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## Evaluation of a portable gas chromatograph with photoionization detector under variations of VOC concentration, temperature, and relative humidity

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### Abstract

The objective of this present study was to evaluate the performance of a portable gas chromatograph-photoionization detector (GC-PID), under various test conditions to determine if it could be used in occupational settings. A mixture of 7 volatile organic compounds (VOCs)—acetone, ethylbenzene, methyl isobutyl ketone, toluene, *m*-xylene, *p*-xylene, and *o*-xylene—was selected because its components are commonly present in paint manufacturing industries. A full-factorial combination of 4 concentration levels (exposure scenarios) of VOC mixtures, 3 different temperatures (25°C, 30°C, and 35°C), and 3 relative humidities (RHs; 25%, 50%, and 75%) was conducted in a full-size controlled environmental chamber. Three repetitions were conducted for each test condition allowing for estimation of accuracy. Time-weighted average exposure data were collected using solid sorbent tubes (Anasorb 747, SKC Inc.) as the reference sampling medium. Calibration curves of Frog-4000 using the dry gases showed  $R^2 > 0.99$  for all analytes except for toluene ( $R^2 = 0.97$ ). Frog-4000 estimates within a test condition showed good consistency for the performance of repeated measurement. However, there was ~41–64% reduction in the analysis of polar acetone with 75% RH relative to collection at 25% RH. Although Frog-4000 results correlated well with solid sorbent tubes ( $r = 0.808$ – $0.993$ , except for toluene) most of the combinations regardless of analyte did not meet the <25% accuracy criterion recommended by NIOSH. The effect of chromatographic co-elution can be seen with *m*, *p*-xylene when the results are compared to the sorbent tube sampling technique with GC-flame ionization detector. The results indicated an effect of humidity on the quantification of the polar compounds that might be attributed to the pre-concentrator placed in the selected GC-PID. Further

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investigation may resolve the humidity effect on sorbent trap with micro GC pre-concentrator when water vapor is present. Although this instrument does not fulfill the accuracy criterion specified in the NIOSH technical report No. 2012-162, it can be used as a screening tool for range finding monitoring with dry gases calibration in the occupational setting rather than compliance monitoring.

## Keywords

Photoionization detector (PID); portable gas chromatography; VOCs

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## Introduction

Volatile organic compounds (VOCs) are of concern because of their potential adverse health effects. The conventional measurement of human exposure to VOCs in air samples requires the use of sorbent tubes, or passive badge samplers, for integrated air sampling. A weakness of conventional integrated air sampling methods is that each collected sample requires subsequent laboratory analysis, which inevitably delays communication of risk data back to the industrial hygienist, or worker. Air samples are usually desorbed and then analyzed by gas chromatography (GC) with different detection methods, including flame ionization, electron capture, photoionization detector (PID), and mass spectrometry. Bench scale GC-based instruments can unambiguously identify multi-species in a complex chemical mixture. Portable direct-reading monitors (PDRM) are being widely used to obtain rapid estimates of employees' exposures to chemical hazards and to enable immediate actions that are necessary to reduce exposures.<sup>[1-3]</sup> They provide powerful on-the-spot information in a wide variety of applications, ranging from leak detection to evaluation of control measures. A general survey monitor such as a handheld PID without a separation step can detect total VOCs at intervals of a few seconds with low detection levels (parts per billion (ppb)) in first responder scenarios.<sup>[4]</sup> There are also a few portable GC/PIDs including Explorer portable GC (Inficon Inc., East Syracuse, NY) and BTEX Analyzer (Series 8900, Baseline-MOCON Inc., Lyons, CO) that can specify individual VOC compounds. However, these instruments are not suitable for collecting worker's breathing zone exposure data due to their bulk (weight > 14 lb). A portable GC/PID, called Frog-4000 (Defiant Technologies, Albuquerque, NM), has been recently commercialized with support from U.S. Environmental Protection Agency (EPA)'s Small Business Innovation Research (SBIR) Program. In contrast to all other commercial portable/transportable GC-based instruments, Frog-4000 (weight < 5 lb) uses ambient air as a carrier gas by attaching cartridges of active carbon/carbon molecular sieve to scrub VOCs and water vapor in the air. This is a great advantage compared to other GC/PIDs which require a separate carrier gas. The Frog-4000 is intended for rapid VOC identification in the outdoor environments and might be able to measure a worker's breathing zone exposure. However, this instrument has not been fully evaluated via laboratory and field performance tests. A high degree in variability of instrument performance has been observed with PDRM's subjected to variations of temperature, relative humidity (RH), and concentration levels.<sup>[5]</sup> The data presented here characterize the performance of the Frog-4000 GC-PID under such variations.

## Experimental methods

### Targeted volatile organic compounds

The seven analytes of interest in the present study were selected because they are commonly present in paint manufacturing industries. They included acetone, ethylbenzene, methyl isobutyl ketone (MIBK), toluene, *m*-xylene, *p*-xylene, and *o*-xylene.

### Test setup and environmental conditions

A glass-type test chamber ( $\sim 0.004 \text{ m}^3$ ) was placed in a  $22 \text{ m}^3$  walk-in environmental chamber (Nor-Lake Enviroline; Nor-Lake Scientific, Hudson, WI) similar to that previously described.<sup>[5,6]</sup> A dynamic atmosphere system was used to produce a constant, known concentration mixture of the 7 analytes of interest at various levels of humidity and temperature using a Miller-Nelson flow-temperature-humidity control system (Model HCS-501, Assay Technology Inc., Livermore, CA) and a certified specialty gas mixture (part No. BL1506056, Ideal Speciality Gases and Analytical Services, Houston, TX) controlled by mass flow controller (Aalborg Instruments Inc., Orangeburg, NY). The proportion of 7 selected analytes for each exposure scenario were chosen based on the relative levels of OSHA's Permissible Exposure Limit (PEL) for the individual compounds, i.e., initial concentrations of each compound were  $1000 \text{ ppm} \pm 2\%$  for acetone,  $200 \text{ ppm} \pm 2\%$  for toluene, and  $100 \text{ ppm} \pm 5\%$  for the other compounds. As shown in Table 1, four different concentration levels (1x, 2x, 4x, and 8x) of diluted gas mixtures were selected to be within the normal operating range of the selected portable GC-PID as recommended by the manufacturer. Three different temperatures (T;  $25^\circ\text{C}$ ,  $30^\circ\text{C}$ , and  $35^\circ\text{C}$ ), and 3 relative humidities (RH; 25%, 50%, and 75%) were selected. Environmental information was recorded through a traceable humidity/temperature meter (Model 4080, Control Company Inc., Friendswood, TX) during each sampling period.

The atmosphere flow rate was approximately  $20 \text{ L min}^{-1}$  within the 4-L volume test chamber. Prior to conducting each experimental trial, a FTIR (DX-4040, Gasmeter Technologies Inc., Finland) and a handheld PID (MiniRAE 2000, RAE Systems, US) were used to ensure the test atmosphere mixed with conditioned environmental air had properly entered the test chamber. Preliminary sorbent tube analysis results showed all 7 analytes were uniformly delivered across all sampling ports. A full factorial experimental design was chosen and performed in the present study. For each test condition, at least 3 replicates of each condition were performed. The total number of experimental trials was 108. One sorbent tube sample and 5 consecutive measurements measured by 2 independent Frog-4000s were performed for each of the 108 experiments (4 concentrations  $\times$  3 temperatures  $\times$  3 relative humidities  $\times$  3 replicates).

### Calibration curves of analytes of interest and instrument settings

Standard calibration curves of each GC-PID for each analyte were established through a gas sample diluter (Defiant Technology Inc.) that blended a certificated gas mixture (Ideal Speciality Gases and Analytical Services, Houston, TX) and a pure dry air (Zero air level, Butler Gas, McKees Rocks, PA), controlled by calibrated rotameters. Both rotameters were periodically calibrated over 15 nominal flow rates by a primary gas flow calibrator (DryCal

DC Lite-M, or DryCal Defender 220-L, BIOS, Butler, NJ). At least 7 atmospheres at different desired nominal concentration for each analyte were measured and the flow rates to deliver the desired concentration were calculated using a volume-concentration equation with atmosphere pressure adjustments provided by the manufacturer. The primary gas flow calibrator was used to confirm the desired nominal flow rate within 5% through a whole completed analytical cycle of the Frog-4000 instrument. User-defined calibration curves ranged in concentration from 0.08–18.1 ppm for acetone ( $R^2 = 0.992$ ); 0.01–1.81 ppm for ethylbenzene ( $R^2 = 0.997$ ); 0.41–3.59 ppm for MIBK ( $R^2 = 0.996$ ); 0.02–3.62 ppm for toluene ( $R^2 = 0.967$ ); 0.02–3.62 ppm for *m, p*-xylene ( $R^2 = 0.995$ ); and 0.01–1.81 ppm for *o*-xylene ( $R^2 = 0.994$ ). A few concentrations of each analyte were checked periodically for daily variation was found to be within  $\pm 25\%$  during the experiments. In the operating manual provided by manufacturer, it is stated the default settings are best for the analysis of benzene, toluene, ethylbenzene, and xylenes (BTEX), but the settings can be altered for analyzing a wide variety of compounds and concentrations. The current instrument operational settings are listed below: hold time at initial GC temperature (38°C) for 400 sec; ramp time from GC cold to GC hot temperature (120°C) over 90 sec; hold time at hot GC temperature for 60 sec; collection time of VOCs onto preconcentrator (60 sec); cleaning time of pre-concentrator by heating (4 sec); time allowed for pressure to stabilize before pre-concentrator fire (4 sec); and time of heating pre-concentrator to release VOCs (6 sec).

### Sorbent tube sampling and analytical methods

Anasorb 747 sorbent tubes (Cat. No. 226–83, SKC Inc., Eighty Four, PA) were selected for all experimental conditions because coconut shell active carbon has been shown to be a rather poor sorbent for polar vapors in air, demonstrating a relatively low recovery performance when high humidity conditions are present.<sup>[7]</sup> Sorbent sampling took place from a sampling port within the glass chamber close to the sampling probes of the Frog-4000s. Samples from the challenge atmospheres were pulled through the Anasorb 747 tubes at a flow rate of 200 mL min<sup>-1</sup> for a sampling time ranging from 30–60 min. A DryCal® DC-Lite device was used to ensure that the difference between pre- and post-sampling flow rates was within  $\pm 5\%$ . Sorbent samples were analyzed by a commercial laboratory in accordance with the NIOSH Manual of Analytical Methods (NMAM) 1501 modified to include the additional analytes.<sup>[8]</sup> In each sampling campaign, 2 or 3 field blank samples were collected to ensure no handling contamination. All field blank samples showed results lower than limit of detection (LOD). The LOD ranged from 0.4–0.9  $\mu\text{g}$  for all 7 analytes. The LOQ ranged from 1.3–4.9  $\mu\text{g}$  for all 7 analytes. The analytical ranges were between 0.4 and 870  $\mu\text{g}$  for all 7 analytes. A few samples (6 out of 123 trials) showed less than the LOQ. Five samples were lost during handling.

### Data analysis

All data were analyzed using JMP software version 12.1.0 (SAS Institute, Cary, NC). First, descriptive statistics on concentration of each analyte for both sorbent samples and Frog-4000 were calculated. Replicate measures that were collected for each independent Frog-4000 result (or Anasorb 747 result) and variable combination were averaged prior to the analysis. Measured concentration values from Anasorb 747 and Frog-4000 were compared with theoretical and mean ratios were calculated. Second, a three-way factorial

analysis of variance was performed to determine whether there were any effects of environmental parameters on quantification by both near real-time and sorbent sampling methods. Lastly, Pearson's correlation coefficients were calculated to see how well paired samples (Frog-4000 vs. Anasorb 747) correlated with each other. Bias, precision, and accuracy were calculated per NIOSH technical report No. 2012-162: Components for Evaluation of Direct-Reading Monitors for Gases and Vapors.<sup>[9]</sup> These values were used to determine whether the Frog-4000 met the NIOSH accuracy criterion (measurements are within  $\pm 25\%$  of the true concentration with 95% confidence). Finally, a contour plot was used to show the relationship between accuracy, bias, and precision.

## Results

### Effect of environmental factors on Anasorb 747 and Frog-4000 data

Figure 1 shows the mean ratios of measured values normalized with theoretical values obtained from Anasorb 747 with the different test conditions. The mean ratios in each analyte of interest were slightly lower than 1 and did not vary much as the target concentration level increased (Figure 1a). The effect of concentration level was significant because of the tight precision ( $p$ -value  $< 0.05$ ). The change in the ratios of each analyte of interest with temperature (Figure 1b), and with relative humidity (Figure 1c) are not visually apparent except that acetone was most affected by water vapor adsorption, as can be seen from a noticeable decrease of normalized ratios as relative humidity increased. Nevertheless, except for the interaction of acetone with relative humidity, temperature and relative humidity can be considered to have no effect on ratios of individual compounds since the differences in least square means for each comparison were small and the differences in observed ratios of each analyte of interest were negligible.

Figure 2 shows the normalized ratio results obtained from Frog-4000 between concentration level, and between the temperature, and between the relative humidity as presented in Figure 1. Statistical differences for each main effect of parameters were observed over their corresponding levels, ( $p$ -value  $< 0.0001$ ). ANOVA results of the 3 or 5 replicates for Frog-4000 within each test condition showed a good consistency on the performance of repeated measurement. When the observed ratios are plotted by concentration level (Figure 2a), the Frog-4000 produced noticeably different results that varied widely by analyte, whereas the mean ratio results collected by Anasorb 747 were relatively flat and close to 1. This scatterplot matrix showed significant differences in the normalized ratios of each analyte over the range of test levels of temperature and relative humidity, indicating strong interaction among the above test parameters, which also can be seen in Figure 3. For example, the reduction in the ratios of acetone with 75% RH relative to collection at 25% RH was ~41–64%. As can be seen especially for the higher acetone concentration levels the reduction in Frog-4000 response is related to the absolute humidity (e.g., 25% relative humidity at 25°C contains 5 g of water per Kg of air, while the same relative humidity at 35°C contains 9.3 g/Kg). Calibration of the Frog-4000 uses dry-air concentrations delivered by a mask. It is possible that there are differences between the Frog-4000 response for a calibration sample delivered by the mask and the Frog-4000 response in a dry chamber environment at the same concentration. If there is no difference then the serious effects of

humidity on response seen in Figure 3 may extrapolate to no effect at zero humidity, but it is not possible to demonstrate this without a zero-humidity chamber experiment. Such an experiment would require room air to be dried, which is difficult to achieve.

### Correlation between Anasorb 747 and Frog-4000 data

Figures 4a–f illustrates the scatterplots of concentration in each analyte of interest in this study between Anasorb 747 and Frog-4000 readings. Overall, these relationships showed the Frog-4000 analysis correlated well with the traditional sorbent-based method ( $r = 0.808$ – $0.993$ ) for most analytes of interest with the exception of toluene. Toluene had the weakest association between direct-reading and the traditional sorbent-based method ( $r = 0.733$ ) (all  $p$ -values  $< 0.05$ ). With Anasorb 747 used as an independent variable, the regression analysis showed slopes varied from 1.31–2.34, indicating ~43–76% lower concentration magnitudes by the Frog-4000 depending on analyte. In addition, most of measurements of analytes of interest showed different correlations between two different instrument units (at least  $r > 0.903$ ) but this is least notable in the acetone ( $r = 0.980$ ) and o-Xylene ( $r = 0.999$ ) results.

### Estimation of accuracy, bias, and precision suggested by NIOSH method

The estimation of accuracy, bias, and precision of the Frog-4000 for direct concentration measurement of 7 analytes under the selected test combinations were calculated using the average of the 2 unit results per NIOSH technical report (No. 2012–162).<sup>[9]</sup> The measurement of each analyte from the monitors were compared to the reference sampler (i.e., Anasorb 747). Note that variances of both bias and precision were significantly different at varied levels of test concentration, temperature, and relative humidity. Overall, most of the combinations regardless of analytes (192 out of 216 runs; 36 trials with 3 replicates for each analyte) generated accuracy exceeding the 25% criterion specified in the NIOSH technical report No. 2012–162.<sup>[9]</sup> The bias of each analyte for the selected VOCs monitor was relatively high ( $>50\%$ ) and varied by temperature ( $p < 0.05$ ), humidity ( $p < 0.05$ ), and concentration level ( $p < 0.05$ ) whereas precision of each analyte was in general less than 9.8% regardless of analytes and test conditions (211 out of 216 runs). These accuracy results in 95% confidence limits are given by equation specified by NIOSH technical report and as indicated in a contour plot for illustration by using toluene as an example (Figure 5a). Because bias is non-homogeneous, we cannot provide a point estimate of the overall monitor accuracy over the range of environmental factors and exposure scenarios using pooled values for bias and precision. Figure 5b illustrates accuracy, bias, and precision of same GC-PID obtained from the same test conditions but the GC-PID measurements were compared to the target values (i.e., theoretical values with dilution correction). The results of accuracy, bias, and precision presented the same trend of variation indicated in contour plot as the findings shown in the Figure 5a (i.e., Frog-4000 Vs. Anasorb 747). Relative small ranges of bias were found while the GC-PID measurements were compared to target values (from  $-0.8$  to  $0.2$ ) rather than Anasorb 747 (from  $-0.8$  to  $0.4$ ).

## Discussion

### Humidity effect on sorbent trap with pre-concentrator and sorbent tube

Within the GC is a sorbent, which acts as a focuser to introduce the sample as a sharp pulse into the GC column; as shown in Figures 6a and 6b, it is the serpentine trace on the top side of the pre-concentrator. There is an integrated heater on the pre-concentrator without trapping temperature control and no membrane filter or sampler over the pre-concentrator. A previous study by Sanchez and Sacks (2005) preconcentrated organic vapors through a multibed on-line sorption trap prior to injecting the analytes onto a GC column and observed that the presence of water vapor in samples affects the retention of polar compounds by carbon-based multiple sorbent traps.<sup>[10]</sup> The current study confirmed that there is an effect of humidity on the quantification of the polar compounds that might be attributed to the adsorbent in the pre-concentrator in the Frog-4000. The sorbent in the pre-concentrator is reported by the manufacturer to be a silica gel (with other additives that give it some preferential selectivity) produced using a sol-gel coating process. In general, silica gel is a widely used adsorbent for polar compounds whereas non-polar compounds are preferentially adsorbed onto activated charcoal or molecular carbon sieves. However, silica gel absorbs water vapor much more intensively than most organic compounds.<sup>[11]</sup> Note that the silica gel coating here is referred to as an aerogel and not as a pure silica gel. Thus, it is not certain whether the type of adsorbent in the pre-concentrator can explain why the GC-PID measurements are depressed in comparison to the reference method (i.e., Anasorb 747 > Frog-4000). Many factors should be carefully considered when selecting different adsorbents for use of in the pre-concentrator as a trap, such as strong affinity with analytes, low activation energy of desorption, large capacity and good binding with pre-concentrator substrate.<sup>[12,13]</sup>

The effect of the adsorption of water vapor on all aspects of the sampling and analysis of polar molecules is of such importance as to require detailed discussion. Harper et al.<sup>[7]</sup> evaluated the effect of humidity on the breakthrough of acetone collected by three different sorbents, including Anasorb 747, carbon molecular sieve (Anasorb CMS), and active charcoal (Lot 120) and reported that the effect of humidity on breakthrough is most marked in the case of carbon molecular sieve, followed by active charcoal and Anasorb 747. Here it should be noted that silica gel exhibits greater affinity for water vapor than the other carbon compounds. It is likely that the acetone is initially absorbed by the silica, but is displaced by water while the pre-concentrator is collecting sample. This displaced acetone is lost to the system before the pre-concentrator is heated and its burden of adsorbed molecules injected into the GC. Those reasons might explain why the acetone concentration magnitude obtained from Frog was always lower than that from the Anasorb 747.

Another common interference for GC detection arises from the simultaneous introduction of water onto the column, which can cause retention time shifts. In the present study, a noticeable shift was observed in the retention time window at 75% RH for all 7 analytes. However, there are many practical improvements to reduce the water uptake of selected sorbent traps during the GC analysis procedure: (1) reducing sample volume; (2) reducing the adsorbent mass; and (3) heating the adsorbent during the air sampling.<sup>[14-16]</sup> Users can

choose either the above practical instrument adjustments, where possible, or conduct calibration with standards under the same condition of humidity as the air sample as recommended by Sanchez and Sacks.<sup>[10]</sup>

### Co-elution effect

Co-elution of analytes is another critical concern in the application of portable GC-based instruments. Haghghi et al.<sup>[17]</sup> reported that the most frequently reported stationary phase used by micro capillary column on-a-chip is polydimethylsiloxane (PDMS). The portable GC-PID in the present study uses a 4.8 m long 316 stainless steel column whose interior surface is coated with a 0.8  $\mu\text{m}$ -thick PDMS stationary phase (OV-1, Ohio Valley Specialty, OH). Theoretically, PDMS should be able to separate VOCs such as light alkanes or aromatic compounds (BTEX) below 40°C. Unfortunately, we found co-elution with *m*- and *p*-xylene. In general, a PDMS stationary phase can separate many VOC analytes, but it is well known that there are some analytes that co-elute with virtually any stationary phase.

### Accuracy

Similar research by Chen et al., using Arizona State University (ASU) VOC sensors, gave an accuracy higher than 81% compared with NIOSH 1501 modified method when benzene samples were analyzed by NMAM 1501 with  $275 \pm 35$  ppb. However, they also stated “further efforts to improve the VOC sensor accuracy and statistical significance of correlation of VOC sensor results with reference methods are on going”<sup>[18]</sup> Research by Romero-Trigueros et al. (2017) also observed the influence of humidity on benzene measurement with a transportable GC-PID. They found the bias in reading was 33% and 47% for a reference concentration of benzene in air of 5 and 40  $\mu\text{g}/\text{m}^3$ .<sup>[19]</sup> In the present study, most of the combinations regardless of analytes generated accuracy >25%, exceeding the criterion specified in the NIOSH technical report No. 2012–162<sup>[9]</sup> when GC-PID measurements were compared to either reference samples or target values. The results of accuracy, bias, and precision presented a similar trend of variation when the GC-PID was compared to either the reference sampling method or the theoretical target concentration, but there was a large variation in biases between these two comparison methods because of effect of water vapor on either reference sorbent tube or pre-concentrator with the selected GC-PID.

### Conclusions

The present study evaluated a commercial portable GC-PID against various temperatures, relative humidities and exposure scenarios in comparison to the Anasorb 747 sorbent tube method. This instrument does not fulfill the accuracy criterion criteria specified in the NIOSH technical report No. 2012–162 but it could be used as a screening tool with dry gas calibration in occupational settings to identify VOCs present in the workplace air. Further investigation may resolve the humidity effect on sorbent trap with micro GC pre-concentrator when water vapor is present. Although this GC-PID can only measure exposure levels up to ~16 ppm (acetone), an inline dilution probe could allow application to the higher concentrations more likely occurring in the workplace.

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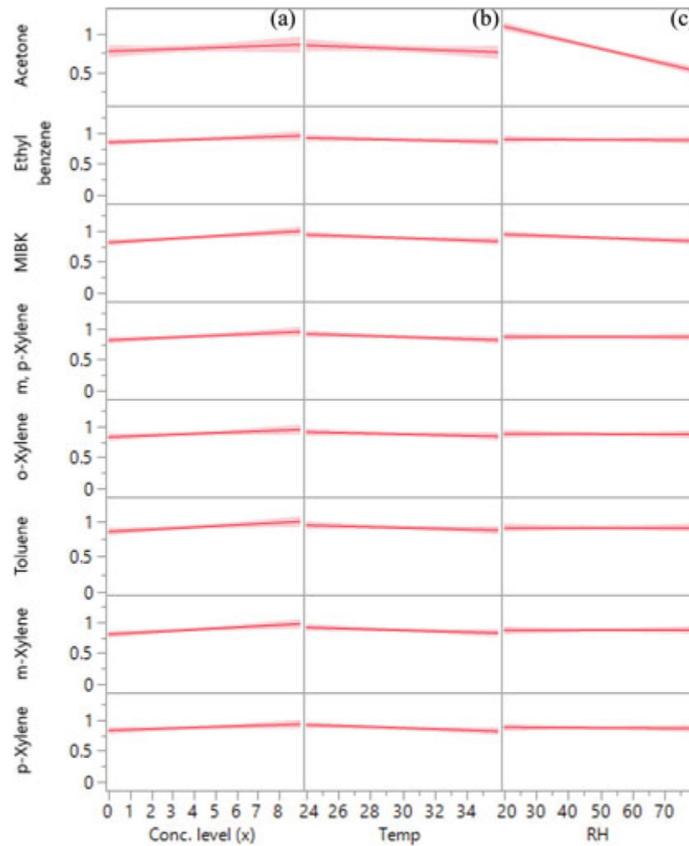
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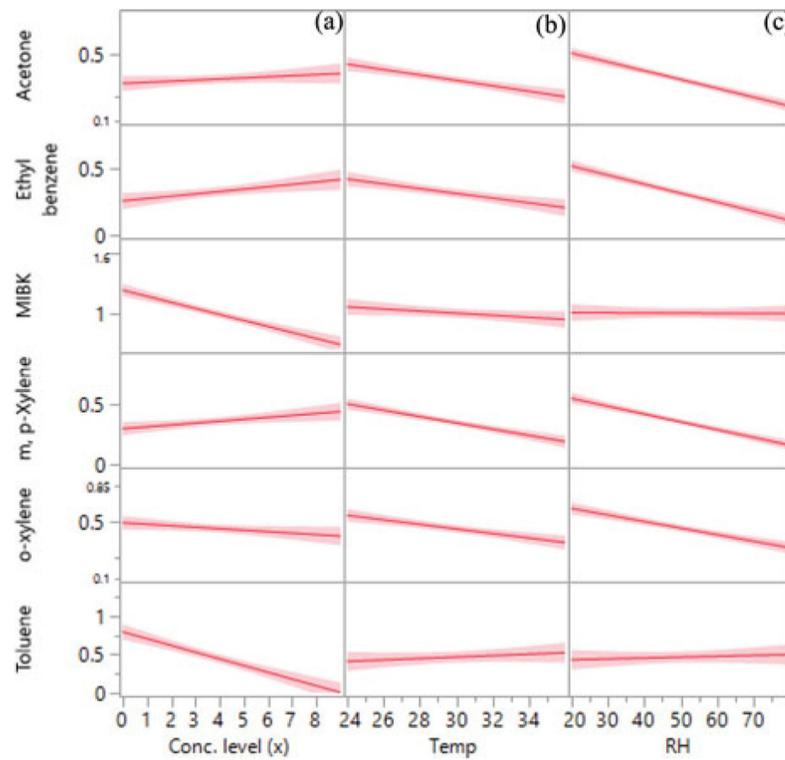
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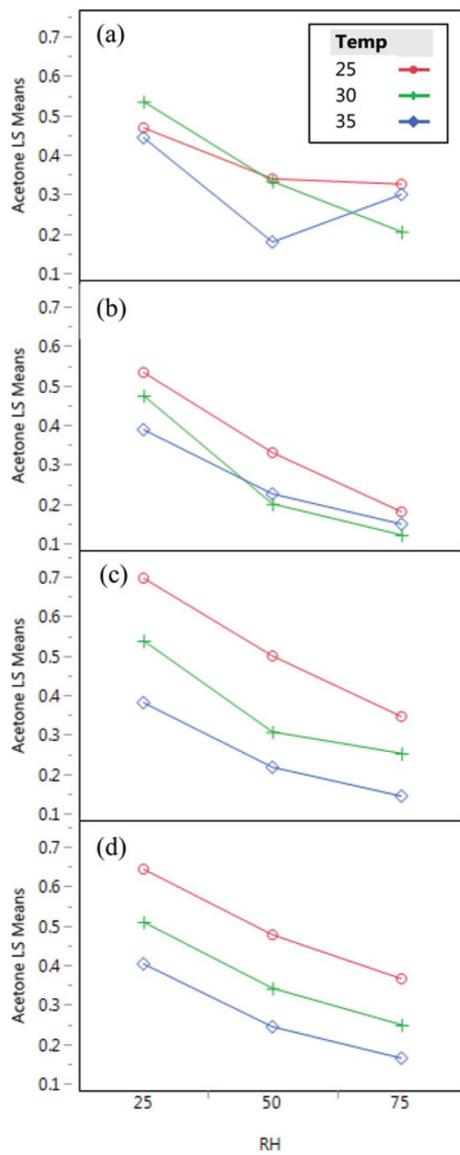


**Figure 1.** Mean ratio of measured/theoretical concentration of 7 analytes against environmental factors (sample collected by Anasorb 747). Note that red line indicates mean values through least square method. The Concentration Level (x) values in the abscissa refer to the sets of environmental testing parameters (1x, 2x, 4x, or 8x) listed in Table 1. The value of an ordinate point is the mean ratio of measurements of an analyte to its applied value. The mean is taken over the environmental factors of temperatures and relative humidities in Table 1 (25°C, 30°C, and 35°C) and (25%, 50%, 75%), respectively. The theoretical value is calculated from its concentration in the standard and the dilution factor.



**Figure 2.**

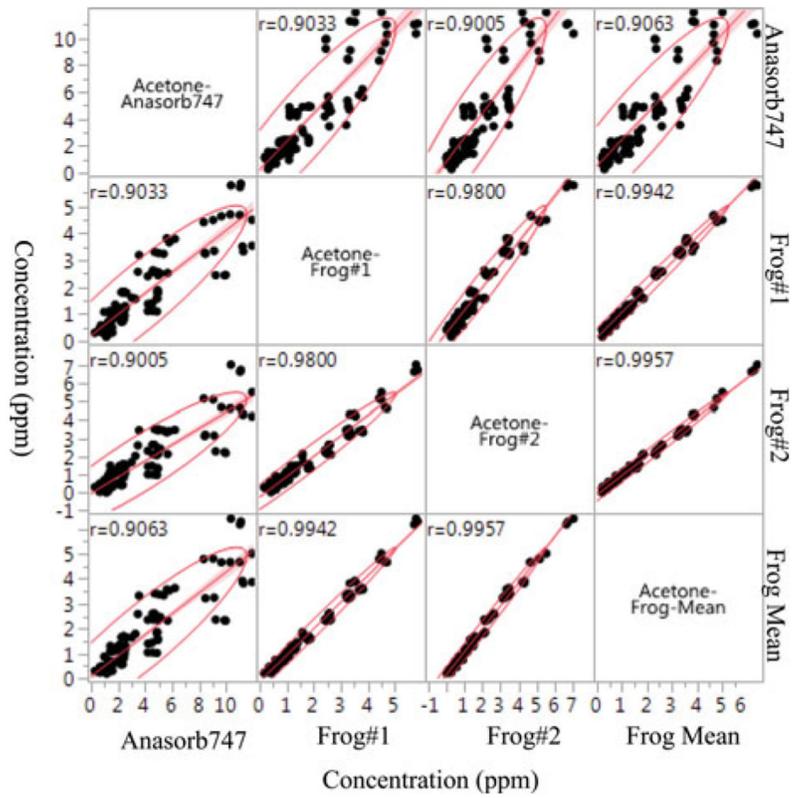
Mean ratio of measured/ theoretical concentration of 7 analytes against environmental factors (sample collected by FROG). Note that red line indicates mean values through least square method. The Concentration Level (x) values in the abscissa refer to the sets of environmental testing parameters (1x, 2x, 4x, or 8x) listed in Table 1. The value of an ordinate point is the mean ratio of measurements of an analyte to its applied value. The mean is taken over the environmental factors of temperatures and relative humidities in Table 1, (25°C, 30°C, and 35°C) and (25%, 50%, 75%), respectively. The theoretical value is calculated from its concentration in the standard and the dilution factor.



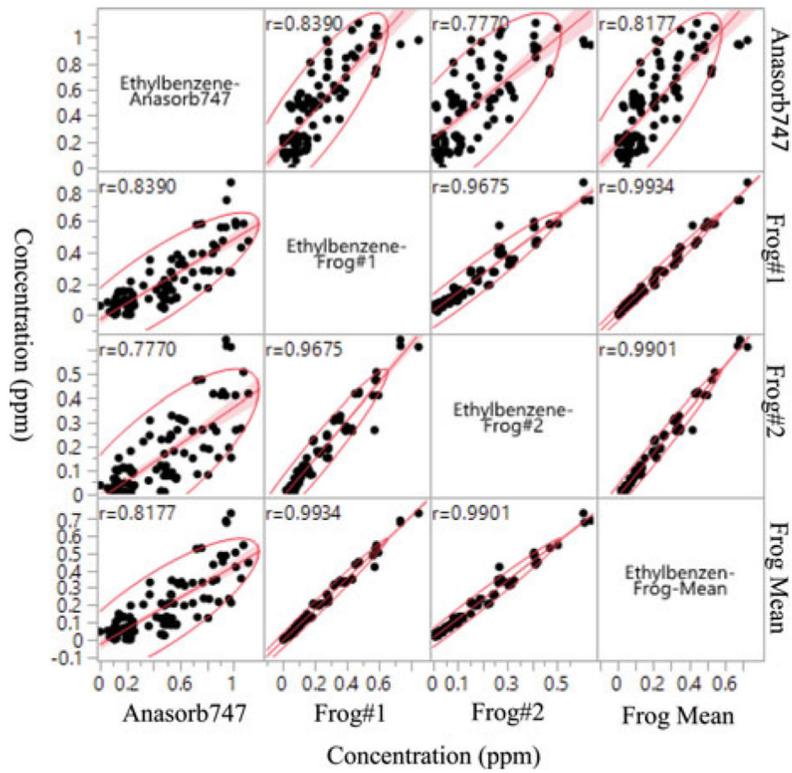
**Figure 3.** Effects of concentration level, temperature, and relative humidity on mean ratio of measured acetone normalized with theoretical values using the selected GC-PID: (a) 1x concentration level; (b) 2x concentration level; (c) 4x concentration level; and (d) 8x concentration level.

	Frog #1-Anasorb 747	Frog #2-Anasorb 747	Frog Mean-Anasorb 747
Anasorb 747-Frog #1		Frog #2-Frog #1	Frog Mean-Frog #1
Anasorb 747-Frog #2	Frog #1-Frog #2		Frog Mean-Frog #2
Anasorb 747-Frog Mean	Frog #1-Frog Mean	Frog #2-Frog Mean	

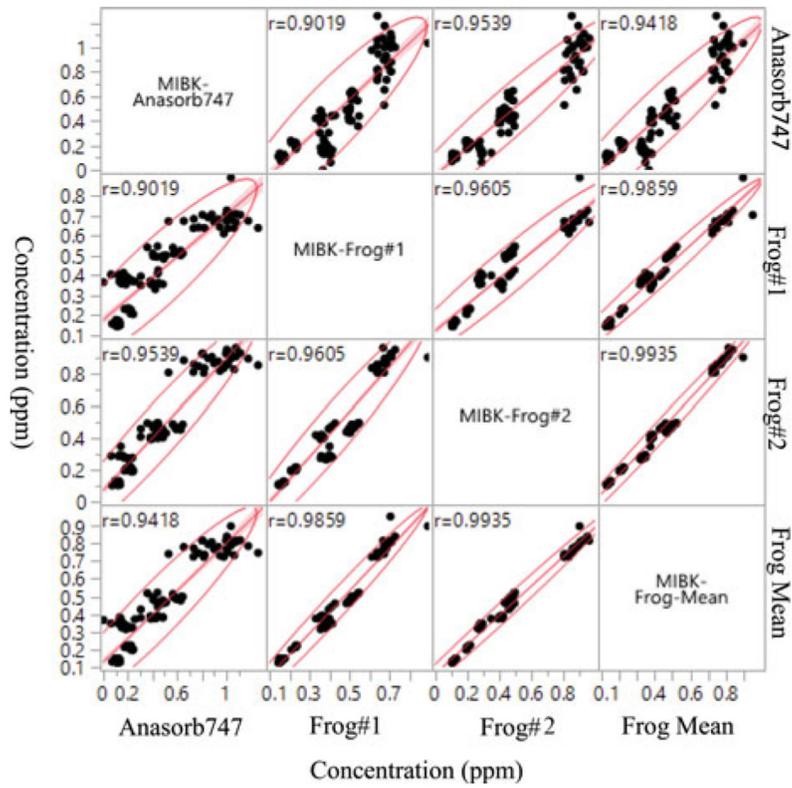
**Figure 4.**  
Key to Figures 4(a)–(f).



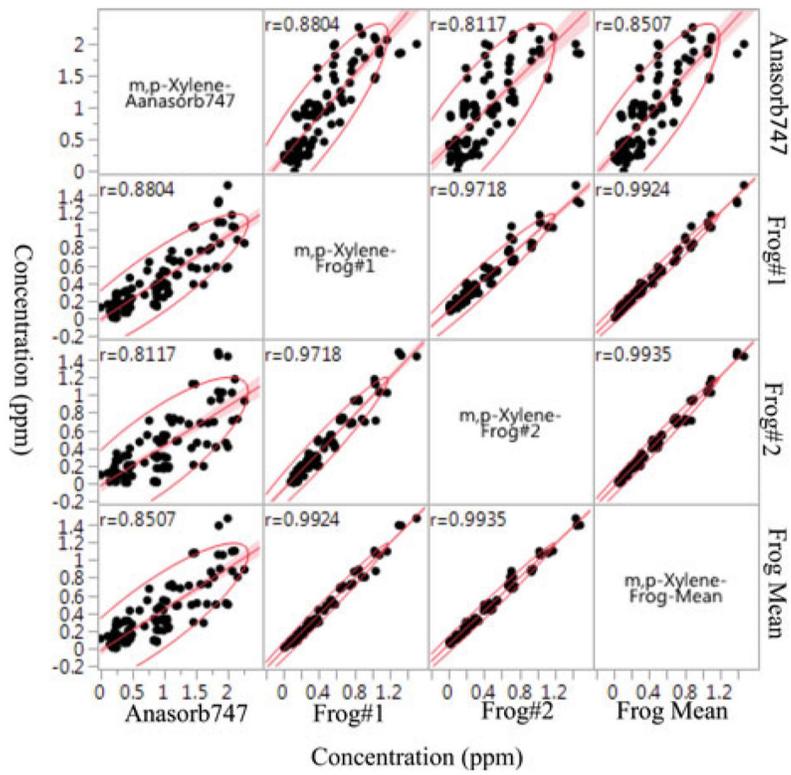
**Figure 4a.** Scatterplot matrix of correlation between Anasorb747 and Frog-4000 data: Acetone. See key for each column/row comparison.



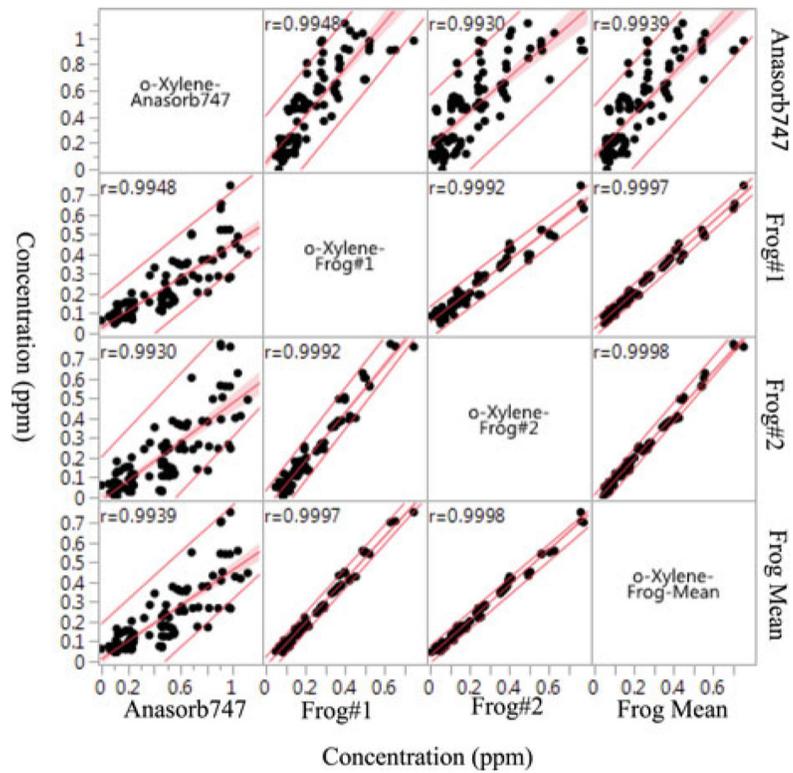
**Figure 4b.** Scatterplot matrix of correlation between Anasorb747 and Frog-4000 data: Ethylbenzene. See key for each column/row comparison.



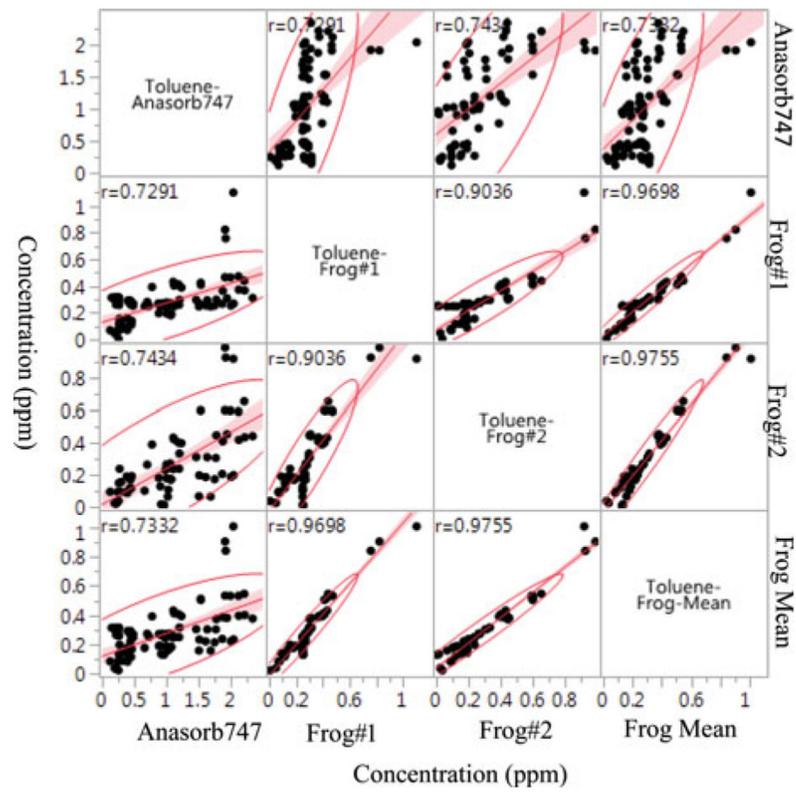
**Figure 4c.** Scatterplot matrix of correlation between Anasorb747 and Frog-4000 data: MIBK. See key for each column/row comparison.



**Figure 4d.** Scatterplot matrix of correlation between Anasorb747 and Frog-4000 data: *m, p*-Xylene. See key for each column/row comparison.

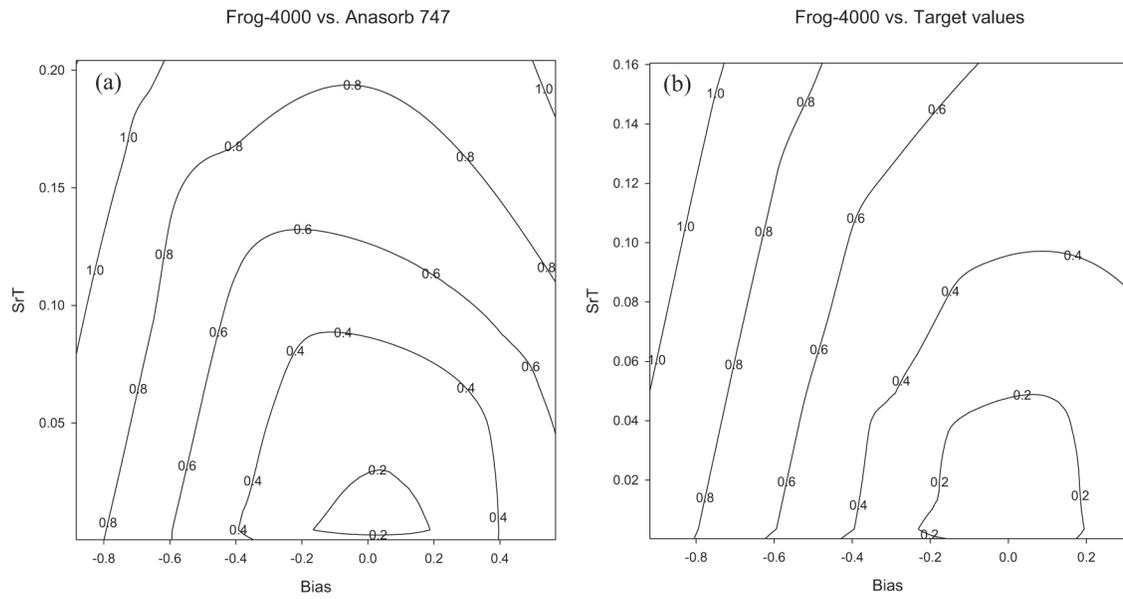


**Figure 4e.** Scatterplot matrix of correlation between Anasorb747 and Frog-4000 data: *o*-Xylene. See key for each column/row comparison.



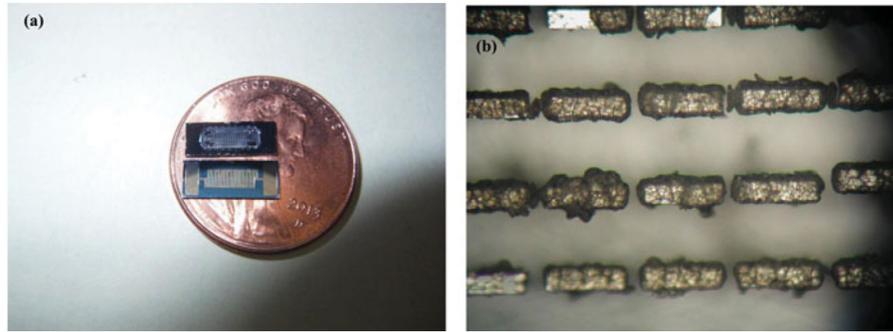
**Figure 4f.**

Scatterplot matrix of correlation between Anasorb747 and Frog-4000 data: Toluene. See key for each column/row comparison.



**Figure 5.**

Accuracy for an analyte “Toluene” as function of Bias ( $B$ ) and precision ( $SrT$ ) according to the NIOSH technical report (No. 2012–162). Note that each curve shows all values of  $B$  and  $SrT$  yielding the corresponding accuracy as indicated on the contour plot. (a): Frog-4000 vs. Anasorb 747 and (b): Frog-4000 vs. Target values.



**Figure 6.** (a) The chip-based pre-concentrator and micro-GC column made through microelectromechanical system (MEMS) batch fabrication technology and (b) the silica gel aerogel coated fins on the pre-concentrator.

**Table 1.**

Environmental testing parameters and instruments involved in the laboratory evaluation.

<b>Testing instruments and reference samplers</b>	
Portable GC-PID	Frog-4000 (Defiant Technology Inc., NM)
Reference	Anasorb 747 (Sorbent tube, 400 mg/200 mg, SKC Inc., PA)
<b>Environmental testing parameters</b>	
Concentration levels (X) in a mixture (ppm)	8x: Acetone 10, Toluene 2, others 1 4x: Acetone 5, Toluene 1, others 0.5 2x: Acetone 2.5, Toluene 0.5, others 0.25 1x: Acetone 1.25, Toluene 0.25, others 0.125
Temperature (°C)	25, 30, and 35
Relative Humidity (RH, %)	25, 50, and 75

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