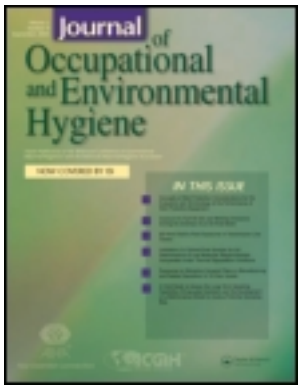

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The performance of three MIRAN SapphIRe Portable Infrared Ambient Air Analyzers and three Century Portable Toxic Vapor Analyzers equipped with photoionization (PID) and flame ionization (FID) detectors was compared with charcoal tube sampling. Relationships were investigated using two different calibration methods at four cyclohexane concentrations, three temperatures, and four relative humidities. For the first method, the TVA monitors were calibrated with a single concentration of methane for the FID, and isobutylene for the PID. The SapphIRe monitors were zeroed and the monitor's manufacturer-supplied library was used. For the second method, a five-point cyclohexane calibration curve was created for each monitor. Comparison of the monitor results of each calibration method (pooled data) indicated a significant difference between methods (t-test, $p < 0.001$), The SapphIRe group had results closer to the charcoal tubes with the second calibration method, while the PID and FID monitor groups performed better using the first calibration method. The PID monitor group's performance was affected only at the 90% relative humidity (RH) condition. Using the first method, the monitor readings were compared with the charcoal tube average using mixed linear model analyses of variance (ANOVAs) and regression. The ANOVA results showed there was a statistically significant difference among readings from all monitor types ($p < 0.0001$). The regression results demonstrated that the SapphIRe ($r^2 = 0.97$) and FID ($r^2 = 0.92$) monitor groups correlated well with the charcoal tubes. The PID monitor group had a similar correlation when 90% RH was excluded ($r^2 = 0.94$) but had a weaker correlation when it was included ($r^2 = 0.58$). The operator should take care when using these monitors at high concentrations and the PID monitors at high humidities, consider the variability between units of the same monitor, and conduct performance verification of the monitor being used.

[Supplementary materials are available for this article. Go to the publisher's online edition of the Journal of Occupational and Environmental Hygiene *for the following free supplemental resources: a program listing, schematic diagrams, and other design details for the test automation system.]*

Keywords direct-reading organic vapor monitors, flame ionization detector, photoionization detector, SapphIRe, toxic vapor analyzer

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INTRODUCTION

An essential part of any health and safety risk assessment is the accurate characterization of exposure. Direct-reading organic vapor monitors are valuable tools for the detection and assessment of worker exposure to inhalation hazards or hazardous material emergency response incidents. Organic vapor monitors can be used for area, process, and even personal monitoring with certain monitors. Some advantages of organic vapor monitors include (1) instantaneous or near instantaneous readings, (2) data logging of changes in concentration, and (3) both peak and time-integrated concentrations. These advantages allow more informed decisions to be made regarding the need for any exposure control measures (administrative controls, environmental controls, and/or respiratory protection) and workers to modify work habits during a shift.

The specific application will dictate the appropriate monitor performance requirements. When a monitor is used as a survey tool to detect sources of organic vapor emissions or to assess the overall volatile organic compound concentration on site, the performance requirements may not be as stringent as for a monitor being used to determine compliance with an occupational exposure limit. Monitors for compliance must have greater reliability in terms of accuracy and precision of

the measurements, and any bias and/or potential interferences must be identified and characterized. Accuracy is the degree of agreement between a measured value and the accepted reference value (i.e., accepted sampling and analytical methods such as charcoal tubes analyzed by gas chromatography with a flame ionization detector [CT method]) within the range of environmental conditions specified by the manufacturer. Precision is the repeatability or reproducibility of individual measurements expressed as the standard deviation or relative standard deviation. Bias is the difference between the average measured value and a reference value.[1]

Only a few researchers have compared the outputs of direct-reading organic vapor monitors with analytical results from integrated sampling methods (e.g., charcoal tubes).[2–4] Coy et al. compared a direct-reading photoionization detector (PID, model "Professional PID"; RAE Systems Inc., San Jose, Calif.) with standard charcoal sorbent tube sampling of 26 breathing zone samples collected during a variety of construction painting tasks.[2] The sample concentration range was from 2 ppm to 1390 ppm. A linear regression between the log concentration of the methods found them to be highly correlated ($r^2 = 0.95$). Drummond compared the reading from a MiniRAE (RAE Systems) equipped with a PID with a charcoal tube as part of a method to measure or confirm a PID response factor in the field.[3] He found that the charcoal tube sample collected from the outlet of the MiniRAE was representative of the air drawn into the instrument.

Poirot et al.[4] compared the readings from a Photovac 2020 PE PID instrument (Thermo Scientific, Waltham, Mass.) with charcoal tubes both in the laboratory and at two different worksites (house painting and site reclamation). In the laboratory, they used two different mixtures: Stoddard solvent (0 to 100 ppm) and *p*-xylene, *m*-xylene, styrene, and ethylbenzene (0 to 500 ppm) for times ranging from 5 to 120 min. They found the results to be highly correlated ($r^2 \geq 0.99$) for the mixtures. The house painters were sampled for petroleum spirits (a mixture of C_8 to C_{12} hydrocarbons). The remediation workers were exposed to a mixture of industrial solvents (chlorinated hydrocarbons, ketones, naphthenes, and so on). The detected concentrations ranged from 0.1 to 4.8 ppm depending on the compound. Similar to the laboratory testing, a good correlation ($r^2 \geq 0.97$) was found between the charcoal tubes and the direct-reading instrument in the field samples. A drawback of this was that the environmental conditions for the workplace sampling were not noted.

Barsky et al.[5] investigated the effect of high humidity on two PID monitors (H-Nu Model PI-101 with a 10.2 eV lamp, and an AID Model 580 Portable Organic Vapor meter with an 11.8 eV lamp), and a Century Model OVA-128 Portable Organic Vapor Analyzer containing a flame ionization detector (FID). The study found the PID monitors were suitable for use in low humidity (0%) conditions but inappropriate for sampling in humid (90%) environments. The FID was not affected by the high humidity. Lee et al.[6] also examined the effect of humidity on the OVA-128 and the PI-101.[6] They also determined that the PID was affected by humidity but the FID was not. None of the above studies evaluated the performance of multiple units of the same monitor or investigated extensive variations in challenge environmental conditions, such as concentration and temperature.

The Department of the Army tested two MIRAN SapphIRe Portable Ambient Air Analyzers under various temperatures and relative humidity (RH) conditions against chemical warfare agents (tabun, sarin, and sulfur mustard).[7] The researchers found that the SapphIRe monitor does not provide sufficient warning to ensure the safety of emergency responders when exposed to chemical warfare agents. This inability to provide sufficient warning may have been due to the relatively high limit of detection for the SapphIRe compared with other field detection methods. They also found that interferents and high humidity negatively affected monitor performance. In another study, the same researchers tested a Century Portable Toxic Vapor Analyzer (TVA), having a PID and FID, using the same three chemical warfare agents.[8] The researchers found that the PID was easily contaminated and needed frequent cleaning, which is impractical in the field. The FID was strongly affected by chemical interferents. Neither the PID nor the FID could be relied on for the detection of chemical warfare agents, and other contaminants adversely affected their performance.

A National Institute for Occupational Safety and Health (NIOSH) study[9] investigated the effect of environmental condition on performance of multiple units of five portable direct-reading organic vapor monitors: ppbRAE, IAQRAE, and MultiRAE; Century Portable Toxic Vapor Analyzer; and MIRAN SapphIRe Portable Ambient Air Analyzers. The monitors were evaluated at three temperatures (4°C, 21°C, and 38°C), RH (30%, 60%, and 90%), and two hexane concentrations (5 ppm and 100 ppm). The 4-hr time-weighted average (TWA) readings from the monitors were compared with the average of two charcoal tube concentrations. A pairwise comparison criterion of ±25% measurement agreement was used. The results indicated that none of the five different types of monitors used in this study provided accurate and precise measurements in comparison with charcoal tube samples of hexane. The monitors' variability prevented conclusive determinations about the effects of concentration, temperature, and RH on monitor performance. This lack of information on the effect of environmental condition on direct-reading organic vapor monitors was one of the driving factors for conducting the current study.

Aside from the recent NIOSH study,[9] no studies that tested the SapphIRe and TVA monitors against non-CWA vapors were found. Since most real-world situations (especially emergency response) involve multiple gases and/or vapors, it is necessary for users to know how interferents affect the performance of the instruments in detecting the gas/vapor of interest. Emergency responders can use these two monitors to: differentiate between contaminated and non-contaminated zones, determine the level of personal protective equipment needed by personnel entering a contaminated area, define evacuation radii, and determine when re-entry/re-occupancy of

a space can occur. To perform these functions, responders need to have detailed knowledge of the monitors' capabilities.[10,11]

The purpose of the current study was to assess the performance of direct-reading organic vapor monitors under different environmental conditions of chemical concentration, temperature, and RH using two different calibration methods. The aims of the study were to (1) compare monitor measurements with an accepted TWA charcoal tube sampling method, (2) investigate the variability among multiple units of the same monitor, and (3) investigate the response relationships between the three detector types.

This study differs from the previous NIOSH study[9] by using a wider range of concentrations and relative humidities. A more sophisticated statistical analysis was used in the current study. This analysis in conjunction with more controlled environmental parameters would allow a better determination of the effect of environmental condition on instrument performance that was not possible with the previous study. Although it focuses on a single contaminant (cyclohexane), it serves as a prelude to studies using multiple vapors.

MATERIALS AND METHODS

Monitors

This study evaluated three MIRAN SapphIRe Portable Ambient Air Analyzers (Series 205B, Model XL; Thermo Fisher Scientific, Franklin, Mass.) and three Century Portable Toxic Vapor Analyzers (Model TVA-1000B, Thermo Fisher Scientific). The SapphIRe is a single-beam dispersive infrared spectrophotometer with a stated accuracy of ±10% of the reading for cyclohexane.[12] The TVA monitors contain both a FID and a PID. The TVA FID uses ultrahigh purity hydrogen (Butler Gas Products, McKees Rocks, Pa.) as the combustion gas and has a stated accuracy of ±25% of the reading or ±2.5 ppm, whichever is greater, in the range of 1.0 to 10,000 ppm. The TVA PID uses a 10.6 eV lamp and has a stated accuracy of ±25% of the reading or ±2.5 ppm, whichever is greater, in the range of 0.5 to 500 ppm. This PID lamp is capable of ionizing cyclohexane since its ionization energy is 9.88 eV.[13] The TVA monitors were equipped with a Watertrap Probe Filter in the sampling probe.[14]

Environmental Conditions

Four concentrations (30, 150, 300, and 475 ppm) of cyclohexane (certified ACS grade, catalog number C556-1, Fisher Scientific, Pittsburgh, Pa.) were used to challenge the monitors. Cyclohexane was selected since it is a high production volume chemical (i.e., having annual production and/or importation volumes above 1 million lbs).[15] Therefore, there should be a need to sample this chemical with direct-reading monitors. It is also used to test Chemical, Biological, Radiological, and Nuclear (CBRN) air-purifying respirator canisters instead of actual chemical agents.[16] The four concentrations were selected to be within the normal operating range of the monitors as well as to encompass the NIOSH recommended exposure limit (REL) and the Occupational Safety and Health Administration's (OSHA) permissible exposure limit (PEL) of 300 ppm.[12–14,17] Tests at a zero ppm concentration (i.e., clean air) were conducted as a control, and the data were processed separately from the other four concentrations.

Three temperatures (5°C, 21°C, and 38°C) and four relative humidities (15%, 30%, 60%, and 90%) were chosen to challenge the monitors since they cover the operative limits of the monitors and represent conditions found in industrial environments.[12,14] Five replicates, each lasting 30 min, were performed for each of the 96 experimental conditions (4 concentrations × 3 temperatures × 4 RH × 2 calibration methods) with an additional 24 conditions for the zero ppm control concentration. All five replicates at each combination were conducted consecutively to minimize the time required for acclimatization of the environmental chamber between environmental conditions and to reduce potential variability.

Monitor Calibration

All six monitors were calibrated by the respective manufacturers prior to the study. In addition, they were calibrated daily in the environmental chamber at the same temperature and RH conditions as during the sampling tests. The monitors were allowed to equilibrate to each different environmental condition at least overnight before being calibrated. The temperature and humidity compensation modes were off during the testing, since (1) the monitors were preconditioned and calibrated at the test temperature and RH, and (2) the environmental chamber held the temperature and RH constant (±3% of target).

Manufacturer-Recommended Calibration Method—Calibration Method 1

The built-in library supplied with the SapphIRe monitors was used with a Gas High Range Limit (HRL) of 500 ppm. The SapphIRe monitors have a detection limit of 6 ppm for cyclohexane when a wavelength of 11.156 μm and a path length of 12.5 m are used.[12] They were zeroed every day using a zero particulate filter (Part Number TR101ZU, Thermo Fisher Scientific) and a zero gas chemical filter (TR101PU, Thermo Fisher Scientific).

The TVA monitors were calibrated by filling separate 100 L Tedlar polyvinyl fluoride bags (CEL Scientific Corporation, Santa Fe Springs, Calif.) with a zero gas (zero grade air, Butler Gas Products) and span gases (500 ± 2% ppm methane in air (Scott Specialty Gases, Plumsteadville, Pa.) for the FID and 1000 ± 2% ppm isobutylene in air (Scott Specialty Gases) for the PID). The stability of the gas concentrations in the bags was investigated. The concentrations in the bags were checked daily for a week using a TVA that was calibrated using the span gases directly from the cylinders. The results showed that the concentrations in the bags were within 5% of the cylinder concentration at the end of the week.

The bags were then placed in the environmental chamber and left at least overnight for equilibration before being used

for calibration. The stability of the concentrations of the gases in the bags was checked prior to the start of the study. The TVA monitors were challenged with the zero gas. After zeroing, they were challenged with the span gases to obtain a second calibration point. As an indication of the success of the daily field calibration of the TVA instruments, the "zero" (counts expected when a zero gas is applied to the detector) and span detector counts (counts expected when a span gas of known concentration is applied to the detector) were recorded.

Chemical of Interest Calibration Method—Calibration Method 2

For each SapphIRe monitor, a new single-gas library was created for cyclohexane. This new library used the same wavelength and path length as the manufacturer's installed library used in Calibration Method 1. For this method, a closed loop system (i.e., the inlet of the SapphIRe monitor was connected to the outlet) that contained a tee with a septum for injecting the cyclohexane was used. Four injection volumes corresponding to 125, 250, 375, and 500 ppm cyclohexane were calculated using the equation provided by the manufacturer.[12] The absorbance at each concentration (0, 125, 250, 375, and 500 ppm) was then used to establish a user-defined calibration curve within each SapphIRe in accordance with the manufacturer's procedures.[12]

The TVA monitors were challenged with the same concentrations of cyclohexane as the SapphIRe monitors. This was accomplished using 100-L Tedlar polyvinyl fluoride bags (CEL Scientific Corporation), which were filled with zero grade air (Butler Gas Products) and injected with the appropriate amount of cyclohexane determined using the same equation as used for the closed loop calibration. The bags were then placed in the environmental chamber and left at least overnight for equilibration before being used for calibration. The concentration of analytes in the bags was checked prior to calibration through charcoal tube sampling with laboratory analysis, and the results showed that the concentrations were within 5% of the theoretical concentration. The concentrations and the corresponding counts were entered into each TVA monitor in order to develop response curves.

Test Setup

All testing was conducted in a 22 m^3 walk-in environmental chamber (Nor-Lake ENVIROLINE; Nor-Lake Scientific, Hudson, Wisc.). Temperature and humidity conditions were monitored in the environmental chamber by a Model HX94V Relative Humidity/Temperature Transmitter, Duct Style (Omega Engineering, Inc., Stanford, Conn.) that was calibrated prior to the start of testing with a HX90-CAL (Omega Engineering) humidity calibration kit.

A 0.4 m^3 Rochester-style (exposure) chamber was placed inside the environmental chamber (Figure 1). The cyclohexane vapor inside the exposure chamber was generated by pumping the liquid from an enclosed reservoir to a three-necked flask on the inlet of the exposure chamber using a Chem-inert M50 liquid handling pump (Valco Instruments Company Inc., Houston, Texas) and an insulated liquid transfer line (Figure 1) heated to approximately 32°C. The three-necked flask contained glass beads and was heated (Thermo Scientific Electrothermal Mantle with Stainless-Steel Liner and Controller Model EM 1000/CEX1, Thermo Scientific Barnstead, Dubuque, Iowa) to assist the evaporation of the liquid cyclohexane. Conditioned environmental chamber air entered the exposure chamber through the inlet located at the top (Figure 1). To accomplish this, air was removed from the bottom of the exposure chamber using a standard overhung multistage centrifugal blower (Model 075-1/3; The Spencer Turbine Company, Windsor, Conn.). Prior to the blower, the air passed through a single fan filter housing (model FS4000; Flow Sciences, Wilmington, N.C.) equipped with an organic solvent bed filter (model FS4251; Flow Sciences) to remove the cyclohexane before entering the blower and returning to the environmental chamber (Figure 1). The flow rate of the blower was approximately 20 L/min[1] to maintain negative pressure (–0.4 inches water-column height) in the exposure chamber as compared with the environmental chamber. A micromanometer (Model DM1; Infiltech, Waynesboro, Va.) was used to monitor the differential pressure between the exposure and environmental chambers.

To ensure the cyclohexane concentration was uniform across all the sampling locations, the exposure chamber had two mixing fans (Model 12-13185-03; Howard Industries, Milford, Ill.) located at opposing bottom corners. Two charcoal tubes, approximately 3 cm apart, were placed in the middle of the chamber. The tubes were the reference standard to which the monitor readings were compared. The monitor inlets were placed near the center of the chamber with enough separation to prevent interference. The distance between the SapphIRe inlets was 16 cm, while the TVA inlets were 6 cm apart. The TVA inlets were located 36 cm from the SapphIRe inlets and 12 cm from the tube inlets. A preliminary assessment of the concentration variability at the various sampling inlet locations was conducted to ensure spatial concentration uniformity. For this, charcoal tubes were placed at monitor inlets as well as their normal positions. Cyclohexane was then generated and sampled by the charcoal tubes. The charcoal tube concentrations among the eight locations had a relative standard deviation of 3.1%. This confirmed the concentration uniformity.

For each replicate, cyclohexane vapor was sampled using two Anasorb coconut shell charcoal sorbent tubes (catalog number 226-01, 6 × 70 mm size, 2-section, 50/100 mg sorbent; SKC Inc., Eighty Four, Pa.) connected to personal sampling pumps (model GilAir-5 with 800518 Constant Flow Low Flow module; Sensidyne LP, Clearwater, Fla.) set to a flow rate of 0.1 L/min. The pumps were calibrated at the start and end of each day using a NIST-traceable primary calibrator (Model 4146 Primary Calibrator; TSI, Incorporated, Shoreview, Minn.). The pumps were operated on a charger controlled by the test automation system.

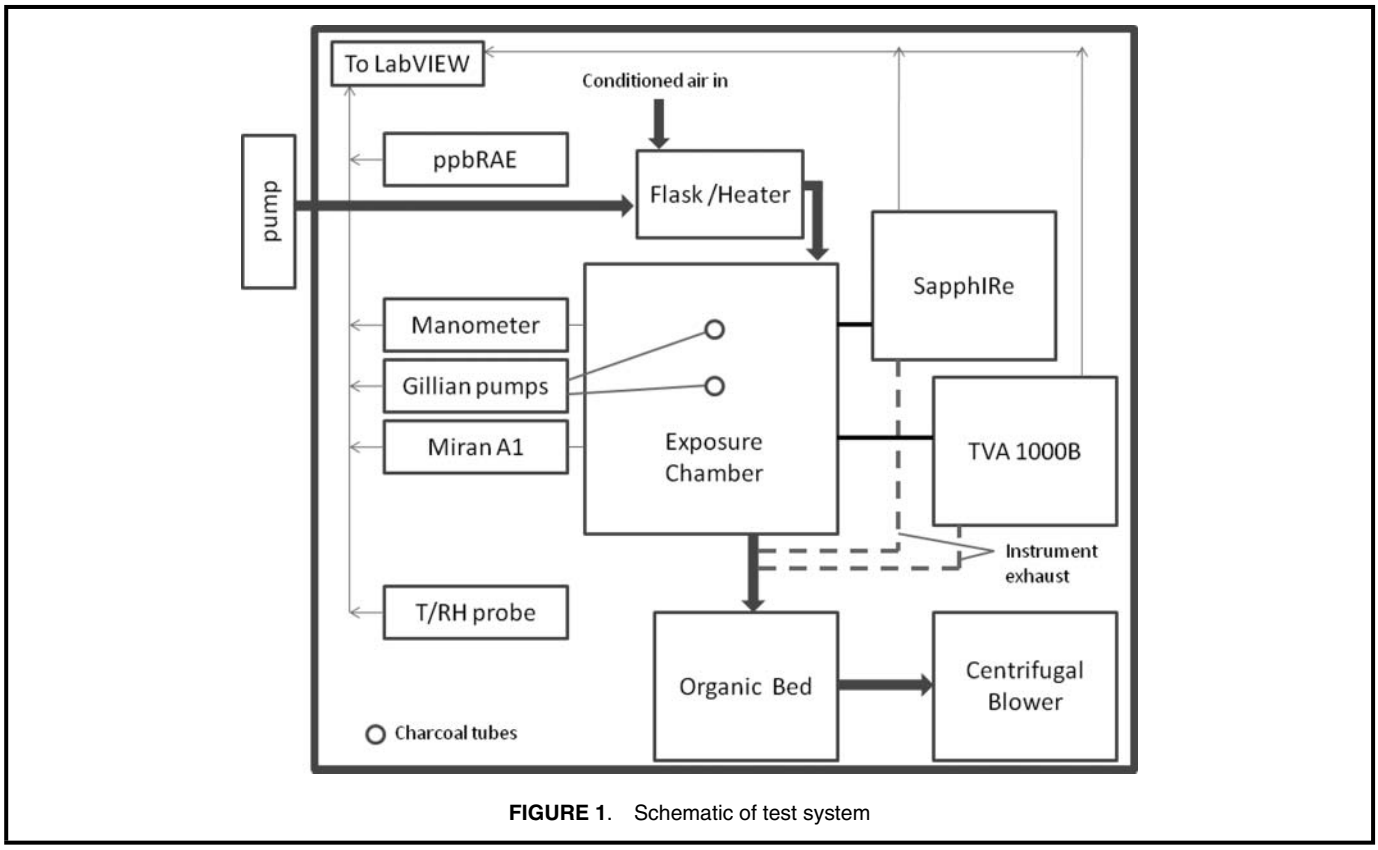

FIGURE 1. Schematic of test system

Charcoal Tube Analysis

The CT method consisted of charcoal tubes analyzed in-house using NIOSH Method 1500 for Hydrocarbons, BP 36°–216°C[18] with an Agilent 6890N gas chromatograph with a FID (Agilent Technologies, Santa Clara, Calif.). The following operating parameters were modified from those stated in Method 1500: 0.2 μL injection volume; 100% dimethyl polysiloxane fused silica capillary column with dimensions of 60 m × 0.32 mm ID × 1.00 μm film (Rtx-1; Restek Corporation, Bellefonte, Pa.); and a 20:1 split flow. In addition, 167 ng of p-cymene 99+% (Acros Chemicals, Thermo Fisher Scientific, Geel, Belgium) was added to each sample as an internal standard. Two five-point response factor calibration curves (both $r^2 = 1$) were developed (3.05 ng/sample to 61.1 ng/sample and 61.1 ng/sample to 763.7 ng/sample). The limit of detection for the modified method was considered to be 3.05 ng. No cyclohexane was detected on the back sorbent section at any of the environmental conditions.

Test Automation System

The testing was automated using LabVIEW 2009 (National Instruments Corporation, Austin, Texas) running on a laptop computer connected to a National Instruments NI cDAQ-9174 CompactDAQ chassis equipped with an NI 9205 32-channel analog input, an NI 9481 4-channel relay, and an NI 9472 8-Channel Digital Output module. Three digital interfaces were built to monitor, decrypt, and reformat the information from the three TVA monitors and forward this processed information in real-time to the computer. The test system collected two data points per second. A program listing, schematic diagrams, and other design details for the test automation system are available in the online supplement (Tables SI and SII and Figures S1 through S10).

DATA ANALYSIS

An average of the 3600 data points from each monitor was calculated for a 30-min TWA. The TVA monitor results obtained using Calibration Method 1 were multiplied by the appropriate response factor (Table SI in the online supplement), since the TVA monitors were calibrated using isobutylene and methane but used for sampling cyclohexane.[19] The results of the nine monitors were compared with the average of two charcoal tubes (analyzed using the CT method described above)[17,18] for each of the tests. All monitor readings and charcoal tube values less than the limit of detection (LOD) value were set to one-half the LOD. The LOD values were: charcoal tubes, 2.9 ppm (determined experimentally); SapphIRe, 6 ppm, [12]; PID, 0.5 ppm[14]; and FID, 1 ppm.[14]

Descriptive Statistics

The means, relative standard deviations, and percent of charcoal tube value (monitor reading/corresponding charcoal tube value × 100) were computed for the charcoal tubes (n = 120), individual monitor (n = 60), and each monitor group (n = 180) at the nominal concentrations of 30, 150, 300, and 475 ppm for both calibration methods. Outliers such as

false negative responses were not removed since the monitor appeared to calibrate properly. A Student's t-test was used to determine whether Calibration Method 1 or 2 resulted in monitor readings closer to the charcoal tube values.

To investigate the relationship between monitors (inter-monitor variability), a mixed linear model analysis of variance (ANOVA) with Tukey's test was employed. The overall relationship between monitors was observed by pooling data regardless of nominal concentration, temperature, and RH.

Regression is another method that can be used to investigate the correlations between the monitor and charcoal tube values. Both variables (monitor and charcoal tube values) have error that needs to be considered. Typical regression analysis assumes only one of the variables has an associated error. To account for the error associated with both variables, the SAS procedure CALIS was used.[20] The output of the model regression is α (intercept), β (slope), and r^2 (coefficient of correlation). The overall correlations among monitors were observed by pooling data regardless of nominal concentration, temperature, or RH.

To determine if an environmental condition (i.e., concentration, temperature, or RH) had an effect on the performance of the monitors, the data were grouped by calibration method, nominal concentration, temperature, and RH to elucidate their effect on monitor performance. The percent differences between the charcoal tube values and the readings from each of the individual units of each monitor type were calculated.

RESULTS

False Positives

Of the 60 control tests (0 ppm) performed with Calibration Method 1, there were two for which the charcoal tube average was above the limit of detection. They occurred at 38°C and 90% RH directly after a 475-ppm trial and were presumably due to residual cyclohexane in the chamber. The tube average concentrations were 5.3 and 3.1 ppm. For these tests, two of the SapphIRe monitors did not detect any cyclohexane, while the third registered 22.6 and 25.1 ppm. The three PID monitors did not detect any cyclohexane. All three FID monitors registered concentrations of 2.0 to 7.7 ppm. The remaining 58 tests had at least one monitor registering cyclohexane when none was present (Table SII in the online supplement). SapphIRe 3 and FID 3 had the highest percentage of false positive readings (i.e., registering cyclohexane when none was present) during the control tests (0 ppm). In 95% of the control tests, SapphIRe 3 registered cyclohexane, while in 81% of the tests FID 3 registered cyclohexane. These false positives occurred at all temperatures and relative humidities. The descriptive statistics for each monitor's false positive tests are contained in Table SIII in the online supplement.

All charcoal tube values for the zero ppm condition conducted using Calibration Method 2 were below the LOD. When Calibration Method 2 was used, PID 2 and FID 2 readings were below the LOD for the zero ppm concentration control tests. Five percent of PID 3 and FID 3 readings were above the LOD. Approximately 10% of the SapphIRe 1 and 2 and PID 2 readings were above the LOD. FID 1 and SapphIRe 3 had the highest percentage of control test readings above the LOD (around 46%). These false positives also occurred at all temperatures and relative humidities (Table SIV in the online supplement). The descriptive statistics for each monitor's false positive test are contained in Table SV in the online supplement.

False Negatives

In the non-zero ppm concentration atmospheres using Calibration Method 1, the PID monitors provided negative or zero concentration readings in 36% (87/240) of the tests (Table SVI in the online supplement). All three PID monitors had approximately the same number of tests with negative or zero values. There were two conditions during which all three PID monitors gave zero values for all five replicates: 21°C/90% RH/30 ppm cyclohexane and 38°C/90% RH/475 ppm cyclohexane. None of the FID monitors had any false negatives. None of the SapphIRe monitors had any false negatives except SapphIRe 2 at 21°C/15%RH/30 ppm cyclohexane concentration. Using Calibration Method 2, the PID monitors had the highest percentage of zero and negative readings (25% to 55%). The percentage of FID and SapphIRe monitor zero and negative readings were substantially lower than the PID (0% to 10%). These occurred at all concentrations, temperatures, and humidities (Table SVII in the online supplement). At 38°C and 90% RH, all three PID monitors provided a zero or negative reading at all four nominal cyclohexane concentrations.

Descriptive Statistics

The overall mean ratios and relative standard deviations (RSDs) for the monitor groups for Calibration Method 1 including false negatives were as follows: SapphIRe 111 ± 32%, FID 107 ± 19%, and PID 96 ± 51%. The mean ratio and RSD of the CT method to the nominal concentration were 90 ± 16%.

For Calibration Method 2, the overall mean ratios and RSDs for the monitor groups including false negatives were as follows: SapphIRe 115 ± 56%, FID 211 ± 153%, and PID 123 ± 45%. The mean ratio and RSD of the CT method to the nominal concentration were 91 ± 13%.

For both calibration methods, the RSDs for all monitors were higher at the 30 ppm nominal concentration than at the other concentrations (Tables I and II). The following relationships exclude the 30 ppm nominal concentration. For Calibration Method 1, the SapphIRe and FID monitor groups had similar RSDs across concentrations (∼20%) while the PID monitor group had higher RSDs (∼45%). For Calibration Method 2, the SapphIRe monitor group RSD was slightly lower (∼14%) when compared with Calibration Method 1. The RSDs for the FID group were higher (∼35%) in Calibration Method 2. The RSDs for the PID group were similar between calibration methods. However, the percent of charcoal tube value remained fairly consistent for the monitor groups using both calibration methods across the four nominal cyclohexane

TABLE I. Means, Relative Standard Deviations, and Percent of Charcoal Tube Value of Monitors and Charcoal Tubes by Nominal Cyclohexane Concentration Using Calibration Method 1

	Nominal Cyclohexane Concentration											
	30 ppm			150 ppm			300 ppm			475 ppm		
Monitor[A]	Mean (ppm)	RSD[B]	% of CT Response[C]	Mean (ppm)	RSD	% of CT Response	Mean (ppm)	RSD	% of CT Response	Mean (ppm)	RSD	% of CT Response
Charcoal Tubes	29.1	20.0	NA	132.1	6.0	NA	252.0	10.1	NA	421.7	13.0	NA
SapphIRe 1	28.4	32.1	97.7	147.1	15.0	111.4	292.4	21.1	116.1	492.3	19.8	116.7
SapphIRe 2	25.5	46.9	87.6	144.3	20.5	109.3	281.5	21.7	111.7	473.2	20.5	112.2
SapphIRe 3	52.9	51.3	182.0	164.6	15.3	124.6	302.7	14.7	120.1	484.8	14.3	115.0
SapphIRe Group	35.6	60.9	122.4	152.0	17.9	115.0	292.2	19.4	116.0	483.4	18.4	114.6
PID 1	11.4	99.7	39.1	112.5	44.6	85.2	231.5	41.2	91.9	371.2	51.7	88.0
PID 2	29.1	56.9	100.1	135.7	47.5	102.7	250.5	45.7	99.4	422.7	41.9	100.2
PID 3	20.0	61.5	68.9	118.7	41.7	89.8	208.8	46.9	82.9	381.8	38.0	90.5
PID Group	20.2	76.1	69.5	122.3	45.6	92.6	230.3	45.1	91.4	391.9	44.2	92.9
FID 1	32.6	26.5	112.1	143.6	18.0	108.7	293.0	16.4	116.3	458.0	25.1	108.6
FID 2	25.8	29.9	88.6	117.5	14.8	88.9	216.4	16.1	85.9	371.8	23.5	88.2
FID 3	36.2	22.3	124.4	160.0	11.6	121.1	293.6	12.3	116.5	487.7	12.2	115.7
FID Group	31.5	29.2	108.3	140.4	13.8	106.2	267.7	20.1	106.2	439.1	23.3	104.1

[A]n = 120 for charcoal tubes, n = 60 for individual monitors and n = 180 for groups.
[B]RSD = percent relative standard deviation.
[C]% of CT Response = percent of charcoal tube response (monitor mean/charcoal tube mean*100).

TABLE II. Means, Relative Standard Deviations, and Percent of Charcoal Tube Value of Monitors and Charcoal Tubes by Nominal Cyclohexane Concentration Using Calibration Method 2

	Nominal Cyclohexane Concentration											
	30 ppm			150 ppm			300 ppm			475 ppm		
Monitor[A]	Mean (ppm)	RSD[B]	% of CT Response[C]	Mean (ppm)	RSD	% of CT Response	Mean (ppm)	RSD	% of CT Response	Mean (ppm)	RSD	% of CT Response
Charcoal Tubes	25.5	18.5	NA	139.8	8.4	NA	281.0	10.7	NA	429.8	9.1	NA
SapphIRe 1	24.9	48.0	97.7	153.8	9.4	110.0	304.6	10.2	108.4	469.9	11.1	109.3
SapphIRe 2	26.7	42.5	104.7	161.5	19.4	115.5	303.7	11.6	108.1	477.6	13.1	111.1
SapphIRe 3	30.5	83.8	120.0	160.1	18.9	114.5	320.0	15.9	113.9	492.1	12.9	114.5
SapphIRe Group	27.4	64.4	107.6	158.5	16.8	113.3	309.4	13.1	110.1	479.9	12.5	111.7
PID 1	7.1	150.9	27.7	160.7	35.3	114.9	352.0	32.5	125.2	535.9	35.4	124.7
PID 2	48.9	55.4	192.2	210.4	51.3	150.4	447.0	55.3	159.1	689.6	54.3	160.4
PID 3	18.4	123.8	72.1	165.3	49.9	118.2	356.9	32.7	127.0	546.0	34.3	127.0
PID Group	24.8	111.5	97.4	178.8	48.9	127.9	385.3	45.6	137.1	590.5	46.2	137.4
FID 1	50.2	75.1	197.3	241.6	22.9	172.8	451.0	21.8	160.5	666.2	27.4	155.0
FID 2	58.1	115.9	228.2	265.4	26.0	189.8	590.3	45.1	210.0	1004.2	55.1	233.6
FID 3	55.0	192.7	216.1	240.1	9.6	171.7	461.5	11.4	164.2	791.3	27.7	184.1
FID Group	54.4	138.4	213.7	249.0	21.6	178.1	501.0	35.4	178.3	820.5	46.8	190.9

[A]n = 120 for charcoal tubes, n = 60 for individual monitors and n = 180 for groups.
[B]RSD = percent relative standard deviation.
[C]% of CT Response = percent of charcoal tube response (monitor mean/charcoal tube mean*100).

concentrations except for the PID monitor group at the 30 ppm nominal cyclohexane concentration.

Student's T-tests

Since the large number of t-tests performed could result in the rejection of the null hypothesis when it is true (i.e., a "Type I" error), the Bonferroni correction was used with a p-value of 0.001, which is the typical p-value of 0.05 divided by 45, the maximum number of hypotheses being tested.[21] The results of the Student's t-tests comparing all the monitor means from Calibration Method 1 (173.7 ppm) with those from Calibration Method 2 (244.7 ppm) on all the data indicated that the two calibrations provided significantly different results ($p < 0.0001$). A t-test using the difference between the monitor group readings and the corresponding charcoal tube values was also performed. Again, there was a significant difference ($p < 0.0001$) between the two calibrations for all three monitor types. Measurements of the PID and FID monitor groups were closer to the charcoal tube values using Calibration Method 1. The SapphIRe group measurements were closer to the charcoal tube values using Calibration Method 2. These relationships were maintained when data were grouped by concentration, temperature, and RH.

Monitor Relationships

For Calibration Method 1, the results of the ANOVAs comparing the monitor readings with the charcoal tube average showed there was a statistically significant difference between all three monitor group means ($p < 0.0001$) ignoring concentration, temperature, and RH effects. For Calibration Method 2, the ANOVA showed the FID monitor group was significantly different from the PID and SapphIRe monitor groups that were not statistically different from each other. The FID and PID monitor group means were significantly different from the charcoal tube mean ($p < 0.0001$), while the SapphIRe monitor group mean was not significantly different. Based on the t-test and ANOVA results, all further analyses were performed only on the data obtained using Calibration Method 1.

The regression results (Table III) demonstrated that the FID and SapphIRe monitors agreed well with charcoal tube values since they had slopes, intercepts, and r^2 values closest to a one-to-one association (i.e., slope and r^2 value of 1 and an intercept equal to 0). The PID monitors had the worst overall association with the charcoal tubes ($r^2 = 0.58$), which may be a result of numerous false negative measurements. The regression results based on target RH (Table IV) indicated the performance of the SapphIRe and FID monitor groups was not affected by RH (i.e., the slope and r^2 values were approximately the same regardless of humidity). The association of the PID monitor group with the charcoal tubes was substantially lower at 90% RH compared with the other three humidities. The regression results based on target temperature showed no effect on the association (data not shown).

Figure 2 is a plot of the mean percent difference between the monitor group and the charcoal tubes by nominal cyclohexane concentration, temperature, and relative humidity using Calibration Method 1. Error bars are 95th percentile confidence intervals. As the nominal cyclohexane concentration increased, the mean percent difference between the PID monitor readings and the charcoal tube values decreased. For the FID and SapphIRe monitors, the mean percent difference did not vary greatly with nominal cyclohexane concentration. The FID and SapphIRe monitors always had a positive bias in relation to the charcoal tube values. The PID monitors had a negative bias only at 30 ppm cyclohexane concentration.

TABLE III. Regression Results for Calibration Method 1: Charcoal Tube Values vs. Monitors

Monitor	β (slope)	α (intercept)	r^2 value
SapphIRe 1	0.99	0.15	0.98
SapphIRe 2	0.99	0.15	0.98
SapphIRe 3	0.99	0.17	0.97
SapphIRe Group	0.99	0.17	0.97
PID 1	0.74	0.67	0.55
PID 2	0.78	0.63	0.60
PID 3	0.78	0.62	0.62
PID Group	0.76	0.65	0.58
FID 1	0.94	0.33	0.89
FID 2	0.98	0.19	0.97
FID 3	0.99	0.12	0.99
FID Group	0.96	0.29	0.92

Note: All concentrations, temperatures, and relative humidities conditions combined.

While regression results showed no temperature effect, the mean percent difference between the monitor readings and the charcoal tube values demonstrated temperature did have an effect on monitor performance (Figure 2). The mean percent difference between the PID monitor readings and the charcoal tube values decreased as temperature increased, but there is no statistically significant difference. The mean percent difference between the FID monitor readings and the charcoal tube values was greatest at 38°C. The mean percent difference between the SapphIRe readings and the charcoal tube values was approximately three times greater at 5°C (32%) than at the other two temperatures (10%).

For the PID monitors, the mean percent differences trended toward positive bias with increasing RH up to 60% and then decreased to –48% at 90% RH (Figure 2). Of the three monitor types, the FID monitors were least affected by humidity. The mean percent difference range for the SapphIRe monitors tended to decrease as humidity increased up to 60%RH and then increased slightly at 90%RH.

DISCUSSION

The largest variability between the CT and nominal concentrations (19.9%) was found at the 30 ppm nominal

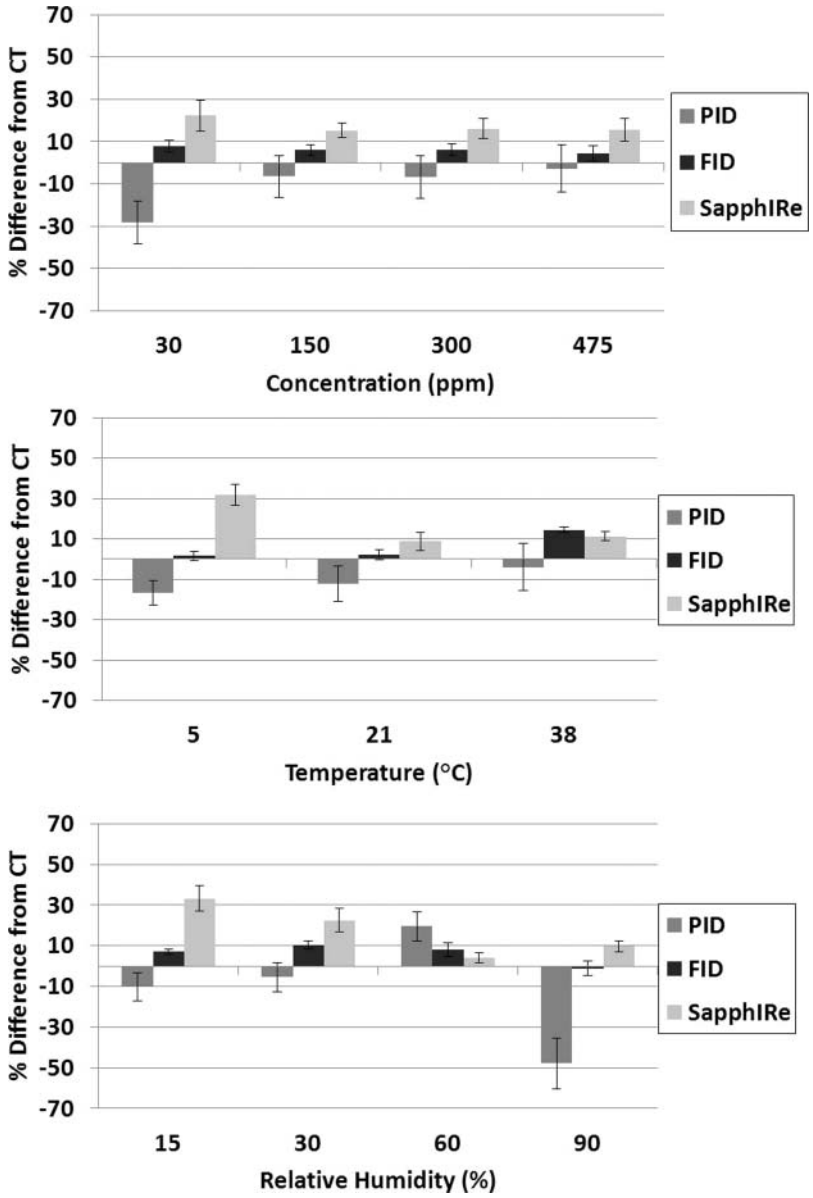

FIGURE 2. Percent difference between monitor group cyclohexane readings and charcoal tube values using Calibration Method 1 at the four nominal cyclohexane concentrations, three temperatures, and four relative humidities. Error bars are 95th percentile confidence intervals.

concentration. The M50 liquid handling pump output may have been less consistent at this concentration due to the small volumetric flow rate of cyclohexane needed to produce a concentration of 30 ppm.[22]

All monitor types had reliability issues evidenced by the number of false positive and false negative readings. False positives may have occurred due to sensor contamination from calibration gas or erroneous readings from electronic noise. False negatives may have occurred due to sensor failure or internal pump failure. This could not be confirmed since no indication of either was noted.

Many discrepancies were noticed when comparing the performance of individual monitors of the same type (Tables I and II). While monitors of the same type did not agree at certain test concentrations, there was no consistent pattern. This may be due to the individual monitors responding differently during a given test condition making the direct comparison of results from multiple monitors challenging. Regardless of calibration method, the SapphIRe and FID monitor readings were fairly consistent relative to the charcoal tube value across the four nominal concentration levels (Tables I and II). These monitor groups performed well since they were within $\pm$ 25% of the charcoal tube value. The PID also performed well with $<$ 10% difference compared with charcoal tube values at 150, 300, and 475 ppm conditions for Calibration Method 1 and at 30 ppm for Calibration Method 2. While the 30 ppm condition falls

TABLE IV. Regression Results for Calibration Method 2: Charcoal Tube Values vs. Monitors Segmented by Relative Humidity

	Target RH											
	15% RH			30% RH			60% RH			90% RH		
Monitor Group	β (slope)	α (intercept)	r^2 value	β (slope)	α (intercept)	r^2 value	β (slope)	α (intercept)	r^2 value	β (slope)	α (intercept)	r^2 value
SapphIRe	1.0	0.09	0.99	0.99	0.14	0.98	0.99	0.10	0.99	0.97	0.24	0.94
PID	0.97	0.26	0.93	0.98	0.19	0.96	0.97	0.27	0.94	0.41	0.91	0.17
FID	0.98	0.18	0.97	0.97	0.25	0.94	0.95	0.31	0.90	0.95	0.32	0.90

within the manufacturer's dynamic range, more variability was observed at this concentration presumably due to decreased signal-to-noise ratio.

Calibration Method 1 is easier and quicker for the user to perform than Calibration Method 2. Based on the results of the overall t-test (all monitors and all environmental conditions), the monitor mean from Calibration Method 1 (173.7 ppm) was closer to the overall charcoal tube mean of 171.2 ppm. Regardless of whether the data were segmented by nominal cyclohexane concentration, temperature, or RH, Calibration Method 1 provided better results than Calibration Method 2. When the data were segmented by monitor group, the FID and PID monitors performed better with Calibration Method 1. For the SapphIRe monitors, Calibration Method 2 (chemical of interest calibration method) provided readings that were closest to the actual cyclohexane concentration but Calibration Method 1 results were still adequate. Calibration Method 1 did provide results (a mean difference of 33.8 ppm between the monitor readings and the charcoal tube value) that were close to the mean difference (24.2 ppm) for Calibration Method 2. Since the differences between the two calibration methods were small for the SapphIRe monitors, users could use Calibration Method 1 for all three monitor types.

Based on the coefficients of correlation, the SapphIRe monitors ($r^2 = 0.97$) had the least variability in readings between the monitors and the charcoal tubes. The FID monitors ($r^2 = 0.92$) had slightly more variation. The PID monitors had the most variability between the monitor readings and the charcoal tubes. The reason the PID monitors had the worst overall association with the charcoal tubes may be a result of numerous false negative measurements.

Another reason may be their poor performance at the 90% relative humidity condition (Table III). Based on the regression results, temperature did not show an effect on monitor performance, while the percent difference from CT values (Figure 2) did demonstrate an effect for the FID and SapphIRe monitors. These conflicting results may be due to the inability of a regression to recognize subtle variations in performance (e.g., some data can provide coefficients of correlation and slopes near one even when the data are highly variable depending on the distribution of the error variation around the regression function).

Tedlar bags are permeable to water vapor, so their interior will equilibrate quickly with that of the environmental chamber.[23] The added water vapor might partially explain the negative bias in the CT values relative to the target values.

The PID monitor group was adversely affected by the 90% RH condition as seen in the regression results (Table IV). This could be due to lamp fogging.[24,25] The response of the 10.6 eV lamp in the PID of the TVA monitors can be reduced in the presence of high relative humidity even though the ionization energy of water is 12.62 eV.[26] Another potential explanation is that the water molecules may collide with the photoionized molecules of the compound of interest inside in the detector. These collisions may deactivate photoionized compounds.[24] The water vapor also absorbs, deflects, and scatters the ultraviolet light. When ultraviolet light is scattered, less light reaches the compound of interest for ionization. This results in less of the compound being ionized and a lower reading on the PID meter.[25,27]

CONCLUSION

A number of false negatives may have influenced this assessment and can certainly influence monitor performance in a real-world setting. False positives were also prevalent throughout the study indicating a measurement of cyclohexane concentration when none was present. Given these issues, monitor reliability should be considered prior to use in the field. Although a statistical difference was observed between some monitor results using the two calibration methods, Calibration Method 1 (manufacturer's recommended span calibration) is suitable for use with all three monitor types. Monitor results obtained using Calibration Method 1 were all within 16% of the charcoal tube values except for the 30 ppm condition. The PID group was drastically affected by the 90% RH condition, while the FID and SapphIRe monitor groups were not affected.

Direct-reading organic vapor monitors do have utility as survey meters to identify exposure sources or concentration profiles. Further research is needed to completely ascertain the performance of these monitors as compared with the charcoal tube method, including 8-hr TWA values under varying environmental conditions. A study is currently being conducted on

the effect of various interferent vapors on the performance of these monitors.

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