indoor air quality (IAQ) in real time and to control ventilation based on the information.

The Information and Communications Technology (ICT) Sector of the National Research Council Canada launched a multi-institute project titled “ICT sector indoor air quality project” in 2008. The major goal of the project is to develop new indoor air quality sensor system technologies that maximize occupant health and safety and minimize energy use. Formaldehyde has been chosen as the target compound to demonstrate the sensor system. Improving commercial sensors is planned within the project in addition to developing new prototype sensors. As a first task, five formaldehyde COTS sensors were tested for their

performances, including linearity, hysteresis, repeatability, stability and selectivity. This paper summarizes the experimental set-up and most recent performance test results.

METHODS

Formaldehyde COTS sensors

Five COTS sensors were selected for the test. Four sensors were purchased and one was donated by a manufacturer. Three of them (COTS_1, 2 and 3) are electrochemical sensors, while two of them (COTS_4 and 5) are photoelectrical photometry-based sensors. Replaceable coloring tape or tablet is used as a sensing medium for COTS_4 and 5, respectively. Table 1 summarizes characteristics of the selected COTS sensors.

Table 1. Characteristics of formaldehyde COTS

	COTS_1	COTS_2	COTS_3	COTS_4	COTS_5
Sensor Type	Electro-chemical	Electro-chemical	Electro-chemical	Photoelectric Photometry	Photoelectric Photometry
Warming-up time	< 80 sec	< 60 sec	2-3 min	< 60 sec	No Warm-up
Measuring Range	0-10 ppm	0-10 ppm	0-30 ppm	0-1.0 ppm	0-1.0 ppm
Detection Time	Instant after warm-up	< 60sec	User defined (normal: 3 min)	15 – 30 min	15 - 30 min
Resolution	0.01 ppm	0.01 ppm	0.01 ppm	0.01 ppm	0.01 ppm
Uncertainty of measurement	-	+/- 25% of the reading	-	+/- 20% of the reading + 1 digit	+/- 10% of the reading
Repeatability	<2% of signal	-	0.015 ppm	-	-
Zero Shift	0.25 ppm	-	<0.002 ppm/min (continuous op.)	-	-

Experimental set-up

The experimental set-up is comprised of multiple gas generation units, a humidification unit, a glass mixing bottle (600 mL), a glass testing bottle (600 mL) with multiple sampling ports, and a data acquisition unit. A commercial permeation tube unit (Dynacalibrator #340, VICI Metronics) was dedicated to formaldehyde generation. Interfering gases were individually generated using a permeation tube or diffusion vial housed in the gas generation unit, which consists of a glass chamber enclosed in an insulated metal block, a heating pad with a temperature controller, and mass flow controllers for gas flow control. An external pump was used to introduce the gas stream from the testing bottle to COTS_1. The other sensors with an internal pump were connected to the sampling port of the testing bottle. Within a period of one hour under one test condition, multiple sensor readings were recorded and then averaged.

Test plan

In reference to Fahlen et al. (1992), the laboratory tests for linearity, stability and repeatability were conducted in the range between 0 and 0.6 ppm. The formaldehyde concentration increased from the lowest to highest gradually and from the highest to lowest to determine linearity as well as hysteresis. Linearity was calculated as the maximum deviation between any measured value and an expected concentration assuming linearity. The expected concentration was calculated from a straight line between the lowest and the highest concentration. Hysteresis was calculated based on two sensor readings measured at one concentration, which was tested twice in the increasing and decreasing order of concentration. For the repeatability test, the sensors were tested at two concentrations (0.09 vs. 0.8 ppm)

alternatively 4 times. The repeatability is defined as the maximum deviation between any measured value and the corresponding mean value for the respective test points. The repeatability test is to assess the presence of memory effects of sensors. The sensors were exposed to one concentration (0.5 ppm) for ~24 hours for the stability test. Stability is defined as the maximum deviation between any measured value and the mean value during the measuring period. The levels of temperature and relative humidity were varied at five levels from 10 to 39 ^{o}C and from 9 to 95%, respectively. The effect of environmental variables was calculated as the deviation from the value obtained under the standard condition (23 ^{o}C, 50 ~ 60% RH).

To determine the selectivity, organic chemicals that that have similar chemical characteristics to formaldehyde (aldehydes, alcohols and ketones) and that are relatively abundant indoors (toluene and limonene) were introduced to the chamber at the same time with formaldehyde. The target concentrations were chosen to represent the concentrations encountered indoors (reference level). The concentration was further increased to get one or two higher levels from the reference level. The concentrations of interfering gases were confirmed with sampling on an adsorbent tube (Tenax or Carbotrap 300) and GC/MS analysis. The formaldehyde concentration was verified with DNPH cartridge sampling and subsequent HPLC analysis.

RESULTS

Linearity, accuracy and hysteresis

Figure 1 presents the results of the linearity tests conducted at 0, 0.05, 0.17, 0.4 and 0.6 ppm of formaldehyde under the standard condition. The concentration was varied from the low to high level in Figure 1 (a), while the order of concentration was reversed in the test presented in Figure 1 (b). All tested sensors generally showed linear responses to formaldehyde between 0 and 0.6 ppm. The maximum deviations between any measured value and an expected concentration assuming linearity are summarized in Table 2. COTS_1 showed the best performance in linearity with a maximum deviation of 13%. COTS_4 and COTS_5 showed good linearity with the maximum deviation less than 50% in the test with decreasing concentrations, but not in the test with increasing concentrations. The opposite was observed for COTS_3. Due to the erratic behavior, including an error message at 0.6 ppm and fluctuations in sensor readings, it was difficult to evaluate the performance of COTS_2.

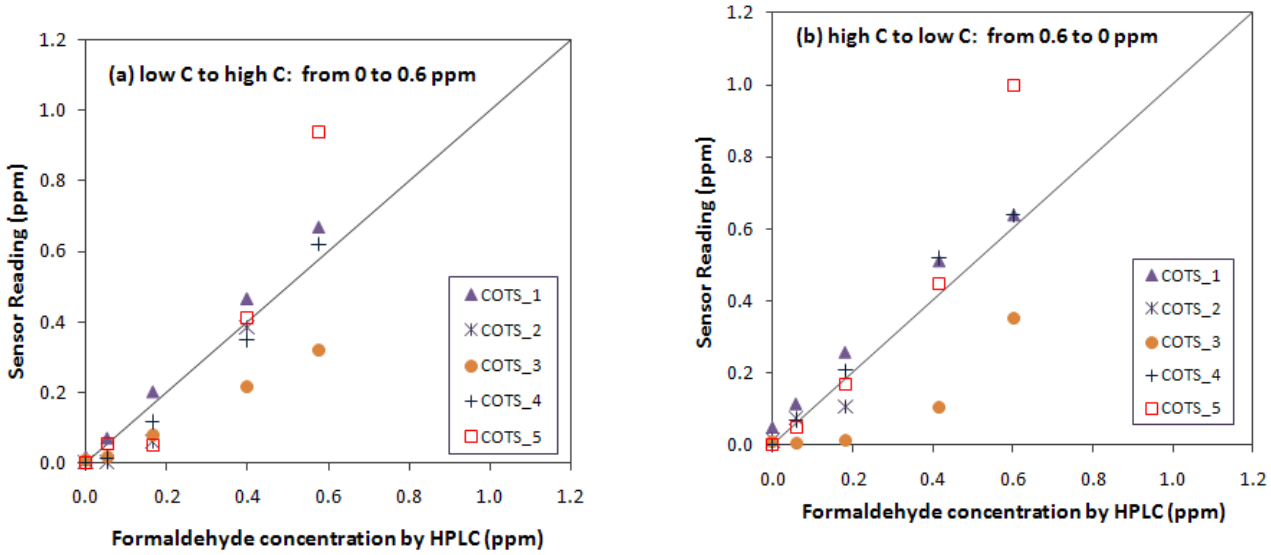

Figure 1. Sensor characteristics curve: a) tested in an increasing, b) decreasing order of concentration at five formaldehyde levels (0, 0.05, 0.17, 0.4 and 0.6 ppm).

The maximum deviations for accuracy and hysteresis characterization are also included in Table 2. All sensor readings were within ±100% of the reference formaldehyde concentration obtained from the HPLC analysis. COTS_1 and 5 showed the best accuracy in the test with increasing and increasing concentrations, respectively. COTS_1, 4 and 5 generally showed better accuracy than COTS_3. COTS_1 showed the least amount of hysteresis. All sensors except COTS_2 (no data) showed hysteresis less than 10% at 0.6 ppm. COTS_1 and 4 generally showed less hysteresis than COTS_3.

Table 2. Maximum deviation (%) for various performance criteria

	COTS_1	COTS_2	COST_3	COTS_4	COST_5
Linearity (0.05 to 0.6 ppm)	**8**		52	78	82
(0.6 to 0.05 ppm)	**13**		88	18	49
Accuracy (0.05 to 0.6 ppm)	**33**		65	76	70
(0.6 to 0.05 ppm)	97		92	25	**15**
Hysteresis (at various conc)	**64**	2150	82	460	240
Repeatability at 0.09 ppm	21	29	78	**5**	**6**
at 0.9 ppm	**1**	7	16	13	
Stability at 0.5 ppm	**7**	16	90	11	27
Temperature at 0.05ppm	**15**	100	117	**16**	29
RH at 0.05 ppm	**13**	77	49	73	32

Repeatability

Figure 2 presents the repeatability test results at 0.09 and 0.8 ppm and Table 2 includes the maximum deviation from the mean value of sensor readings. No deviation was calculated for COTS_5 at 0.8 ppm due to oversaturation of the coloring tab. At 0.09 ppm, COTS_4 and 5 showed the smallest deviation from the mean value, followed by COTS_1. Overall, COTS_1 and 4 showed good repeatability at both concentrations. With COTS_2 and COTS_3, an increasing trend with time can be clearly seen until the third repetition (Figure 2).

Stability

Sensors were exposed to 0.5 ppm of formaldehyde for ~24 hours (Figure 3). The deviations from the mean value of sensor readings are summarized in Table 2. All sensors showed the maximum deviation bigger than that of the formaldehyde concentration measured with HPLC. COTS_1 and 3 showed the smallest (7%) and biggest deviation (90%), respectively. COTS_2, 4 and 5 had good stability (11%, 16%, and 27%, respectively).

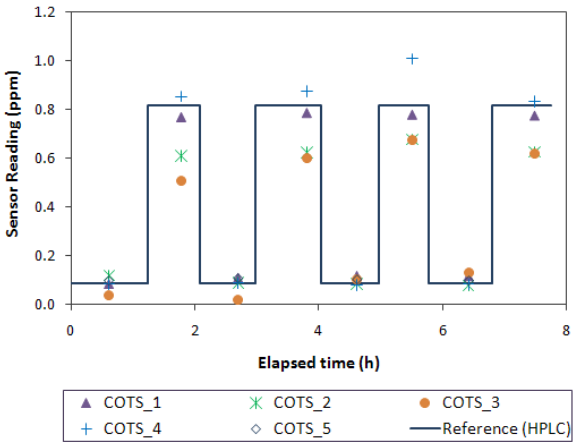

Figure 2. Sensor readings from the repeatability test at 0.09 and 0.9 ppm

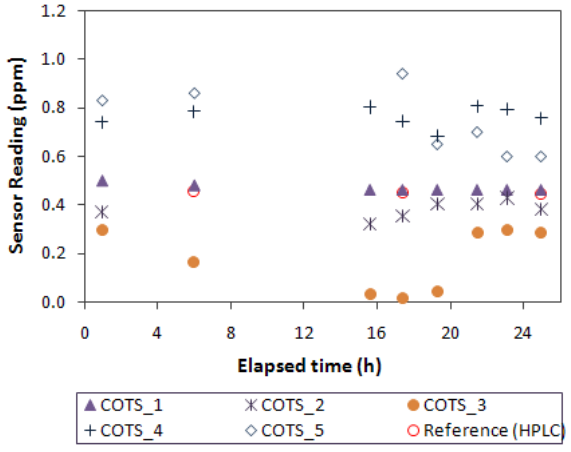

Figure 3. Sensor readings from the stability test at 0.5 ppm

Relative humidity effect

Figure 4 presents the results of three sensors that responded linearly to relative humidity (9 – 95%) under 0.05 ppm formaldehyde and 23 ^{o}C. The RH effect was the most noticeable with COTS_3 and 5 with a decreasing trend with increasing RHs. The readings of COTS_4 also decreased with increasing RHs, but the magnitude of the RH effect was not significant (Table 2) in comparison to the variations in the formaldehyde concentration. No trend was found for COTS_2. The results are surprising for COTS_5 since no effect RH was reported between 30 and 70% in Suzuki et al. (2003) with a photometry similar to COTS_5. It appears that water molecules react with sensing materials, leading to decreased sensor readings.

Temperature effect

Figure 5 presents the readings of two sensors that responded linearly to temperature (10 – 39 ^{o}C) under 0.05 ppm formaldehyde and 50% RH. The maximum deviations from the mean value are included in Table 2. A decreasing trend was observed with increasing temperature for COT_4 and 5. The temperature effect on a COTS_5 type sensor was also reported in Suzuki et al. (2003). They reported the temperature correction was possible using the themistor in the hand-held photometry. It appears that the mechanism for the temperature correction was not available or functional for COTS_4 and 5.

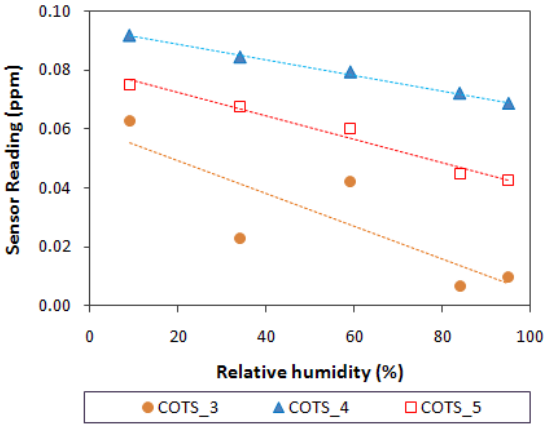

Figure 4. Sensor readings from the relative humidity test at 0.05 ppm

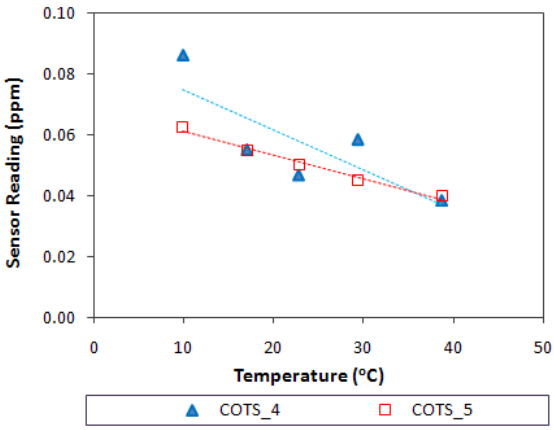

Figure 5. Sensor readings from the temperature test at 0.05 ppm

Cross-sensitivity

COTS_1 showed the cross-sensitivity to various interfering gases, including aldehydes (9% for acetaldehyde and 11% for hexanal), alcohols (33% for ethanol, 30% for 2-propanol, and 12% for 1-butanol) and limonene (29%). Two example graphs are given for COTS_1 in Figure 6. The improved selectivity of COTS_3, which is another electro-chemical sensor, appears to be the result of a chemical filter installed. No evaluation on cross-sensitivity was made for the third electro-chemical sensor, COTS_2, due to the instability of sensor readings. Two photoelectric photometry based sensors showed good selectivity due to the selective nature of the coloring tablet and tape. No sensors showed significant cross-sensitivity to ketones (acetone and 2-butanone) and toluene in the range of 0.02 to 0.6 ppm.

CONCLUSIONS

Formaldehyde commercial-off-the-shelf (COTS) sensors were shown to have good performance in the concentration range of 0 to 0.6 ppm and were sensitive enough to detect 0.05 ppm of formaldehyde. COTS_1 (electrochemical sensor) performed best in linearity, hysteresis, repeatability, stability, and environmental effect tests. COTS_4 (photoelectric photometry) showed good performance in linearity, repeatability, stability and sensitivity.

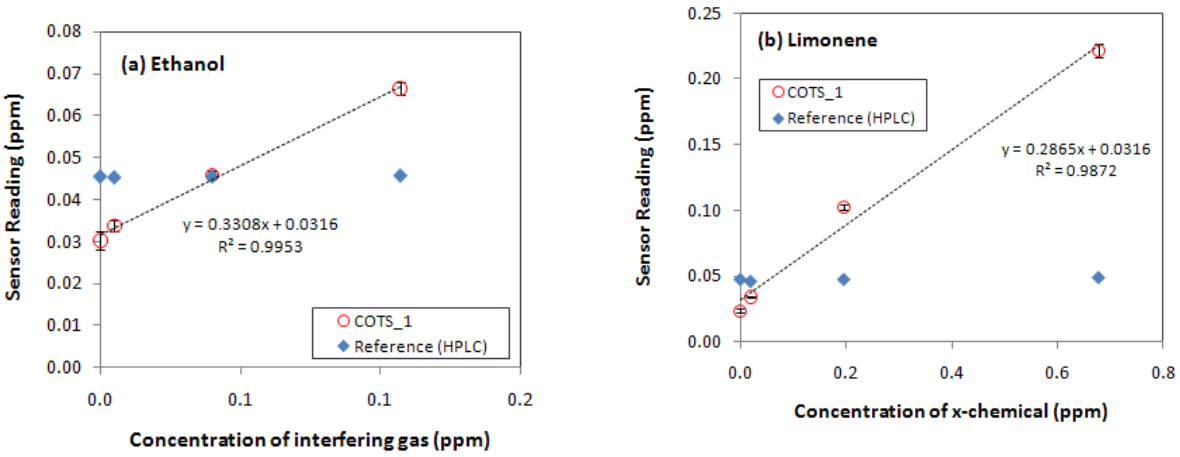

Figure 6. Cross-sensitivity of COTS_1 to ethanol (a) and limonene (b)

However, each sensor showed its own weakness. COTS_1 responded to organic gases including aldehydes (acetaldehyde and hexanal), alcohols (ethanol, 2-propanol and 1-butanol) and limonene, while COTS_4 showed linear responses to temperature and relative humidity.

The acceptance of COTS_4 as continuous measurement equipment is currently limited due to an inherent problem with impracticality of using a coloring tape. As the coloring tape is expensive, more practical solutions are required for continuous monitoring. In consequence, COTS_1 can be a better candidate for continuous monitoring if measures can be implemented to improve selectivity towards common organic compounds in indoor air. One potential solution is using a chemical filter to remove any interfering gases as demonstrated with COTS_3.

Similar types of performance tests are in progress in a lower formaldehyde range (< 0.1 ppm) that can reflect the typical indoor concentrations more closely. The cross-sensitivity test will be expanded to testing more diverse compounds individually (e.g., carbon monoxide) and testing multiple compounds simultaneously. Concurrently, selected sensors (e.g., COTS_1) will be tested in a full-scale chamber where their signals will be fed to a dedicated ventilation system for ventilation flow control in more realistic conditions (e.g., in a passive operation mode for COTS_1).

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