Assessing flammable storage cabinets as sources of VOC exposure in laboratories using real-time direct reading wireless detectors

Herein we present the results of measurements using wireless direct-reading photoionization detector-based gas sensors to quantify concentrations of vapors of volatile organic compounds (VOCs) in and around flammable storage cabinets containing common organic solvents, including acetone, dichloromethane, trichloroethylene, and benzene. Such cabinets are commonly employed in laboratories to contain flammable liquids. A sensor array was deployed in a series of flammable storage cabinets in working laboratories. Measurements in cabinets containing bottles of typical solvents demonstrate that vapor concentrations gradually increase upon closing the cabinet door. The results suggest that these storage units can be a source of vapors of VOCs in laboratories and the unnecessary exposure of laboratory workers to chemical vapors. Ventilation of cabinets tended to lower maximum concentrations of VOCs. However, the efficacy of this engineering control was found to depend on the quality of the cabinet door seal, as well as having debris-free flame arrestors. Opening cabinet doors resulted in release of vapors to the laboratory atmosphere, which represents an unnecessary exposure risk for workers. A countermeasure aimed at improving the seal of previously opened solvent bottles reduced measured concentrations of VOCs in cabinets below the detector's limit of detection.

By Amie E. Norton, Amos Doepke, Fariba Nourian, William B. Connick, Kenneth K. Brown

Amie Norton is affiliated with Department of Chemistry, University of Cincinnati, P.O. Box 210172, Cincinnati, OH 45221-0172, United States.

Amos Doepke is affiliated with NIOSH (National Institute for Occupational Safety and Health), 1090 Tusculum Ave., Cincinnati, OH 45226, United States.

Fariba Nourian is affiliated with NIOSH (National Institute for Occupational Safety and Health), 1090 Tusculum Ave., Cincinnati, OH 45226, United States.

INTRODUCTION

In the laboratory, chemists are at risk of occupational exposure to hazardous vapors of volatile organic compounds (VOCs), which include many of the common solvents and organic compounds used in chemistry procedures. ^{1–3} Exposure to VOC vapors can have adverse effects on human health, including eye/nose/

William B. Connick is affiliated with Department of Chemistry, University of Cincinnati, P.O. Box 210172, Cincinnati, OH 45221-0172, United States.

Kenneth K. Brown is affiliated with NIOSH (National Institute for Occupational Safety and Health), 1090 Tusculum Ave., Cincinnati, OH 45226, United States (Tel.: 513 841 4364; fax: 513 841 4500; email: krb1@cdc.gov).

throat irritation, headaches, fatigue, respiratory irritation, trouble breathing, blurred vision, loss of coordination, nausea, hearing loss, cardiac stress, and loss of consciousness. Long-term exposure can result in damage to the liver, kidney, and central nervous system. Moreover, common laboratory solvents such as benzene are known carcinogens, and others (e.g., dichloromethane, trichloroethylene, tetrachloroethylene) are reasonably suspected of being human carcinogens.^{4,5} In most laboratories, volatile organic compounds are stored in flammable storage cabinets (FSCs), which are a laboratory safety measure intended to protect the contents from ignition sources and to prevent the contents from contributing to a fire outside the cabinet. The high density of VOCs stored in FSCs raises the concern that these cabinets may be a significant point source of chemical vapors in laboratories. Therefore, the

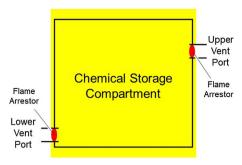


Figure 1. Schematic showing the principle elements of a flammable storage cabinet.

configuration and performance of a given FSC can reasonably be expected to influence the release of chemical vapors into the laboratory and the subsequent exposure of workers.

FSCs typically consist of a steel cabinet that serves as a storage compartment for chemical containers (Figure 1). Cabinets often are equipped with one or more shelves to maximize storage capacity. Vent ports may be open or closed using a steel bung. Typically, each port is equipped with a stainless steel flame arrestor in order to prevent the propagation of flame into or out of the storage compartment. The National Fire Protection Association (NFPA) has provided a set of OSHA-enforceable standards for use of FSCs, and ventilation for fire protection purposes is not recommended. The NFPA has warned that cabinets are not generally tested with venting, and therefore venting could compromise the ability of the cabinet to protect its contents from involvement in a fire. Given these circumstances, the NFPA recommends that vent ports be sealed. However, if venting is used, the NFPA minimal design requirement is that "the vent openings be ducted directly to the outdoors or to a suitable treatment device designed to control VOCs and ignitable vapors." State or local codes, institutional policies, insurance carriers and other authorities having jurisdiction also may have specific requirements for configuring FSCs.

In our experience, we have found that the vast majority of laboratory workers are unaware of recommendations surrounding FSC ventilation. Moreover, we have observed that the configuration of vent ports varies widely, even within institutions and individual laboratories. One of the most common configurations involves ventilation with a lower vent port under negative pressure and an upper vent port closed. Ventilation is a conceptually appealing engineering control because it is expected to reduce release of vapors to the laboratory atmosphere. On the other hand, FSCs without external ventilation also were

commonly encountered. In those cases, we have typically found that upper and lower ports were both closed, in compliance with NFPA recommendations under non-vented conditions.

In the study described here, we evaluated a series of differently configured FSCs as point sources for VOCs in operational laboratories and examined the influence of various parameters on the release of VOCs. Traditional methods for measuring concentrations of VOCs (e.g., EPA TO-17, NIOSH 1501, NIOSH 2549) were deemed impractical for this purpose, because they require days to organize, carry out, and cannot deliver real-time monitoring.⁷⁻⁹ Therefore, commensurate with the ongoing goal of establishing direct-reading methods (DRMs) using devices that provide accurate and near instantaneous measurement of workplace exposures, we have used wireless sensors to monitor VOC concentrations in and around flammable storage cabinets in working chemistry laboratories. The identities of VOCs released from chemical containers in these cabinets were confirmed using a field portable gas chromatographymass spectrometer. The results demonstrate that surprisingly straightforward countermeasures resulted in reductions in levels of VOCs.

EXPERIMENTAL

Figure 2 shows the eight Toxi-Rae Pro (Rae Systems, Mobile, Alabama) wireless photoionization detector (PID)



Figure 2. Eight PID gas sensors wirelessly connected to long range modems wired to a laptop with data acquisition software.

gas sensors (10.6 eV lamps) used to measure VOCs in air, the long-range modems, and laptop base station with data acquisition software. The accuracy, precision, LOQ (limit of quantitation) and LOD (limit of detection) of these sensors were determined using a previously established NIOSH statistical protocol.¹⁰ The PID sensors were calibrated using an average of six measurements of certified isobutylene standards in nitrogen (Wright Brothers Gas, Montgomery, OH), at 0.00, 0.101, 0.994, 10.6 and 100 ppm. For the eight ToxiRae Pro PID sensors used in this study, the average and standard deviation of the LOQ was 10 ± 4 ppm and the LOD was 3 ± 1 ppm isobutylene; thus, a measurement at the LOD was designated as 3 with only one significant figure in the tables.

Levels of vapors of VOCs were measured in eight FSCs located in the National Institute for Occupational Safety and Health (NIOSH) Alice Hamilton Laboratory (Cincinnati, OH, USA). These included four right-handed door Justrite (Justrite, Mattoon, IL) (labeled: LS316, LS291, LS315, LS313), one French-door Eagle (Eagle Manufacturing Company, Wellsburg, WV) 30-gallon (labeled: LS166), one French-door Justrite 30gallon (labeled: LS521), and two under-counter, French-door Hamilton (Hamilton Scientific Inc., Two Rivers, WI) 24-gallon (model no. 950S744: labeled: H1, H2) flammable storage cabinets. In all FSCs, the upper port was located on the upper right side of the cabinet, and the lower port was located on the lower left side of the cabinet (Figure 1). The Justrite 30-gallon and two under-counter Hamilton 24-gallon FSCs were not vented. The under-counter models were fit snugly under fume hoods, but not connected to the fume hood exhaust system; all other cabinets were free-standing. Each of the remaining cabinets had the lower port connected to a 2-in. diameter rigid PVC pipe, which was under negative pressure and vented to the outdoors. The upper ports of these vented cabinets were closed. The negative pressure resulted in an airflow in the ventilation pipe of ~ 20 cubic feet per minute (cfm). For example, for the LS316 Justrite 22-gallon



Figure 3. An array of PID gas sensors positioned along the front edges of 4 of 5 shelves of the LS316 FSC.

cabinet, the airflow was determined to be 22 cfm (TSI VelociCalc model 9535 air velocity meter, Shoreview, MN) with the cabinet door closed and the upper port closed, which was above the minimal flow standard of 3 cfm recommended by NFPA code 91.¹¹ Airflow through vented ports was visualized using a Wizard Stick (Zero Toys, Concord, MA) fog generator. A ninth unvented FSC (Justrite 22-gallon, 4 shelves, right-handed door; labeled: LS424) was used to evaluate measures for slowing release of vapors from solvent bottles.

For evaluation of levels of VOCs in FSCs, PID gas sensors were positioned along the front edge of the shelves. When five shelves were present there were no sensors on the second shelf from the bottom. For example, in the case of the Justrite 22-gallon LS316

cabinet, two sensors were positioned at the front left and front right edges of each shelf, except the second from the bottom (Figure 3). For the two-shelf LS166 cabinet, four sensors were evenly distributed in a line across the width of and along the front edge of each shelf.

To evaluate vapor concentrations released from the LS316 cabinet when the door was open, a CEMWIP (Chemical Exposure and Monitoring with Indoor Positioning by Measure-Net Technology, Cincinnati, Ohio) sensor, equipped with a 10.6 eV PID sensor (Baseline MOCON, Lyons, CO)¹² was positioned outside the cabinet, at 0.18, 0.40, and 0.49 and 0.56 m along a line originating at the front left edge of and perpendicular to the door of the cabinet. The sensor was placed on a tripod at a height of 1.6 m. The identities of the VOCs in the cabinet

atmosphere were determined using a HAPSITE-ER (Inficon, Syracuse, NY, USA) portable GC-MS with a sample probe attachment while the cabinet door was closed. A room-air blank was analyzed, and then the cabinet atmosphere was sampled on the left side of the top shelf using HAPSITE-ER in situ probe technique. ¹³ Chemicals identified by GC-MS were consistent with the flammable storage cabinet inventories.

Solvent bottles contained in FSCs were mainly from Sigma Aldrich and Fisher Scientific. An inventory of LS316 is provided in the Supporting Information. Evaluated measures for reducing release of VOCs included: (1) placing solvent bottles in plastic bags, (2) wrapping each solvent bottle neck and cap with Parafilm (Sigma–Aldrich, St. Louis, MO), and (3) wrapping the threads of each solvent bottle with two layers of Teflon tape (0.75 in. wide, Thomas Scientific, Swedesboro, NJ).

RESULTS AND DISCUSSION

To evaluate levels of vapors of VOCs in working laboratory conditions, we

examined eight FSCs in 6 operational laboratories. The manufacturer-stated capacities of the FSCs ranged from 15 to 30 gallons (56.8-113.6 L). Each FSC contained at least 22 chemical storage containers with a minimum total volume of >30 L of liquid organic compounds (Table 1). For most containers, the manufacturer's seal previously had been broken. In each cabinet (except for LS313), there were mostly lowboiling point solvents, such as acetone and dichloromethane. The number of storage shelves per cabinet ranged from 2 to 5. The three models with only two shelves (LS166, H1 and H2) had identical inventories in this study, because the contents were transferred back and forth for measurements. Those three cabinets were unventilated, meaning that the upper and lower ports were sealed with metal bungs. The two-shelf, under-cabinet, French door H1 and H2 cabinets were situated underneath fume hoods, but not connected to the hood exhaust system. The five remaining cabinets were ventilated, meaning that the lower port was under negative pressure and vented to the outdoors, and the

upper port was closed. In order to ensure adequate airflow, the flame arrestors were cleaned with a wire brush to remove accumulated debris.

Table 1 shows the highest concentration of vapors of VOCs recorded by each Toxi-RAE gas sensor in an array of 4–8 sensors distributed along the front edges of shelves in each of the eight FSCs (Figure 3). Readings were recorded with the cabinet door(s) closed for 20 min and then open for 5 min. While closed for 20 min, vapor levels gradually increased (Figure 5). The cycle was repeated 3 times for each cabinet, and the maximum value is reported in Table 1.

Several key observations emerge from Table 1 and are supported by the full set of time-dependent data. First, vapor levels in unvented cabinets were higher than those in vented cabinets, in accord with expectations. For example, of the two-shelf cabinets having identical contents, maximum vapor concentrations were more than two times lower in the vented LS166 cabinet as compared to the unvented H1 and H2 cabinets. This conclusion also was supported by measurements made

Table 1. Highest PID Sensor Readings (ppm)^a at Distributed Locations on Shelves Within 8 Different Flammable Storage Cabinets Over a 20-min Period.

Sensor Position ^b	Justrite22	Justrite22	Justrite22	Justrite22	Justrite30	Eagle30	Hamilton 950S744a	Hamilton 950S744b
	(LS316)	(LS315)	(LS291)	(LS313)	(LS166)	(LS521)	(H1)	(H2)
Top left (TL)	8.2	14.0	<3	<3	<3	3.9	4.6	30.3
Top right (TR)	<3	5.5	< 3	<3	<3	3.4	34.6	27.7
2nd left (2L)	4.7	<3	<3	<3	13.2 (TML)	6.7	NA	NA
2nd right (2R)	3	<3	< 3	<3	10.1 (TMR)	5.6	NA	NA
3rd left (3L)	<3	<3	< 3	<3	<3 (BMR)	3.2	NA	NA
3rd right (3R)	3.7	<3	<3	<3	3.5 (BML)	4.3	NA	NA
Bottom left (BL)	<3	<3	< 3	<3	<3	4.7	4.6	28.2
Bottom right (BR)	<3	<3	<3	<3	<3	7.5	8.8	3
Manufacturer capacity (L)	83	83	83	83	113.6	113.6	56.8	56.8
No. of shelves	5	4	4	4	2	5	2	2
No of containers	104	33	16	23	22 ^c	45	22 ^c	22 ^c
Approximate total volume of liquid (L)	80	50	10	32	83	40°	40°	40°
Ventingd	Yes	Yes	Yes	Yes	Yes	No	No	No

^a The LOD was 3 ppm (detection with 99.7% confidence) and LOQ was 10 ppm. Some entries are designated NA because there were only four sensors deployed in those cabinets.

^b TL = left side of top shelf; TR = right side of top shelf; 2L = left side of second shelf from top; 2R = right side of second shelf from top; 3L = left side of third shelf from top; 3R = right side of third shelf from top; BL = left side of bottom shelf; BR = right side of bottom shelf. TML = top middle left TMR = top middle right BMR = bottom middle right BML = bottom middle left (see text).

^c The contents of the Justrite 30 and two Hamilton models were identical.

d Vented cabinets had open lower ports under negative pressure and closed upper ports; unvented cabinets had both ports closed.

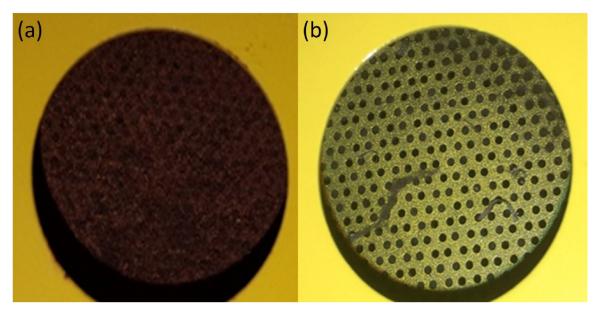


Figure 4. A typically corroded FSC flame arrestor (a) before and (b) after cleaning.

before cleaning flame arrestors, which are surprisingly prone to becoming clogged with debris, resulting in restricted airflow in vented cabinets (Figure 4). For example, cleaning the outlet port flame arrestor of LS316 reduced the maximum vapor levels by 40–60%.

It also was noted that, where vapor concentrations are above the detection limit, the vented cabinets tended to show higher vapor concentrations on the higher shelves, which were further from the vented lower port. Moreover, for the top shelf, the highest levels tended to be on the left side. These observations suggest that the efficiency of vapor removal through venting varies with location in the cabinet. It is

likely that the shelves, as well as the chemical containers, influenced airflow. In the case of the LS316, a portable GC-MS (HAPSITE-ER) was used to verify that the accumulated vapors within the FSC were consistent with the chemical inventory of the cabinet. A complete list of identified vapors is in Table 2 along with their PEL (Permissible Exposure Limits), STEL (Short Term Exposure Limits) and REL (Recommended Exposure Limits). Two of the detected vapors in the LS316 cabinet, dichloromethane and tetrachloroethylene, are recommended to be kept at the lowest feasible concentration (LFC).¹⁴ While NIOSH has a new policy on carcinogens, 15 it is not currently retroactive to

Table 2. VOC Compounds Identified in the Atmospheres of Flammable Storage Cabinet LS316 Using a HAPSITE GC-MS, Along With Various Regulatory Exposure Limits.

Chemical	PEL (ppm)	STEL (ppm)	REL (ppm)
Acetone	1,000	1,000	250
Benzene	1	5	0.1
Dichloromethane	25	125	LFC
Ethylbenzene	100	125	100
Methyl cyclohexane	500	Not listed	400
Hexane	500	Not listed	50
Xylene	100	150	100
Trichloroethylene	100	2	25
Tetrachloroethylene	100	Not listed	LFC
Toluene	200	100	150

LFC = lowest feasible concentration.

compounds found in the pocket guide. So, concentrations are recommended to be kept at LFC, where feasible is technically defined as detection levels listed in the NIOSH Manual of Analytical Methods (NMAM). In two of the cabinets, LS291 and LS313, the concentration of vapors at all locations remained below the detection limit of the Toxi-RAE gas sensors throughout the duration of each cycle. The precise reason for these lower concentrations are not fully understood, but the results are likely related to the efficiency of these cabinets in trapping vapors, as well as the differences in contents and quality of container seals.

PID gas sensor measurements obtained after closing the FSC doors show a gradual increase, eventually reaching a plateau (Figure 5). For example, in the case of the vented and unvented LS316, $t_{1/2}$ values for the rise time are \sim 7 min. By contrast, once the FSC was opened, gas sensor readings dropped rapidly with $t_{1/2} \leq 1$ min. These results suggest that opening of FSC doors resulted in a rapid release of vapors, which could be a significant source of exposure for occupants of the laboratory.

Levels of VOCs Outside FSCs

In order to better assess FSCs containing solvents as potential sources for VOCs, we used a PID-based

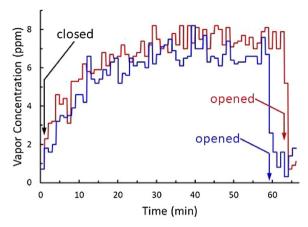


Figure 5. Levels of VOCs recorded by a sensor positioned on the left top shelf the vented (—) and unvented (—) LS316 cabinet over time. In each experiment, the cabinet was closed at \sim 1 min; the vented cabinet was opened at the \sim 59-min time mark, and the unvented cabinet was opened at the \sim 63 min time mark.

CHEMWIP sensor¹² to characterize the plume of VOCs emanating from an open FSC. The sensor was placed on tripod at a height of 1.6 m and at fixed distances along a line from the left edge of and perpendicular to the right-handed door of the LS316 22gallon FSC. Readings were recorded over a 10-min period immediately following opening of the cabinet door. Levels of VOCs were found to vary somewhat erratically due to air currents in the laboratory. However, the peak measured concentration occurred within the first 6 min of opening the cabinet door and the vapor concentration decreased with time, indicating dissipation of the vapors. In addition, the maximum concentrations of VOCs clearly decreased with distance of the sensor from the FSC, as shown in Figure 6. The highest concentrations of VOCs were found at 0.18 and 0.9 m from the open SFC

door (Figure 6). At longer distances, 0.49 and 0.56 m, the signal was near background level (0.12 ppm), presumably due to room air mixing. The results clearly demonstrated that a worker opening the door and reaching into the FSC cabinet is likely to be exposed to elevated levels of vapors that have accumulated in the cabinet.

Efficacy of Control Measures

Vapor release from FSCs is directly related to the efficacy of vapor containment within chemical containers and the efficiency of removing escaped vapors via venting before these vapors are released to the laboratory atmosphere. Because of the comparatively elevated vapor concentrations in the vented LS316 FSC, a series of control measures were examined in order to evaluate their efficacy in reducing concentrations of VOCs inside the cabinet. Specifically, experiments were

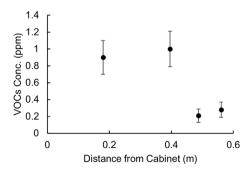


Figure 6. Distance from the cabinet versus maximum VOCs concentration. Error bars represent $\pm 2\sigma$.

undertaken to evaluate the influence of different configurations (i.e., open or closed) of the vent ports, as well as specific measures for sealing chemical storage bottles. When only the lower port was open to ventilation, the airflow in the ventilation exhaust tube was 22 cfm. When the upper port was open, the FSC was opened directly to the laboratory atmosphere (see Figure 1). For each configuration, the door to the FSC was left closed for 24 hours, and subsequently gas sensor measurements were recorded for 2 hours. The highest recorded concentrations for each sensor are reported in Table 3.

Surprisingly, the configuration of the upper and lower ports had comparatively little influence on the maximum vapor levels. Though there were no visible signs of damage to the cabinet, we hypothesized that a contributing factor might be airflow through the FSC where the door meets the cabinet frame, which could reduce the efficiency of venting vapors from inside the FSC. In support of this notion, when we sealed the door on another FSC LS313 (see Supplement) with masking tape while under outlet ventilation only, all detector readings remained below the limit of detection. FSC LS313 was used for this experiment, because LS316 was completely filled with bottles making it inconvenient to add another bottle for a deliberate release experiment. Then, the FSC inlet port was opened and the sensor reading dropped to an instrumental zero. Finally, the inlet port was closed, and tape removed to return the system to normal conditions and VOC rose above LOD. The results demonstrate that the integrity of the FSC door seal has a profound impact on the efficiency of ventilation, and this in turn creates practical challenges for mitigating the risk of FSCs as point sources for vapors of VOCs.

To evaluate methods for minimizing release of vapors from chemical containers, we identified an empty unventilated 22-gallon FSC (LS317) and stored solvent bottles under different conditions. It was found that chemical bottles with manufacturer seals did not emit detectable concentrations of VOCs (<3 ppm). For example, sixteen

Table 3. Highest PID Sensor Readings (ppm) at Distributed Locations on Shelves Within LS316 FSC in Different Configurations.

Upper Port Lower Port Teflon Tape	Closed Closed No	Closed Open No	Open Closed No	Open Open No	Closed Closed Yes	Closed Open Yes	Open Closed Yes	Open Open Yes
TL	6.1	3.0	5.3	11	<3	<3	<3	<3
TR	3.0	5.7	10.1	3	<3	<3	<3	<3
2L	3.6	3	3	<3	<3	<3	<3	< 3
2R	<3	<3	<3	<3	<3	<3	<3	<3
3L	<3	<3	<3	<3	<3	<3	<3	<3
3R	3.2	3	3	<3	<3	<3	<3	<3
BL	<3	<3	<3	<3	<3	<3	<3	<3
BR	<3	<3	<3	<3	<3	<3	<3	<3

previously unopened 4 L solvent bottles (6×4 L methanol, 6×4 L acetonitrile, 4× 4 L acetone) were placed in the FSC. After the cabinet was left closed for 24 hours, vapor concentrations were monitored for a 2-hour period using an array of eight sensors. distributed on the four shelves as described previously. Under these conditions, concentrations of VOCs were below the LOD (<3 ppm). However, we found that a solvent bottle seal was never vapor tight after a bottle was opened. For example, sixteen previously opened 4 L solvent bottles (4× 4 L acetone, 2× 4 L acetonitrile, 1× 1 L xylenes, 4×4 L methanol, 1×1 L 1-hexene, 1× 1L ethanol, 3× 4L dichloromethane) resealed using the manufacturer's supplied cap were stored in the same cabinet. After 24 hours, the vapor levels were monitored for a 2-hour period. The maximum VOC concentration 7.8 ppm. When each bottle was placed in a plastic bag sealed by tying the bag in a knot, the maximum concentration decreased to 5 ppm. Alternatively, wrapping Parafilm around the outside of each bottle cap was slightly more effective, lowering the maximum reading to 3.9 ppm. However, the most effective measure involved wrapping 2 layers of Teflon tape between the threads of each glass chemical storage bottle and the cap. With this measure, the maximum vapor level was below the LOD (<3 ppm). Given these results, we tested the efficacy of the Teflon tape countermeasure on the contents of LS316. As shown in Table 3, when the bottles were sealed with Teflon tape the maximum concentration of vapors dropped to below the

LOD. Thus, of all control measures investigated, wrapping with Teflon tape proved most impactful.

CONCLUSIONS

FSCs were found to be a source of exposure to organic chemicals. In one case, dichloromethane, tetrachloroethylene, and benzene were qualitatively found in the emissions. The National Institute for Occupational Safety and Health (NIOSH) recommends that exposure to dichloromethane and tetrachloroethylene be kept at the lowest feasible concentration. Results showed that it is feasible to lower the concentrations found in FSCs. The carcinogen benzene has an exception to the NIOSH LFC using an OSHA defined short-term exposure limit (STEL) of 1 ppm and total weighted average (TWA) of 0.1 ppm. instead. Ventilation of FSCs tends to lower concentrations of VOCs. Ventilation using both inlet and outlet ports lowered concentrations below the LOD of the PID. However, imperfect cabinet door seals degrade the efficacy of ventilation engineering control measures. In addition, flame arrestors have a tendency to corrode and accumulate debris, which reduces the efficiency of ventilation. Thus, to ensure best performance, ventilated FSCs require maintenance. It also should be noted that, when a worker opens the door of a FSC, there is the additional risk of a release of a plume of vapors, resulting in elevated exposure. Waiting for the plume to dissipate is likely an impractical strategy for minimizing exposure in many cases. With respect to preventing release of vapors from chemical containers, solvent bottles with the original manufacturer seal were not found to be a source of vapors. Moreover, wrapping Teflon tape between the threads of a glass chemical storage bottle and its manufacturer-supplied cap greatly improves containment of vapors in previously opened bottles, suggesting that this is a practical measure for reducing exposure of workers to vapors of VOCs in laboratories. Given that FSCs also are utilized to store many secondary containers (e.g., volumetric flasks, solvent wash bottles, vials) future evaluation of how to best seal such containers would be an asset to the chemist in reducing VOC exposure.

The NFPA has warned that FSCs are not generally tested with venting, and therefore venting could compromise the ability of the cabinet to protect its contents from involvement in a fire. Given these circumstances, the NFPA recommends that vent ports be sealed. The results presented in the Supplement demonstrated that ventilation of FSCs at both ports could reduce carcinogen vapors to LFC. If ventilation was used for this purpose, then there is a need to validate the efficacy of FSCs for flammability safety with ventilation. VOCs present both flammability and toxicity risk, and thus both risks have to be considered with FSCs in the laboratory where VOCs pose both risks to workers.

DISCLAIMERS

The findings and conclusions in this report are those of the author(s) and do

not necessarily represent the official position of the National Institute for Occupational Safety and Health, Centers for Disease Control and Prevention.

Mention of any company or product does not constitute endorsement by the National Institute for Occupational Safety and Health (NIOSH), Centers for Disease Control and Prevention (CDC).

ACKNOWLEDGEMENTS

W.B.C. thanks the National Science Foundation (CHE-1566438) for their generous support. K.K.B. and A.E.N. thank the CDC Center for Control Disease and Prevention for their generous support through the LASSI fund.

APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jchas.2018.01.001.

REFERENCES

- Gustavsson, P.; Reuterwall, C.; Sadigh, J.; Söderholm, M. Mortality and cancer incidence among laboratory technicians in medical research and routine laboratories (Sweden). Cancer Causes Control Pap. Symp. 1999, 10(1), 59-64.
- Kauppinen, T.; Pukkala, E.; Saalo, A.; Sasco, A. J. Exposure to chemical carcinogens and risk of cancer among Finnish laboratory workers. *Am. J. Ind. Med.* 2003, 44(4), 343–350.

- Rachet, B.; Partanen, T.; Kauppinen, T.; Sasco, A. J. Cancer risk in laboratory workers: An emphasis on biological research. Am. J. Ind. Med. 2000, 38 (6), 651-665.
- Karami, S.; Bassig, B.; Stewart, P. A. Lee, K.-M., ; Rothman, N.; Moore, L. E.; Lan, Q. Occupational trichloroethylene exposure and risk of lymphatic and haematopoietic cancers: A metaanalysis. Occup. Environ. Med. 2013, 70(8), 591–599.
- Lynge, E.; Anttila, A.; Hemminki, K. Organic solvents and cancer. *Cancer Causes Control Pap. Symp.* 1997, 8(3), 406–419
- NFPA 30: Flammable and Combustible Liquids Code 2015 Edition, section 9.5.4 (National Fire Protection Association).
- 7. Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air: TO-17; U.S. EPA, https://www3.epa.gov/ttnamti1/files/ambient/airtox/to-17r.pdf (accessed 05.10.17).
- 8. Hydrocarbons, Aromatics Method 1501; NIOSH Manual of Analytical Methods 5th ed.: Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health. https://www.cdc.gov/niosh/docs/2003-154/pdfs/1501.pdf (accessed 05.10.17).
- Volatile Organic Compounds (Screening) Method 2549: NIOSH Manual of Analytical Methods 5th ed.: Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health. https://www.cdc.gov/niosh/docs/2003-154/pdfs/2549.pdf (accessed 05.10.17).

- 10. NIOSH Guidelines for Air Sampling and Analytical Method Development and Evaluation; DHHS (NIOSH) Publication Number 95-117, https://www.cdc.gov/niosh/docs/95-117/pdfs/95-117.pdf (accessed 05.10.17).
- 11. NFPA 91: Standard for Exhaust Systems for Air Conveying of Vapors, Gases, Mists, and Noncombustible Particulate Solids Agency (National Fire Protection Association 2010).
- Brown, K. K.; Shaw, P. B.; Mead, K. R.; Kovein, R. J.; Voorhees, R. T.; Brandes, A. R. Development of the chemical exposure monitor with indoor positioning (CEMWIP) for workplace VOC surveys. J. Occup. Environ. Hyg. 2016, 13(6), 401–412.
- Smith, P. Person-portable gas chromatography: Rapid temperature program operation through resistive heating of columns with inherently low thermal mass properties. *J. Chromatogr. A*, 2012, 1261, 37–45.
- 14. NIOSH Pocket Guide To Chemical Hazards: 2007; DHHS (NIOSH) Publication No. 2005-149, https://www.cdc.gov/niosh/docs/2005-149/pdfs/2005-149.pdf (accessed 05.10.17).
- Whittaker, C.; Rice, F.; McKernan, L.; Dandovic, D.; Lentz, T.J.; MacMahon, K.; Kuempel, E.; Zumwalde, R.; Schulte, P. Current intelligence bulletin 68: NIOSH Chemical Carcinogen Policy; U.S. Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) No. 2017-100, https://www.cdc.gov/niosh/docs/2017-100/pdf/2017-100.pdf (accessed 07.11.17).

Supporting Information for

Assessing Flammable Storage Cabinets as Sources for VOC in Laboratories Using Realtime Direct Reading Wireless Detectors

Amie Norton,† Amos Doepke,‡ Fariba Nourian, ‡ William B. Connick,†* and Kenneth K. Brown‡*

- † Department of Chemistry, University of Cincinnati, P.O. Box 210172, Cincinnati, OH, 45221-0172
- ‡ NIOSH (National Institute for of Occupational Safety and Health), 1090 Tusculum Ave., Cincinnati, Ohio 45226

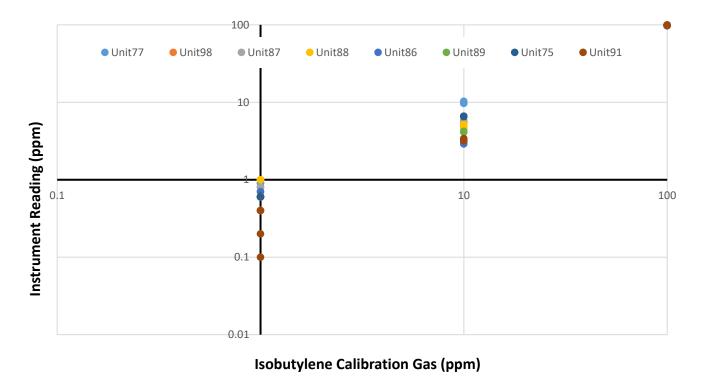


Figure S1. The isobutylene response factor of the ToxiRae Pro PID sensors as the sensor response in ppm versus gas standard concentrations in ppm.

Figure 1 shows the responses from 8 separate ToxiRAE units with each unit being tested against nine standard isobutylene concentrations 3 X 0.994 ppm, 3 X 10.6 ppm, and 3 X 100 ppm for total of 72 data points. The SOP¹⁴ recommends using at least six calibration standards distributed from the expected LOD to no higher than one order of magnitude for estimating LOD and LOQ. In this case, data at 0.994, 10.6, and 100, each level in triplicate, were used for

determining the least squares regression line for estimating and the LOD and LOQ and are shown in Figure S1.

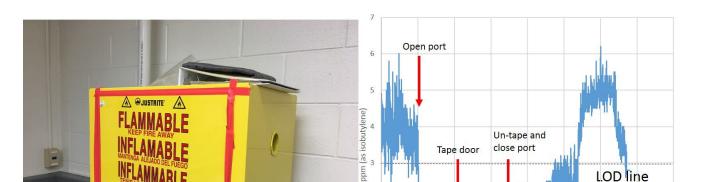


Figure S2. Effect of Flow Through Ventilation on VOC Level.

Figure S2. Effect of Sealing FSC Door with Tape and Opening Inlet Port. (left) Photograph showing the door of LS313 FSC sealed with tape. (right) Effect of sealing the door on readings by the sensor on the left side of top shelf.

1:00:00

3:59:58 Hours

Figure S2 shows the effect of 1) opening the inlet port and 2) sealing the doors of the LS313 FSC upon the PID response from VOCs. The first arrow on the graph from the left axis is when the upper port of the cabinet (shown on the left) was opened, the second arrow is when the door cracks were sealed with tape, and third arrow is when the tape was removed and upper port plugged again. This pilot experiment suggests the potential benefits of further investigations in ventilation configurations for the mitigation of VOCs to the lowest feasible concentration.

Table S1. Chemical Inventory of FSC LS316

Shelf	Compound	Amount	Shelf	Compound	Amount
3	Acetaldehyde	10 mL	2	Ethyl acetate	1 L
2	*Acetone wash bottle capped	250 mL	2	Ethyl acetate	1 L
1	*Benzene	100 mL	2	Ethyl acetate	1 L
1	*Benzene	100 mL	1	Ethyl acetate	1 L
1	*Benzene	1 L	1	*Ethylbenzene	100 mL
4	*Benzene	1 L	2	*Ethylbenzene	100 mL
3	Benzene-D6	5 g	3	2-Furaldehyde	5 mL
3	4-Bromo-2-nitrophenol	5 g	3	2-Heptanone	100 mL
3	Bromoacetonitrile	100 g	2	3-Heptanone	5 mL
3	Bromoform	50 g	2	3-Heptanone	100 mL
3	2-Bromopropane	10 g	2	Hexachloroethane	5 g
2	1,3-Butanediol	100 mL	5	*Hexane	4 L
4	2-Butanol	1 L	3	2-Hexanone	10 g
3	2-Butanone	100 mL	2	4-Hydroxy-4-methyl-2-pentanone	25 mL
1	2-n-Butoxyethanol	500 mL	2	Isopropyl acetate	5 mL
2	Butyl acetate	100 mL	1	Methanol	1 L
3	Butyl acetate	100 mL	2	Methanol washbottle (uncapped)	50 mL
4	Butyl acetate	500 mL	2	Methanol-D4	10 X 0.25 mL
4	Carbon disulfide	500 mL	3	*Methyl cyclohexane	100 mL
3	Chloroacetone	5 g	4	4-Methyl-2-pentanone	500 mL
2	4-Chlorobenzotrifluoride	100 g	4	4-Methyl-2-pentanone	500 mL
4	Chloroform	1 L	3	N,N-Dimethylacetamide	100 mL
2	2-Chlorophenol	5 g	2	Naphthalene	1 g
3	3-Chlorophenol	25 g	2	Naphthalene	1 g
2	4-Chlorophenol	5 g	3	Nonane	100 mL
4	CleanLube II	12 oz	2	2-Nonanone	5 g
1	Cyclohexanone	25 mL	2	3-Nonanone	10 mL
2	Di(ethylene glycol)	25 g	3	5-Nonanone	25 g
2	Di(propylene glycol)	25 g	3	Octane	100 mL
3	Di(propylene glycol) methyl ether	25 mL	3	Pentane	100 mL
2	Dibutyl phthalate	100 g	3	2-Pentanone	100 mL
3	1,1-Dichloroacetone	100 g	2	1,2-Propanediol	25 mL
3	1,1-Dichloroacetone	100 g	1	2-Propanol	100 mL
3	1,2-Dichlorobenzene	100 mL	1	n-Propyl alcohol	4 L
1	1,1-Dichloroethane	1 g	1	n-Propyl acetate	1 L
1	1,1-Dichloroethane	1 g	1	Sodium tetraphenylborate	25 g
3	1,2-Dichloroethane	100 mL	4	1,1,2,2-Tetrachloroethane	5 mL
2	1,2-Dichloroethane-D4	1 g	2	p-Terphenyl-D14	100 mg
1	*Dichloromethane	1 L	3	*Tetrachloroethylene	100 mL
4	*Dichloromethane	1 L	1	*Toluene	100 mL
3	1,2-Dichloropropane	25 g	3	*Toluene	100 mL
3	2-(Diethylamino)ethanol	25 g 25 mL	4	*Toluene	100 IIIL
	, ,				1 L 4 L
2	Diethylene glycol monobutyl ether	100 mL	5	*Toluene	
2	Diethylene glycol monobutyl ether	100 mL	3	Toluene-D8	5 g
3	Diethylene glycol monobutyl ether	100 mL	2	Tri(ethylene glycol)	25 g
4	Diethylene glycol monobutyl ether	1 L	1	1,1,1-Trichloroethane	500 mL
2	Diethyl phthalate	100 g	3	*Trichloroethylene	100 mL
2	2,2-Dimethoxypropane	25 mL	4	*Trichloroethylene	500 mL
1	Dimethyl Sulfoxide	1 L	5	Waste Mixed Chemicals	4 L
3	2,6-Dimethyl-4-heptanone	25 g	5	Waste Mixed Chemicals	4 L
2	2-(Dimethylamino)ethanol	10 g	5	Waste Mixed Chemicals	4 L
3	Dioctyl phthalate	100 mL	2	*Xylenes mixed	500 mL
4	Ethanol	1 L	3	*o-Xylene	100 mL
1	Ethyl acetate	500 mL	4	*o-Xylene	1 L
1	Ethyl acetate	1 L	3	o-Xylene-D10	5 g
2	Ethyl acetate	1 L	3	*p-Xylene	100 mL

^{*}indicates compounds that were identified by GC-MS as listed in Table 3.