



Final Report

Evaluating Vapor Leak Detectors for use in “PERC” Dry Cleaners

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This report was prepared by the Local Hazardous Waste Management Program in King County, Washington, a coalition of local governments. Our customers are residents, businesses and institutions with small quantities of hazardous wastes. The Program's mission is: to protect and enhance public health and environmental quality in King County by reducing the threat posed by the **production, use, storage and disposal** of hazardous materials.

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CONTENTS

Acronyms and Abbreviations	vii
Executive Summary	1
Introduction	3
Local Hazardous Waste Management Program in King County	3
PERC as a dry cleaning solvent	3
Dry cleaning overview	4
Exposure routes for PERC	6
Inhalation	6
Dermal contact	6
Ingestion	6
Health effects of PERC	6
Central Nervous System	7
Respiratory system	7
Liver/Kidney	7
Skin	7
Reproductive system	7
Carcinogenicity	7
PERC in the environment	8
Regulatory and advisory limits	9
Occupational health	9
Environmental protection	9
Leak detection requirements	10
Sources of detector information	11
Current study	12
Methods	13
Detector selection	13
Phase I: Evaluating the detectors' technical capabilities	13
Testing equipment	13
Testing procedures	17
Phase II: Usability testing	20
Selection of detectors	20
Testing apparatus	20
Testing procedures	22
Results	23
Phase I: Technical evaluation of detectors	23
Limit of detection	23
Response time	26
Concentration gradient	29
Laboratory analysis of charcoal tube samples	30
Phase II: Usability testing	32

Selection of detectors for usability testing	32
Timed trials	32
Questionnaire.....	32
Discussion.....	41
Technical capabilities.....	41
Usability.....	41
Limitations of the study	41
Number of response time data points per concentration	41
Relative humidity requirements	42
Limit of Detection measurement accuracy	42
Lower limit of Photoionization Detector above the Limit of Detection of the most sensitive detectors	42
Discrepancy between PID and charcoal tube concentrations	42
Gradient testing	44
Effects on average response time	44
Other potentially suitable leak detectors not evaluated	45
Usability testing not conducted with dry cleaners.....	45
Usability testing apparatus not representative of real dry cleaning machines.....	46
Conclusions.....	46
Future opportunities	47
Acknowledgments.....	49
References	51
Appendix A Usability Questionnaire	55
Appendix B Detector Response Times.....	61
Appendix C Two-Way Analysis of Variance (ANOVA)	65

Figures

Figure 1. The PERC vapor generation system	14
Figure 2. Schematic of the Dynacalibrator Model 450	15
Figure 3. Diffusion vial	16
Figure 4. Schematic of a single usability test unit.....	20
Figure 5. Usability testing apparatus	21
Figure 6. Detector response times	26
Figure 7. Distribution of response times for the ZX model.....	28
Figure 8. Distribution of response times for the XP-1A model.....	28
Figure 9. Distribution of response times for the XL-1A model	29
Figure 10. Detectors selected for usability testing	32
Figure 11. PERC concentration measured by charcoal tubes and PID.....	43
Figure 12. Relationship between matched PID and charcoal tube concentrations.....	43
Figure 13. Average response time with standard errors of the mean at each concentration	45

Tables

Table 1. Kauri-Butanol (KB) values and cleaning performance of dry cleaning solvents	4
Table 2. Summary of dry cleaning machine generations	5
Table 3. Theoretical PERC concentrations and corresponding Dynacalibrator settings	18
Table 4. Detector characteristics	24
Table 5. Leak detector limits of detection	25
Table 6. Detector response time descriptive statistics (seconds).....	27
Table 7. Concentration gradient detection from 25 to 50 ppm.....	30
Table 8. Target concentration, lab result, corrected PID result, identification, and collection date for charcoal tube samples.....	31
Table 9. Detector that felt the best to hold	33
Table 10. Was the light display helpful?	33
Table 11. Detector with easiest light display to understand	34
Table 12. Were instrument sounds helpful in finding the leak?	34
Table 13. Detector with easiest response sounds to understand.....	35
Table 14. Detector with easiest response sounds to understand (among those with a preference)	35
Table 15. Detector with easiest controls to use	35
Table 16. Detector with hardest controls to use	36
Table 17. Detector that was liked the most	36
Table 18. Detector that was liked the least.....	36
Table 19. Which instrument's controls were the easiest to use? (Q.8).....	37
Table 20. Which instrument's controls were the hardest to use? (Q.9).....	37
Table 21. Overall, which detector did you like the MOST? (Q.10)	38
Table 22. Overall, which detector did you like the LEAST? (Q.11).....	39

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ACRONYMS AND ABBREVIATIONS

ACGIH	American Conference of Governmental Industrial Hygienists
ANOVA	Analysis of variance
ATSDR	Agency for Toxic Substances Disease Registry
°C	Degrees Centigrade
CARB	California Air Resources Board
CAS	Chemical Abstract Service
CNS	Central nervous system
DEQ	Oregon Department of Environmental Quality
DNAPL	Dense Non-Aqueous Phase Liquid
DOSH	Division of Occupational Safety and Health
Ecology	Washington State Department of Ecology
EPA	United States Environmental Protection Agency
eV	Electron volt
ft ³	Cubic feet
KB	Kauri-Butanol
IARC	International Agency for Research on Cancer
kg	Kilogram
l	Liter
LED	Light emitting diode
LHWMP	Local Hazardous Waste Management Program in King County
L&I	Washington State Department of Labor and Industries
LOD	Limit of Detection
m ³	Cubic meter
mg/kg	Milligrams per kilogram
ml/min	Milliliters per minute
mg/l	Milligrams per liter
mm	Millimeter
NAS	National Academies of Science
NIOSH	National Institute for Occupational Safety and Health
NRC	National Research Council
OSHA	Occupational Safety and Health Administration
PEL	Permissible exposure limit

PERC	Perchloroethylene
PID	Photoionization detector
ppb	Parts per billion
PPE	Personal protection equipment
ppm	Parts per million
PSCAA	Puget Sound Clean Air Agency
PSI	Pounds per square inch
PTFE	Polytetrafluorethylene
REL	Recommended exposure limit
RH	Relative humidity
SARA	Superfund Amendments and Reauthorization Act
SQG	Small Quantity Generator
STEL	Short term exposure limit
TLV	Threshold limit value
TWA	Time-weighted average

EXECUTIVE SUMMARY

The majority of dry cleaners in King County, Washington continue to use perchloroethylene (PERC) as their primary dry cleaning solvent. Previous investigations conducted by the Local Hazardous Waste Management Program in King County (LHWMP) identified deficiencies in the maintenance of PERC dry cleaning machines. Of particular concern is the leakage of PERC from hoses and gaskets, which occasionally generate hundreds of parts per million of PERC vapor in the breathing zones of dry cleaners. The U.S. Environmental Protection Agency (EPA) requires that PERC-using dry cleaners use a vapor leak detector to routinely scan for leaks in their equipment. However, LHWMP has determined that very few dry cleaners own or use such an instrument. Confounding adoption of leak detectors by this industry is the lack of readily available, easy to understand information that could be used to inform selection and purchasing of instruments.

In order to address these issues, several leak detectors were evaluated using criteria appropriate for dry cleaners. First, their technical capabilities were evaluated by determining their response times and limits of detection (LODs). Second, select detectors were subjected to a usability evaluation. Detectors were purchased in November 2010. The technical evaluation was conducted in February-March 2012 and the usability testing was conducted in May 2012.

This study identified three leak detectors that conformed to required technical specifications. These detectors were manufactured by TIF Instruments, Inc.; model numbers RX-1A, ZX, and XP-1A.

LHWMP will use the information generated by this study to engage the dry cleaning community, with the aim of increasing the use of these detectors by dry cleaners.

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INTRODUCTION

Dry cleaning is the process of cleaning fabrics using an organic solvent rather than water. Perchloroethylene (PERC) continues to be the most frequently used dry cleaning solvent in the United States, despite evidence suggesting that this chlorinated hydrocarbon may pose considerable risk to human health and the environment. Precursors to PERC used in dry cleaning include gasoline, kerosene, benzene, and Stoddard solvent. However, these solvents fell out of favor due to flammability and explosion concerns.⁽¹⁾ PERC is a clear, colorless, chlorinated solvent with a sharp, sweet, chloroform-like odor. PERC is also an important chemical intermediate or starting material for the production of other chemicals. Widely used as a metal-degreaser, PERC may be found in many household products, including water repellants, silicone lubricants, fabric finishers, and brake cleaner.⁽²⁾ Synonyms for PERC include perchloroethylene, tetrachloroethylene, PCE, tetrachloroethene, perclene, perchlor, or the Chemical Abstracts Service (CAS) number 127-18-4.⁽²⁾

Local Hazardous Waste Management Program in King County

The Local Hazardous Waste Management Program in King County (LHWMP) was established in 1990 in response to the Washington State Dangerous Waste Management Act (RCW 70.50.220), which required local governments to address small quantity hazardous waste streams from businesses and households. The program has operated since 1991 to address hazardous materials and to protect the public and the environment from their effects. LHWMP is comprised of over 40 city, county and tribal governments who work together to reduce these threats.⁽³⁾

LHWMP is a non-regulatory program with no enforcement authority. Consequently, the program emphasizes free-of-charge, on-site technical assistance, educational outreach, and incentive programs to achieve its mission.

PERC as a dry cleaning solvent

Michael Faraday first synthesized PERC in 1821, but it would not be until the 1940s that PERC would become the predominant dry cleaning solvent in the United States. PERC was thought to be a safer alternative to the petroleum-based solvents that had been used previously.⁽¹⁾ Because PERC is considered to be non-flammable, the risk of injury to workers and damage to buildings due to fire was negligible compared to that of flammable chemicals such as kerosene or gasoline.

PERC is highly lipophilic and readily breaks down grease, fat, oil, and wax. An index of a solvent's degreasing or cleaning ability is the unitless Kauri-Butanol (KB) number. A high KB value indicates a stronger cleaning ability than that of a low KB value. Solvents with large KB values are typically efficient at removing stains, but they may damage delicate garments.⁽⁴⁾ KB values and a cleaning performance summary of dry cleaning solvents are presented in Table 1.

Table 1. Kauri-Butanol (KB) values and cleaning performance of dry cleaning solvents		
Solvent/Type	KB Value	Cleaning Performance
PERC	92	Oil-based stains, most water-based stains, silks, wools, rayon. Not good for delicate garments.
Stoddard solvent	32-39	Less aggressive than PERC for oil-based stains. Can handle delicate garments.
Pure Dry (hydrocarbon plus a hydro-fluoroether and a perfluorocarbon)	37-40	Less aggressive than PERC for oil-based stains. Can handle delicate garments.
Shell 140 (hydrocarbon)	Not available	Less aggressive than PERC for oil-based stains. Can handle delicate garments.
EcoSolv (hydrocarbon)	26-27	Less aggressive than PERC for oil-based stains. Can handle delicate garments.
DF-2000 (hydrocarbon)	27	Less aggressive than PERC for oil-based stains. Can handle delicate garments.
Green Jet (DWX-44 detergent)	N/A	Less aggressive than PERC. More effective in cleaning sugar, salt, perspiration stains. Good for delicate garments. Not good for heavily soiled garments.
Rynex 3 (propylene glycol ether)	70	Aggressive, cleans water-soluble and oil-based stains.
GreenEarth (siloxane)	<20	Less aggressive than PERC for oil-based stains. Good for water-based stains, delicates.
Carbon dioxide	<10	Good for all stains and most fabrics. Very effective in removing oils, greases, sweats.
Wet Cleaning (water)	Not applicable	Aggressive, good for both oil and water-based stains. Can handle delicate garments.

PERC is also highly stable, which allows it to be filtered, distilled, and re-used. PERC's low solubility in water allows for a faster separation of moisture from the solvent in a dry cleaning machine's water separator.⁽⁵⁾ Unfortunately some of these qualities that make PERC an effective cleaning solvent also contribute to it being an occupational and environmental health hazard.

Dry cleaning overview

The processes involved in commercial dry cleaning typically include pre-treating with a spot cleaner, washing, solvent extraction, drying, and finishing.

Initial spot treatment is done by hand with a variety of chemicals. Depending on the type of chemical used, spot treatment products can contaminate waste streams with additional chlorinated hydrocarbons and other hazardous substances.

The washing step is similar to that of residential laundry except that the machines use organic solvents rather than water.

In modern dry cleaning, the washing and drying cycles are performed in the same machine. This “dry-to-dry” technology has significantly decreased occupational PERC exposures compared to older “transfer” machines, which required the manual transfer of clothing from a washer to a separate dryer.

Finishing a garment is the last step, and can include pressing, steaming, and ironing with pressing and tensioning machines. Tensioning machines are used to stretch, reform, and finish dry cleaned clothing.⁽⁵⁾

Technological advances in the design of dry cleaning machines are referred to as “generations”. Each successive generation incorporates incremental improvements that reduce the amount of PERC lost during operation (see Table 2).

Table 2. Summary of dry cleaning machine generations	
Machine	Summary
1st Generation	Transfer from Washer to Dryer by hand
2nd Generation	Dry-to-Dry Vented, Refrigerated or Water-Cooled
Retrofitted 2nd	Self-Contained, Non-Vented, Refrigerated
3rd Generation	Dry-to-Dry, Self-Contained, Non-Vented, Refrigerated
4th Generation	Machine is Enclosed, Refrigerated, Carbon Absorber
5th Generation	Machine is Enclosed, Carbon Absorber, Vapor Sensor, Vapor Lock Mechanism

A detailed explanation of different solvents and the processes they entail is provided in the California Air Resources Board’s (CARB’s) technical assessment of the dry cleaning industry.⁽⁴⁾

Leaking machine components such as gaskets and hoses can become sources of PERC release. Such releases may expose workers and communities to PERC and may result in fines from regulatory agencies such as the Washington State Department of Labor and Industries (L&I), the Washington State Department of Ecology (Ecology), the Puget Sound Clean Air Agency (PSCAA), and the United States Environmental Protection Agency (EPA). Early detection, through the regular use of vapor leak detectors, can help protect both humans and the environment from the consequences of PERC release.

According to a 2011 EPA estimate, approximately 28,000 dry cleaners used PERC in the United States.⁽⁶⁾ The gradual transition of this industry away from PERC to less toxic

solvents⁽⁷⁾ has contributed to the reduction of occupational exposures and less frequent environmental release.⁽⁸⁾

Exposure routes for PERC

Inhalation

Inhalation of vapor is the major exposure route for PERC in the dry cleaning industry. Inhalation may occur during normal operating procedures, as well as during machine maintenance, filter changing, cleaning of still bottoms, and spot treatments. Inhalation exposures can also result from the off-gassing of PERC from dry cleaned garments, household products containing PERC, industrial emissions, and through vapor intrusion from contaminated groundwater.⁽⁹⁾ Fabric off-gassing varies depending on the generation of machine as well as the type of fabric cleaned. A National Institute for Occupational Safety and Health (NIOSH) study demonstrated that two identical swatches of fabric emitted 31.8 and 1.34 mg PERC/kg cloth after being cleaned in a refrigerated dry-to-dry machine and a 5th generation machine, respectively.⁽⁸⁾

Fabric type has also been shown to influence the retention of PERC. After six cycles through a dry cleaning machine, wool retained nearly four times more PERC than cotton, and twice as much as polyester.⁽¹⁰⁾

Dermal contact

Although PERC is not rapidly absorbed through the skin, it can be measured in exhaled breath after prolonged skin contact.⁽¹¹⁾ Worker's skin may contact PERC during maintenance operations, such as cleaning lint and button traps, changing solvent filters, and disposing of hazardous waste.

Ingestion

Ingestion is not typically considered to be an important occupational exposure route. Drinking contaminated water in community settings is perhaps the greatest source of PERC ingestion. Nursing mothers can transmit PERC to their children through breast milk due to the high fat content and the lipophilic nature of PERC.⁽⁹⁾ PERC may cross the placental membrane and result in the decreased mean birth weight for births to exposed mothers.^(9,12) Studies of food service businesses located in the same building as PERC dry cleaners show an increased concentration of PERC, especially in fatty foods such as deli meats and mayonnaise. PERC concentrations as high as 50 mg/kg were detected in margarine from a business located next to a PERC dry cleaner.⁽¹³⁾

Health effects of PERC

Once absorbed, PERC diffuses into the bloodstream and distributes throughout the body, but primarily to organs and fatty deposits.⁽¹⁴⁾ Most of the absorbed dose is exhaled as unchanged PERC, regardless of whether it is inhaled, ingested, or absorbed.⁽²⁾ A small amount of the absorbed PERC is converted by the liver to its main urinary metabolite, trichloroacetic acid, and excreted through urine.⁽¹³⁾ Elimination of PERC from adipose

tissue is difficult and slow, reflecting its stability, high adipose/blood partition coefficient, and limited delivery from blood to tissue.⁽¹³⁾

Central Nervous System

The most immediate effect of PERC exposure is depression of the central nervous system (CNS), including drowsiness, dizziness, concentration impairment, disorientation, irritability, and unconsciousness.⁽⁹⁾ Evidence from animal and human studies indicates that chronic exposure to PERC can cause a decrease in color vision, reaction time, and other cognitive effects.⁽¹⁵⁾

Respiratory system

PERC causes irritation of the upper respiratory tract and mucous membranes. A survey of dry cleaning workers revealed that upper respiratory irritation was indicated at concentrations as low as 20 ppm.⁽¹⁶⁾

Liver/Kidney

Human exposure to PERC has been associated with abnormal liver function, cirrhosis, and hepatomegaly.⁽⁹⁾ Animal studies have shown that PERC causes damage to both the liver and kidneys. Renal proteins excreted in the urine measured in epidemiologic studies add support to the association between PERC inhalation and chronic kidney disease.⁽¹⁵⁾ Animal studies including multiple species have shown an association between inhalation and ingestion of PERC with an increased liver weight, necrosis, inflammatory cell infiltration, and proliferation.⁽¹⁵⁾

Skin

PERC is an effective degreasing agent and removes the skin's natural oils. Repeated contact can result in drying and defatting of the skin, which can cause dermatitis. Skin irritation leading to redness and blistering is also caused by dermal contact, with symptoms persisting up to several months.⁽¹⁷⁾

Reproductive system

A study of pregnancy outcomes among 419 dry cleaning workers suggested that PERC exposure was associated with spontaneous abortion and developmental abnormalities.^(14,18) Ingesting water contaminated with PERC at Camp Lejeune in North Carolina showed an association between PERC exposure and lower mean birth weight.⁽¹²⁾ However, because the risk estimates from the available studies are considered to be inaccurate due to small sample sizes, the association between PERC exposure and reproductive concerns is generally considered inconclusive.⁽¹⁵⁾

Carcinogenicity

EPA's guidelines for carcinogen risk assessment indicate that PERC is likely to be carcinogenic in humans by all routes of exposure. Epidemiologic studies indicate that PERC exposures may be associated with several types of cancer, including bladder cancer, non-Hodgkin lymphoma and multiple myeloma.⁽¹⁵⁾

Before finalizing the document, *Toxicological Review of Tetrachloroethylene (Perchloroethylene)* (CAS No. 127-18-4) in support of *Summary Information on the Integrated Risk Information System (IRIS)*, EPA requested that the National Research Council (NRC) of the National Academies of Science (NAS) conduct an independent toxicological assessment. The NRC supported EPA's position that PERC is likely to be carcinogenic in humans, due to the weight of evidence of bioassays and less from epidemiological evidence.⁽¹⁹⁾

PERC is classified by the International Agency for Research on Cancer (IARC) as a Group 2A carcinogen.⁽¹³⁾ A Group 2A classification indicates that PERC is probably carcinogenic to humans. PERC is reasonably anticipated to be a human carcinogen on the basis of limited evidence from studies in humans and sufficient evidence of carcinogenicity from studies in experimental animals.⁽²⁰⁾

The American Conference of Governmental Industrial Hygienists (ACGIH) includes PERC in the A3 carcinogenicity category. This category includes confirmed animal carcinogens with unknown relevance to humans.⁽²¹⁾ Animal studies have shown PERC to be carcinogenic, but at concentrations and via exposure routes not likely to be encountered by humans.

PERC in the environment

Because of its volatility, much of the PERC lost due to leaks, spills, and other uncontrolled releases escapes into the atmosphere. Uncontained liquid PERC may also permeate concrete floors, enter into the soil, and may eventually contaminate groundwater and surface water.⁽²⁾

Because PERC does not form strong bonds with soil, contaminated soil can emit PERC vapor into the air. Vapor intrusion from contaminated soils into homes and businesses has been measured in ambient indoor air and in fatty foods.⁽²²⁾

PERC is classified as a Dense Non-Aqueous Phase Liquid (DNAPL) because it is denser than water and is relatively insoluble. PERC tends to sink vertically through sand and gravel aquifers, making removal difficult.⁽²³⁾ PERC can perch between soil layers, eventually creating a large plume due to the effects of gravity and capillary action.

PERC is frequently found in surface and groundwater. Approximately 38% of 9,232 surface water sampling sites in the U.S. have tested positive for PERC.⁽²⁾ PERC has been detected in at least 771 of the 1,430 National Priority List (NPL) sites identified by the EPA.⁽²⁾

As required by the Superfund Amendments and Reauthorization Act (SARA), the EPA and ATSDR compile the Substance Priority List, which is a list of the 275 most commonly found substances at facilities on the NPL. Due to its toxicity and potential for human exposure, PERC is currently ranked 33rd on the 2011 Substance Priority List.⁽²⁴⁾

A 2011 review of the State Cleanup Sites database managed by the Washington State Department of Ecology revealed that approximately 50 current and former dry cleaning sites were under investigation for environmental contamination in King County.⁽²⁵⁾

Regulatory and advisory limits

Occupational health

The Occupational Safety and Health Administration (OSHA) is responsible for developing and enforcing workplace safety and health regulations in the United States. A permissible exposure limit (PEL) is a regulatory limit based on the amount of a substance in the air over an 8-hour time-weighted average (TWA). OSHA has set the PEL for PERC to 100 ppm, the acceptable ceiling concentration to 200 ppm, and the maximum peak for an 8-hour shift to 300 ppm for a maximum of 5 minutes in any 3 hours.⁽²⁶⁾ In 1988, OSHA attempted unsuccessfully to decrease the 8-hour TWA for PERC to 25 ppm. However, in January 1989, the Final Rule on Air Contaminants Project was remanded by the U.S. Circuit Court of Appeals, leaving the 8-hour TWA at 100 ppm.⁽²⁷⁾

NIOSH is responsible for conducting research and making recommendations for the prevention of work-related injury and illness.⁽²⁸⁾ NIOSH has no recommended exposure limit (REL) for PERC, but does recommend minimizing workplace exposures due to PERC's carcinogenic potential.⁽²⁹⁾ When there is no known threshold for carcinogens that would protect 100% of the population, NIOSH recommends limiting occupational exposures to the lowest feasible concentration.

ACGIH is a private, non-profit scientific association that investigates, recommends, and reviews exposure limits for chemical substances. ACGIH has threshold limit values (TLVs) and biological exposure indices as guidelines for decision making. ACGIH recommends an 8-hour TWA of 25 ppm and a short term exposure limit (STEL) of 100 ppm for PERC.⁽²¹⁾

The Division of Occupational Safety and Health (DOSH) within L&I develops and enforces health and safety rules for Washington state.⁽³⁰⁾ DOSH has set the PEL for PERC to an 8-hour TWA of 25 ppm, and a 15-minute STEL to 38 ppm.⁽³¹⁾ These are the legally enforceable occupational exposure limits for PERC in Washington state.

Like federal OSHA, DOSH regulates businesses with one or more employees. Owner-operators who do not enroll in the L&I-administered workers compensation system are exempt from DOSH regulations and are not subject to workplace inspections. In King County, Washington, 26 percent of dry cleaning businesses are owner-operated, with no employees.⁽⁷⁾

Environmental protection

The EPA has criteria for determining whether a PERC-using facility is classified under the regulations for air, hazardous waste, and wastewater. Air regulations depend on the annual amount of PERC purchased, type of machine(s) used, and the year the machine(s) were installed. In both EPA and Washington State regulations (see WAC 173-303-090(8)), wastes with more than 0.7 mg/L PERC designate as dangerous waste for the

toxicity characteristic. Wastewaters that designate as dangerous waste for PERC may not be discharged into the sewer system. Wastewater regulations depend on the amount of PERC discharged to the sewer each month.⁽³²⁾ The EPA has set a maximum contaminant level (MCL) for PERC in drinking water at 0.005 mg/l or 5 parts per billion (ppb).⁽³³⁾

The Puget Sound Clean Air Agency (PSCAA) has jurisdiction over King, Kitsap, Pierce, and Snohomish Counties in Washington state, and requires PERC-using dry cleaning shops to adopt dry-to-dry machines and to perform regular inspections for leaks.⁽³⁴⁾ In 2001, the EPA approved the PSCAA regulation for PERC dry cleaners as equivalent, and thus only one regulatory agency was required. In 2006, however, the EPA updated the emission standards for PERC dry cleaners and the PSCAA regulation lost its equivalent status in 2008. Until the PSCAA withdrew its rule in 2010, PERC-using dry cleaners were required to follow both EPA and PSCAA regulations. Currently, the PSCAA requires PERC dry cleaners provide notification before beginning operations, but does not issue permits or enforce EPA's regulations.

Leak detection requirements

The federal regulation that describes the rules covering topics including leak detection is 40 CFR Part 63 Subpart M--National Perchloroethylene Air Emission Standards for Dry Cleaning Facilities. In Washington state, this regulation is adopted by reference into WAC 173-400-075, which states:

(8) Emission standards for perchloroethylene dry cleaners

(e) Inspection.

(i) The owner or operator must inspect the dry cleaning system at a minimum following the requirements in Table 3 and Table 4

(ii) You must check for leaks using a portable leak detector.

(A) The leak detector must be able to detect concentrations of perchloroethylene of 25 parts per million by volume.

(B) The leak detector must emit an audible or visual signal at 25 parts per million by volume.

(C) You must place the probe inlet at the surface of each component where leakage could occur and move it slowly along the joints.

(iii) You must examine these components for condition and perceptible leaks:

(A) Hose and pipe connections, fittings, couplings, and valves;

(B) Door gaskets and seatings;

(C) Filter gaskets and seatings;

(D) Pumps;

(E) Solvent tanks and containers;

(F) Water separators;

(G) Muck cookers;

(H) Stills;

(I) Exhaust dampers; and

(J) Cartridge filter housings.

(iv) The dry cleaning system must be inspected while it is operating.

(v) The date and result of each inspection must be entered in the operations and maintenance record at the time of the inspection.

Sources of detector information

The California Air Resources Board (CARB) evaluated several leak detectors and photoionization detectors (PIDs) under laboratory conditions to determine their detection accuracy and response times to PERC standards.⁽⁴⁾ However, response times were reported in ranges rather than individual measurements. In addition, because the analysis was conducted in 2005, several of the tested detectors are no longer manufactured.

The Oregon Department of Environmental Quality's (DEQ's) Small Business Assistance Program helps dry cleaners comply with its enhanced leak detection and repair program. TIF XP-1A leak detectors were distributed to dry cleaners who participated in workshops or training sessions.⁽³⁵⁾ While this is not an explicit recommendation of the XP-1A detector by the Small Business Assistance Program, it does project a level of confidence in the performance of this instrument.

In Washington state, the Spokane Regional Clean Air Agency provides support to dry cleaners in Spokane County through their Compliance Assistance Program. The publication titled *"Dry Cleaning & Air Quality Requirements in Spokane County"* states that perceptible leak checks must be performed weekly using sight, smell, and touch. Monthly leak checks must also be performed using a hydrocarbon detector or PERC gas analyzer.⁽³⁶⁾ The sensitivity and price for several halogenated hydrocarbon detectors and PIDs are presented, but the only recommendation was for further research into which detector would be the best for individual facilities.⁽³⁶⁾

The Air Pollution Control Division of the Colorado Department of Public Health and Environment produced *"New Requirements for Leak Detectors and Monitoring Equipment for Perchloroethylene Drycleaning Facilities in Colorado"*, which includes the same basic type of information for nine halogenated leak detectors expected to meet EPA guidelines. No detector-specific recommendations are provided, although useful tips for operating a "typical" halogenated leak detector are included.⁽³⁷⁾

Current study

A survey conducted by LHWMP in 2010 provided valuable insights into the local dry cleaning industry. Surveys were mailed to dry cleaning businesses throughout King County. Results of the survey indicated that 26 percent of the respondents were owner-operated and had no employees; 84 percent self-identified as Korean; 69 percent reported using PERC in their primary dry cleaning machine; and 69 percent did not own and use a PERC leak detector.⁽⁷⁾

This current project was conducted to ultimately increase the number of King County dry cleaners that own and regularly use vapor leak detectors. As described above, there is a lack of readily available, easy to understand information to inform the purchase and use of leak detectors.

Consequently, several readily available leak detectors were evaluated using criteria appropriate for dry cleaners. In Phase I, their technical capabilities were evaluated by determining their response times and limits of detection (LODs). In Phase II, select detectors were subjected to a usability evaluation. Detectors were purchased in November 2010. Phase I and Phase II of this study were conducted in February-March 2012 and May 2012, respectively.

METHODS

Detector selection

The following instruments were selected for testing after reviewing the sources of detector information described previously, contacting the studies' authors, and reviewing the product catalogs of several manufacturers:

- Kanomax USA, Inc. (Andover, NJ). Model: AeroQual Series 200
- NOVA Systems Products, LLC (Aurora, IL). Model: BOLO GRN
- Snap-on Incorporated (Kenosha, WI). Model: ACT760A
- INFICON (Syracuse, NY). Model: TEK-Mate
- TIF Instruments, Inc. (Owatonna, MN):
 - Model: RX-1A
 - Model: XL-1A
 - Model: XP-1A
 - Model: ZX-1

Detectors were purchased in November 2010.

We subsequently learned that TIF Instruments replaced the ZX-1 model with the ZX. Once the ZX was received, it was included in the remaining procedures. Prior to testing, the BOLO GRN model was discovered to be malfunctioning, so it was returned to the manufacturer for repair. A replacement BOLO GRN detector arrived soon after the first day of testing had been completed on the other detectors.

Unlike PIDs, leak detectors do not provide quantitative measurements of chemical concentrations. Rather, they provide a semi-quantitative indication of the presence of a chemical, which is generally sufficient to allow identification of a leak source.

The detectors were evaluated in two phases. Phase I involved laboratory testing to determine the detectors' technical capabilities. Phase II included hands-on usability testing by volunteers.

Phase I: Evaluating the detectors' technical capabilities

Testing equipment

Several concentrations of PERC vapor were generated to test the technical capabilities of the leak detectors in February-March 2012. The configuration of the components used in Phase I is presented in Figure 1.

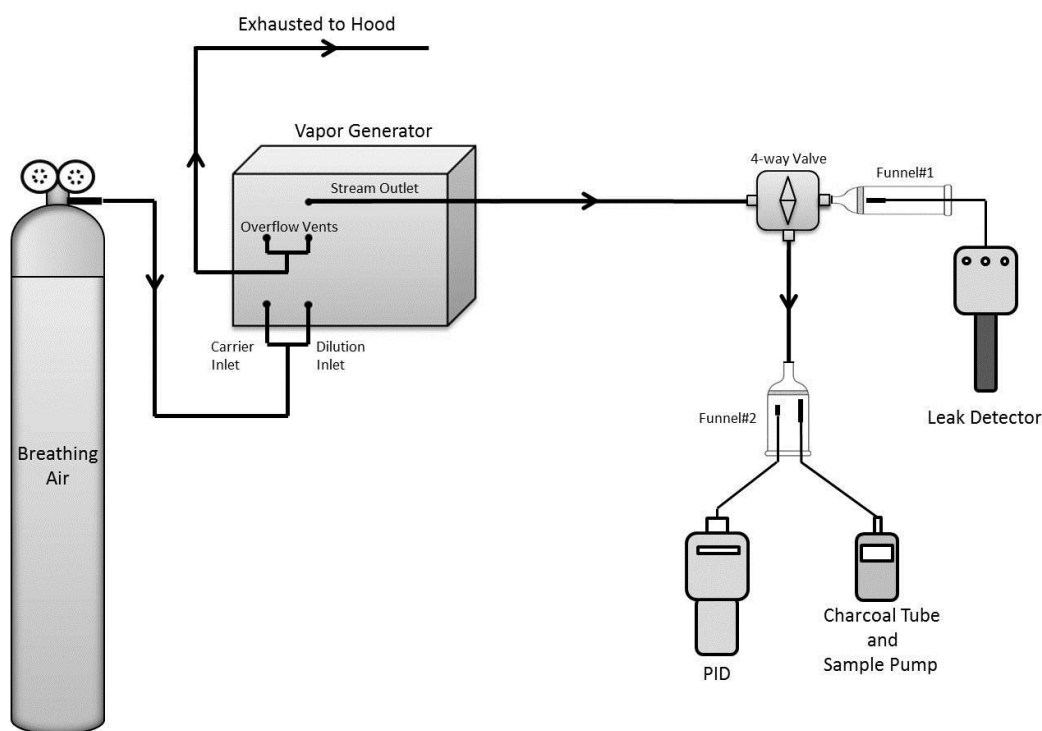


Figure 1. The PERC vapor generation system

Vapor generation

The desired PERC vapor concentrations were generated using a Dynacalibrator Model 450 (VICI Metronics, Poulsbo, Washington), equipped with a diffusion vial.

An external source of breathing air was split into two streams before entering the Dynacalibrator: the carrier stream and the dilution stream. The carrier stream has a fixed flow rate set by the manufacturer, while the dilution stream may be adjusted using two flowmeters. The use of two flowmeters enables the user to create two distinct concentrations by changing the flow rate through the flowmeters. Because the temperature and flow of the carrier stream are unchanged, the flowmeter with the lower flow rate generates the higher concentration.

The carrier stream passes through a temperature-controlled permeation chamber, which houses the diffusion vial that contains the test chemical (PERC). The temperature in the permeation chamber influences the rate at which the liquid in the diffusion vial moves into the vapor phase. At a constant temperature and pressure, vapor diffuses at a steady rate through the diffusion vial's capillary tube. As the carrier stream passes through the permeation chamber, it incorporates the PERC vapor as it leaves the diffusion vial. The carrier stream then joins the dilution stream in a mixing tee and is exhausted through the stream outlet port.

The Dynacalibrator has three settings that were used during testing: Zero, Span1, and Span2. When in the “Zero” setting, the carrier stream travelling through the permeation chamber is exhausted through the overflow vent. The dilution stream travels through the Span1 flowmeter and out the stream outlet. This configuration provides a vapor stream that should have a concentration of 0 ppm. The schematic of flow for the Dynacalibrator 450 is shown in Figure 2.

When set to “Span1”, the carrier stream mixes with the dilution stream that has travelled through the Span1 flowmeter and is exhausted through the stream outlet.

When set to “Span2”, the carrier stream mixes with the dilution stream that has travelled through the Span2 flowmeter and is exhausted through the stream outlet.

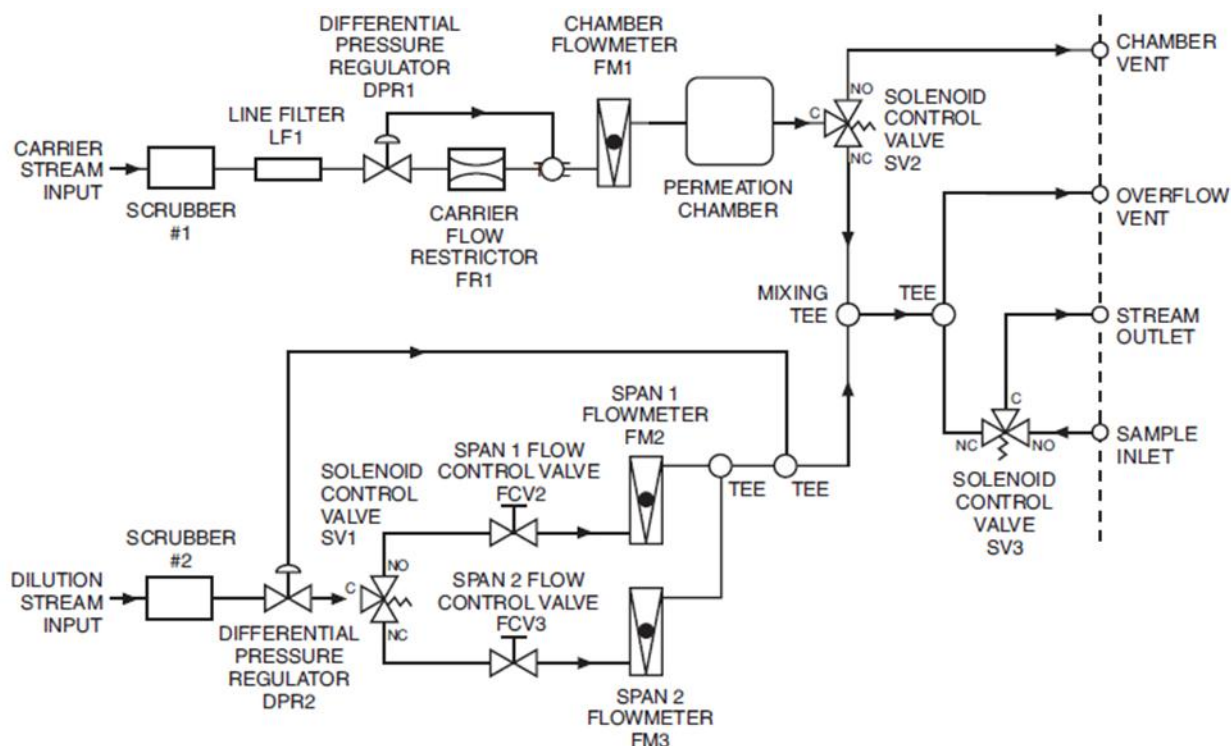


Figure 2. Schematic of the Dynacalibrator Model 450

Diffusion vial

A model ‘D’ VICI diffusion vial was used to generate the PERC vapor. The ‘D’ designation refers to the 5 millimeter (mm) inside diameter of the diffusion vial capillary. The vial had a reservoir length of 75 mm, capillary length of 18 mm, total length of 93 mm, and an inside capillary diameter of 5 mm. A ‘D’ sized diffusion vial similar to that used during testing is shown in Figure 3.

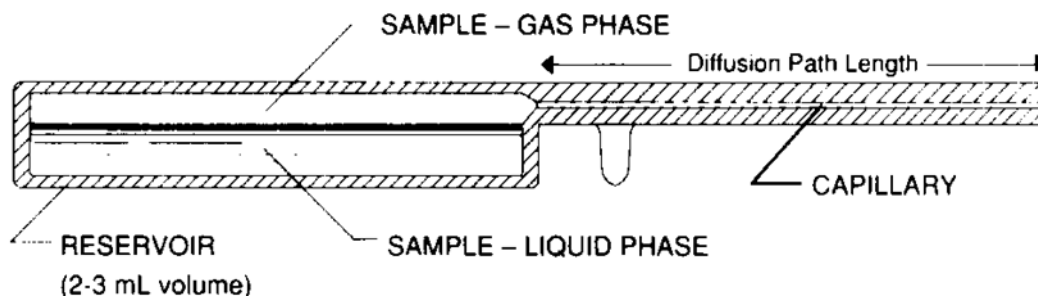


Figure 3. Diffusion vial

Perchloroethylene

A one liter bottle of 99% extra pure PERC was purchased from Acros Organics (Thermo Fisher Scientific; catalog number 138010010).

Air cylinder

A cylinder of compressed medical grade breathing air was used as the source of carrier and dilution streams to ensure chemical consistency and eliminate contamination concerns. A “K” type cylinder (part number AI M-K, with 2200 PSIG and volume of 232 ft³) was purchased from Praxair (Danbury, Connecticut).

Polytetrafluorethylene tubing

Polytetrafluorethylene (PTFE or Teflon®) tubing was used to ensure that PERC would not be absorbed before reaching the exhaust outlet. PTFE has several physical characteristics, such as an extremely low coefficient of friction, that make its use appropriate with solvents and reactive chemicals. All tubing downstream from the point of PERC introduction was constructed exclusively of PTFE.

Tubing/Fittings

Tygon tubing was used to connect the air cylinder to the Dynacalibrator because it is sufficiently flexible and less expensive than PTFE. Tube fittings and hose adaptors were comprised of either ¼” copper or ¼” PTFE. Teflon® tape was used to ensure a tight seal, when necessary.

Fritted filter funnels

Glass fritted filter funnels were attached to the ends of both exhaust stream outlets in order to provide an even distribution of the air stream at the detector probe. Detectable levels of PERC did not accumulate in either of the fritted filters and did not appear to measurably slow the exhaust stream. PERC accumulation in the fritted filters was tested for, after switching settings to “Zero” using the PID and the TIF ZX leak detector. Laboratory results from charcoal tube sampling were below the limit of detection (LOD) of 0.08 ppm.

Hygrometer

An ISO 9001-certified Cole-Parmer Traceable® hygrometer/thermometer was used to measure the relative humidity (RH) and temperature of the air stream. The hygrometer was Traceable® to the National Institute of Standards and Technology (NIST) calibration on 01/03 by Control Company in Friendswood, TX.

Flowmeter calibration

A Bios Defender 520 volumetric primary flow standard was used to calibrate the Dynacalibrator's dual flowmeters. The Defender 520 was used to average the flow rate for up to ten readings.

Concentration measurement: Photoionization detector

A RAE Systems MiniRAE 2000 PID was used to provide a quantitative measurement of the PERC vapor concentration in the exhaust stream. PIDs measure all airborne substances in a vapor that have ionization potentials below the rating of the instrument's vapor discharge lamp. When a vapor enters the PID, it passes by a UV lamp, which breaks the vapor down into positive and negative ions that can be counted with a detector.⁽³⁸⁾

The MiniRae 2000 was fitted with a 10.6 electron volt (eV) gas discharge lamp. Internal memory allowed for the logging of 15,000 data points that could be downloaded for further analysis. The PID is equipped with an internal pump with a regulated flow rate of between 450-550 ml/min, which limits the effect of the outside airstream flow rate. The PID was calibrated using isobutylene calibration gas certified to 100 ppm. A correction factor of 0.57 was applied to the PID readings to obtain the PERC concentration.⁽³⁹⁾

Concentration measurement: Charcoal tubes

SKC® Anasorb® coconut shell charcoal sorbent sample tubes (catalog number 226-01) were used to validate the measurements taken by the PID. Used tubes were stored on ice in a cooler while testing was conducted, and then transferred to a refrigerator until delivered to the laboratory for analysis.

A Gilian dual-mode, low-flow pump was used to draw air through the charcoal tubes. The pump was calibrated to approximately 200 milliliters per minute (ml/min). Air was drawn through the charcoal tubes at approximately 200 ml/min for 15 minutes to yield a sampling volume of 0.003 cubic meters (m³).

The University of Washington's Department of Environmental and Occupational Health Sciences Environmental Health Laboratory performed the analysis of the charcoal tubes. This American Industrial Hygiene Association (AIHA) accredited laboratory used a modified version of the NIOSH method 1003 for analysis of halogenated hydrocarbons.

Testing procedures

Six concentrations of PERC vapor were tested: 5, 10, 25, 50, 100, and 250 ppm. The concentrations were divided into three groups. Two concentrations were assigned to each group, based on the permeation chamber temperature setting shared by the two desired

concentrations. This approach allowed us to keep the chamber temperature the same while being able to generate two different PERC concentrations. The groupings are presented in Table 3.

Table 3. Theoretical PERC concentrations and corresponding Dynacalibrator settings						
Group	Theoretical Concentration	Digital Temperature Setting	Chamber Temperature (°C)	Span #	Float	Rotameter Reading
1	C1 (5 ppm)	700	46	1	Bottom	7.5
	C2 (10 ppm)	700	46	2	Bottom	7.0
2	C3 (25 ppm)	900	65	1	Bottom	5.7
	C4 (50 ppm)	900	65	2	Bottom	3.7
3	C5 (100 ppm)	999	85	1	Bottom	6.8
	C6 (250 ppm)	999	85	2	Bottom	4.0

Tests were conducted in the following order:

1. Limit of detection (LOD)
2. Response time
3. Concentration gradient

This order was chosen because if a detector could not detect PERC at the tested concentration, there was no reason to proceed with testing for the response time or the concentration gradient.

System set-up

The Dynacalibrator Model 450 instruction manual states that an external source of gas must have a pressure between 10-25 pounds per square inch (PSI). The regulator controlling the air cylinder was within the recommended pressure settings at approximately 15 PSI. The diffusion vial was injected with 1 ml of PERC and allowed to equilibrate at the specified chamber temperature. The Dynacalibrator provides a small

light near the temperature controls that serves as a visual cue to indicate that temperature equilibrium has been reached in the permeation chamber.

Concentration setting

Span1 and Span2 flowmeters were set to predetermined flow rates in order to achieve the desired vapor concentrations. To verify the concentrations delivered by the system prior to detector testing, a low-flow sample pump drew the exhaust stream through a charcoal tube for 15 minutes for both Span1 and Span2. Charcoal tubes were then sent to the laboratory for quantitative analysis.

Limit of detection

Before testing at Span1 and Span2, detectors were exposed consecutively to “Zero” air (i.e., no PERC in the “vapor” stream) to ensure against false positive results. Detectors were then exposed consecutively to the first concentration of the current group and their response was recorded as either “Detect” or “Non-Detect”. Once every detector was tested at Span1, the Dynacalibrator was switched to Span2. The detectors were then tested consecutively in the identical manner and results were recorded. The Dynacalibrator was switched back to the Zero setting when the final detector was tested.

Reaction time

Only the detectors that were capable of detecting the PERC concentration during the LOD testing were included in the reaction time procedures for that concentration. The detector’s probe was placed in Funnel#1 and the detector was powered on in order to calibrate in air known to be absent of PERC. The exhaust stream was diverted to Funnel#2 using a Swagelock 4-way valve. The Dynacalibrator was then switched to Span1. Simultaneously, the valve was turned, diverting the exhaust stream to Funnel#1, and a stopwatch was started. Timing was stopped and recorded when the detector reacted to the exhaust stream. This procedure was repeated twice more, for a total of three reaction time measurements per detector. Identical procedures were then performed at the Span2 concentration.

When the last detector was tested at the two concentrations of the current group, identical procedures were performed for both LOD and Reaction Time at the next group’s concentrations. This was repeated until testing had been completed for all three groups.

Concentration gradient

Detectors were tested at 0, 25, and 50 ppm to determine if they would respond to concentration gradients. Detectors were first exposed to 0 ppm, and then switched to 25 ppm and the response was recorded. The concentration was then increased to 50 ppm and the detector’s response was recorded once more. Concentrations were then stepped back down to 25 and 0 ppm with responses recorded at each step.

Phase II: Usability testing

Selection of detectors

Detectors were selected for usability evaluation if they were determined to have a suitably low limit of detection and response time from the Phase I test of technical capabilities. Other features identified by the study investigators as being desirable were also considered in the selection process, such as the ability to manually reset the detector. Phase II was conducted in May 2012.

Testing apparatus

Three identical testing units were assembled to simulate the search for a vapor leak in a PERC dry cleaning machine. Each unit consisted of a sample pump, glass impinger, $\frac{1}{4}$ " tubing, and $\frac{1}{4}$ " fittings. The pump was connected to the impinger with flexible tubing, as was the impinger to a copper union tee. Less flexible tubing was used to connect the copper union tee to five other union tees situated in a circle. Each of the five union tees was separated by approximately 7" of tubing. Each had a length of tube, approximately 1", directed toward the center of the circle. A schematic of one of the three testing units is presented in Figure 4 and a photograph of the complete apparatus is presented in Figure 5. Four of the five outlet tubes were blocked, indicated by an "X" in the diagram, leaving only one outlet for the vapor in the system to escape, as indicated by the arrow. Two of the three identical units were designed so that the vapor was exhausted through a hidden hole in the flexible tubing immediately after traveling through the impinger.

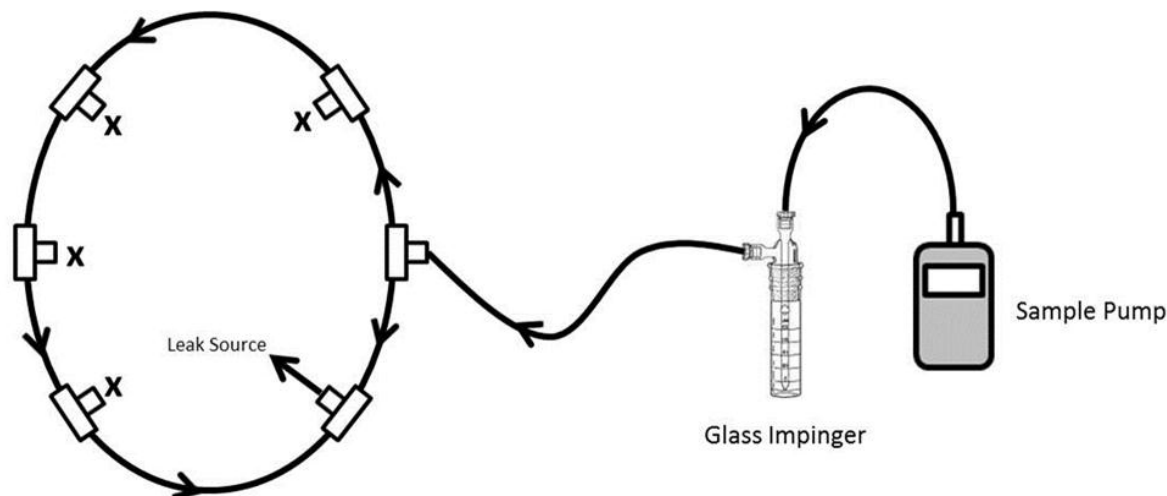


Figure 4. Schematic of a single usability test unit

Sampling pumps

Three low-flow Gilian sample pumps were calibrated to approximately 500 mL/min using the Defender 520 primary flow standard. Factory-supplied adaptors were installed on the pumps in order to switch the direction of flow, allowing them to push air through the impingers and testing units. Pumps were connected to a charging station during testing.

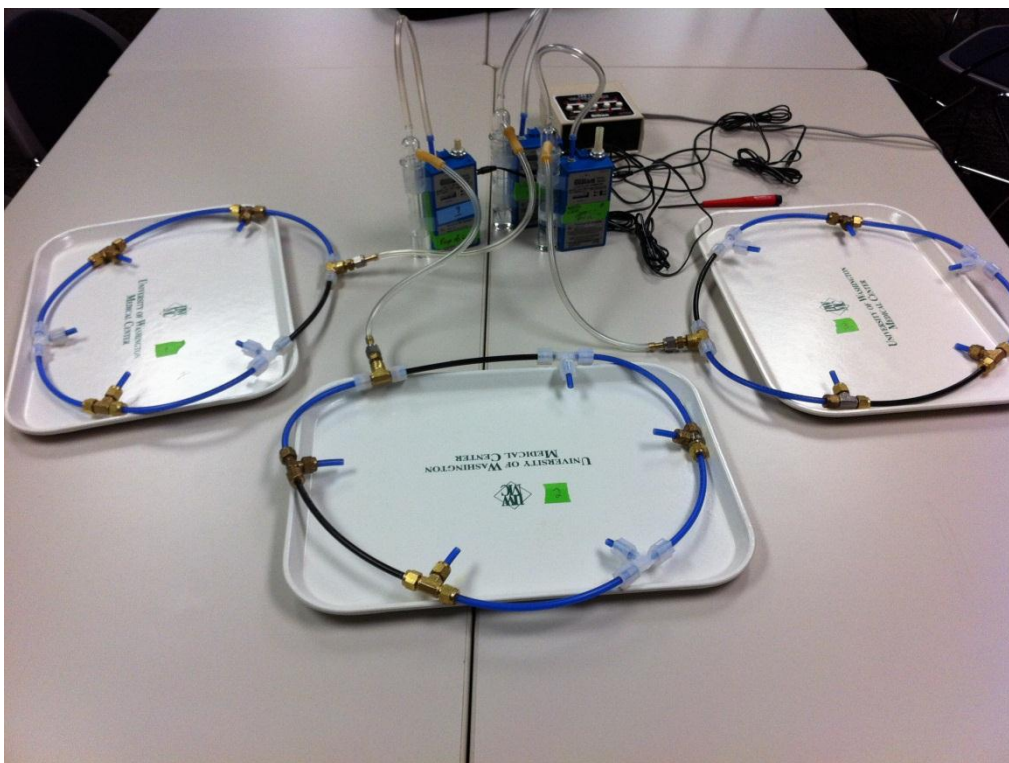


Figure 5. Usability testing apparatus

Test vapor source

Because the usability testing was conducted in an office setting, a chemical less toxic than PERC was needed. Several possible alternatives were evaluated by determining the responsiveness of the leak detectors, but ultimately 91% isopropyl alcohol (consumer-grade rubbing alcohol) was selected. The amount of isopropyl alcohol used (10 ml) and the short duration of testing (approximately 5 minutes) exposed test subjects to minimal airborne concentrations.

Glass impingers

Introduction of isopropyl alcohol into the air stream was achieved by placing glass impingers between the sample pumps and the stream outlet. Two of the impingers contained 10 ml of tap water while the third contained 10 ml of isopropyl alcohol. All impingers and their contents were visually identical.

Trays

A fiberglass cafeteria tray was used to support each of the three test units. Each unit was numbered 1, 2, or 3 to help randomize the leak source location. The trays allowed some of the alcohol carrying vapor to accumulate and partially simulate ambient air contaminated with relatively low concentrations of vapor.

Testing procedures

All research materials were submitted for review to an Institutional Review Board by the Human Subjects Division within the Office of Research at the University of Washington. Documents approved on Human Subjects Application number 42867 were then used during testing.

Subjects included employees from various Seattle & King County programs, L&I, and PSCAA. Subjects were asked to sign a written consent form before testing, and encouraged to ask questions. Once signed, a copy of the consent form was given to the subjects for their personal records.

Upon completion of the written consent form, subjects were provided with a brief tutorial for each of the three detectors tested. The investigator demonstrated how each detector was powered on, how the detector visually and audibly reacted to isopropyl alcohol, and how it powered down.

Following the tutorial, the investigator described the testing apparatus and procedures. Subjects were told that there would be only one leak source out of the 15 possible sources. Subjects were then assured that although the testing would be timed, this was a test of the instrument's usability rather than individual performance. The order in which each subject received the detectors was decided by a random number generator. The plastic cases that contained each detector were labeled with the number 1, 2, or 3. The location of the leak source was also selected by the random number generator that corresponded to the numbered test unit.

Testing commenced once the appropriate detector was selected and powered on. The three sample pumps were also then powered on. When the subjects were instructed to begin, a stopwatch was started and then stopped when the leak was found. The detector was then powered down and returned to its plastic case. The three sample pumps were also powered down. While the subject retrieved and powered up the second detector, the leak source was changed from one test unit to another - as dictated by the random number generator. At this time, the subject was asked to look in the opposite direction while the leak source was changed. This procedure was repeated until the subject found the leak source with the three detectors.

Subjects were then asked to complete a questionnaire, which was designed to gather information about their experience. Questions were asked about the visual and audio responses, which detector they disliked the most, and which they liked the most. The questionnaire is presented in Appendix A.

RESULTS

Phase I: Technical evaluation of detectors

Phase I testing was conducted over three days. Detectors were tested at two concentrations per day due to the time needed to complete the experimental procedures. Measurements were recorded on paper and then entered into a Microsoft Excel 2010™ worksheet.

Basic instrument information provided by the manufacturers and results from preliminary tests, including warm-up time and motion sensitivity are presented in Table 4. Warm-up time was measured from when a detector was powered on to when the warm-up cycle was completed. A detector was deemed sensitive to motion if it yielded an audible or visual response when moved rapidly from an overhead position to waist height with a straight arm.

Limit of detection

At the time of initial testing, two detectors were not available. The BOLO GRN had been returned to the manufacturer upon request of the customer service representative, and a replacement had not yet arrived. The TIF ZX had been ordered but had not yet arrived. When these two detectors were delivered, they were tested at similar concentrations using identical experimental procedures as the previously tested detectors. As measured by the PID, test concentrations of PERC for the last two detectors were within 0.1 ppm of the respective test concentrations of the first group of detectors tested. However, charcoal tube sampling was not conducted while testing the TIF ZX or BOLO GRN.

Detectors were initially tested against the lowest concentration (i.e., 5 ppm). However, because two-thirds of the detectors were able to detect this concentration, additional testing was conducted at nominal PERC concentrations of 1.0, 0.5, 0.3, 0.15, and <0.15 ppm. Charcoal tube sampling was not performed at these concentrations.

The initial procedures increased in concentration from 5 to 250 ppm while the supplementary procedures decreased from 1 to less than 0.2 ppm. Detectors that failed to detect 5 ppm in the initial testing were excluded from testing at lower concentrations. Results of the LOD testing are presented in Table 5. Shaded boxes indicate that the specified concentration was detected.

The TIF XL-1A failed to detect PERC at concentrations below 1 ppm. The remaining five detectors were able to detect PERC at concentrations below the PID's LOD. Lower detection limits of the five remaining detectors were below 0.2 ppm (as measured by the PID). Below 0.2 ppm, a stable reading could not be measured using the PID. A system check using Zero air failed to elicit a detector response and the PID read 0.0 ppm. Switching the Dynacalibrator from Zero air to the PERC-containing air stream caused the detectors to respond while the PID continued to read 0.0 ppm.

Table 4. Detector characteristics										
Manufacturer & Model	Cost (USD) ^{*2}	Warranty (years) ¹	Sensor Lifetime ¹	Sample Delivery ¹	Warm-up Time ¹	Zero or Reset ¹	Sensitivity Adjust ¹	Motion Sensitive ²	Mute ¹	Visual Display ¹
TIF ZX	445	3	100 hrs	Internal Pump	20 sec	Manual & Auto	Yes	No	Yes	Yes
TIF ZX-1	421	25	100-150 hrs	Internal Pump	20 sec	Manual & Auto	Yes	No	Yes	Yes
TIF RX-1A	281	2	20 hrs	Internal Pump	2 sec	Manual	Yes	Yes	No	Yes
TIF XP-1A	310	3	20 hrs	Internal Pump	2 sec	Manual	Yes	Yes	No	Yes
TIF XL-1A	182	2	20 hrs	Internal Pump	2 sec	Manual	No	Yes	No	Yes
Nova Systems BOLO GRN	135	1	10 yrs	Diffusion	30 sec	None	Yes	No	Yes	Yes
Infincon TEK-MATE	200	2	100 hrs	Internal Pump	20 sec	Auto	Yes	Yes	No	No
Snap-On ACT760A	290	3	>300 hrs	Internal Pump	20 sec	Auto	Yes	No	Yes	No
Kanomax AeroQual Series 200	900	1	2-5 yrs	Internal Fan	3-7 min	Manual	No	Yes	Yes	Yes
*Purchased Nov 2010 ¹ Manufacturer information ² Laboratory tested information										

Table 5. Leak detector limits of detection											
Detector	Nominal PERC Concentrations (ppm)										
	<0.15	0.15	0.3	0.5	1	5	10	25	50	100	250
AeroQual 200											
BOLO GRN											
Snap-on											
XL-1A											
RX-1A											
TEK-Mate											
XP-1A											
ZX-1											
ZX											
PID Corrected (ppm)	0.0	0.2	0.3	0.7	1.3	5.5	11.2	28.9	58	110	274
Charcoal Tube (ppm)	N/A	N/A	N/A	N/A	N/A	4.2	7.7	22.1	45	73	173

Response time

Every detector responded to at least one of the eleven PERC concentrations. Of the nine detectors, five responded to all eleven concentrations, while the remaining four detectors responded to seven, three, two, and one concentrations. Detectors that responded to specific concentrations during LOD testing had their response times tested at those concentrations. The concentrations at which the detectors were tested are presented in Table 5. Response times were measured three times per detector at each detectable concentration. Detector response times are presented in box-plot form in Figure 6. Raw data collected during response time testing are presented in Appendix B.

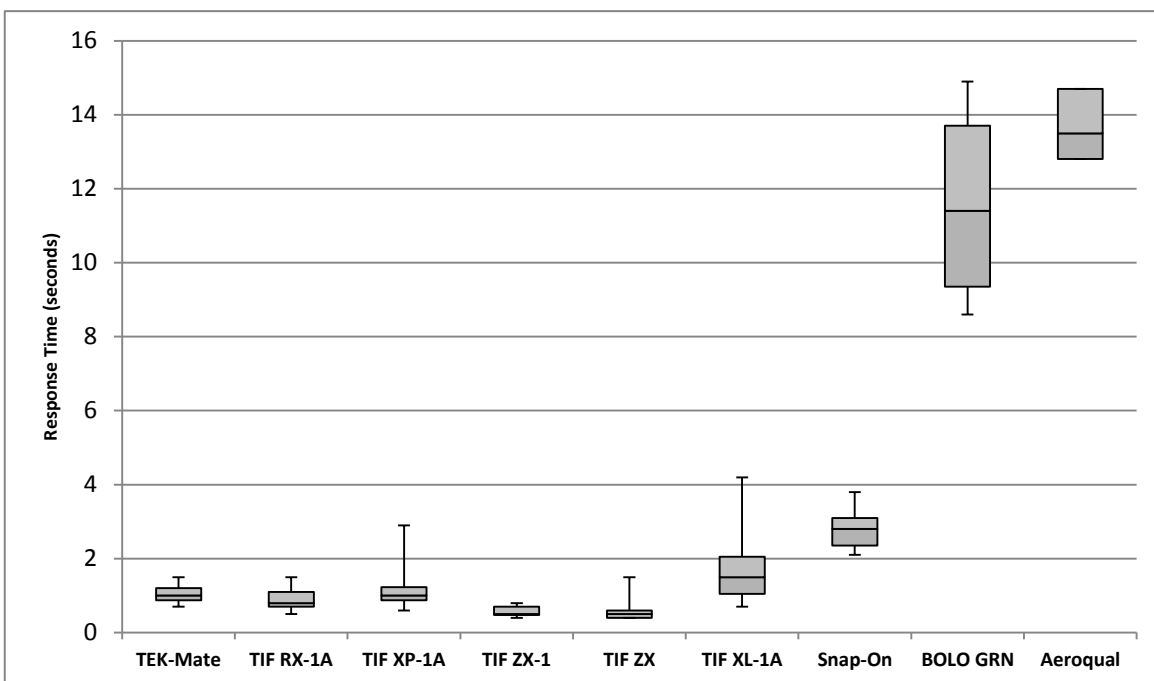


Figure 6. Detector response times

Response time descriptive statistics are presented in Table 6. The difference in response time between the fastest and slowest single measurement was 14.5 seconds. The ZX-1 had the smallest Response time range (0.4 seconds), while the BOLO GRN had the largest range (6.3 seconds).

The TIF ZX, XP-1A, and XL-1A had single response time measurements that skewed their distribution to the right. These outliers are 1.5 seconds, 2.9 seconds, and 4.2 seconds for the ZX, XP-1A, and XL-1A respectively. The distribution of response time measurements for the ZX, XP-1A, and XL-1A are presented in Figures 7, 8, and 9, respectively.

Table 6. Detector response time descriptive statistics (seconds)										
Detector	Count	Mean Response Time (sec)	Standard Error of the Mean	Standard Deviation	Minimum Response Time (sec)	25th Percentile	Median Response Time (sec)	75th Percentile	Maximum Response Time (sec)	Response Time Range (sec)
Aeroqual	3	13.7	0.55	1.0	12.8	13.2	13.5	14.1	14.7	1.9
BOLO GRN	6	11.5	1.01	2.5	8.6	9.7	11.4	13.2	14.9	6.3
Snap-On	9	2.8	0.17	0.5	2.1	2.4	2.8	3.1	3.8	1.7
TEK-Mate	30	1.0	0.04	0.2	0.7	0.9	1	1.2	1.5	0.8
TIF RX-1A	30	0.9	0.04	0.2	0.5	0.7	0.8	1.1	1.5	1.0
TIF XL-1A	21	1.6	0.18	0.8	0.7	1.1	1.5	2.0	4.2	3.5
TIF XP-1A	30	1.1	0.09	0.5	0.6	0.9	1.0	1.2	2.9	2.3
TIF ZX-1	30	0.6	0.03	0.1	0.4	0.5	0.5	0.7	0.8	0.4
TIF ZX	30	0.5	0.04	0.2	0.4	0.4	0.5	0.6	1.5	1.1

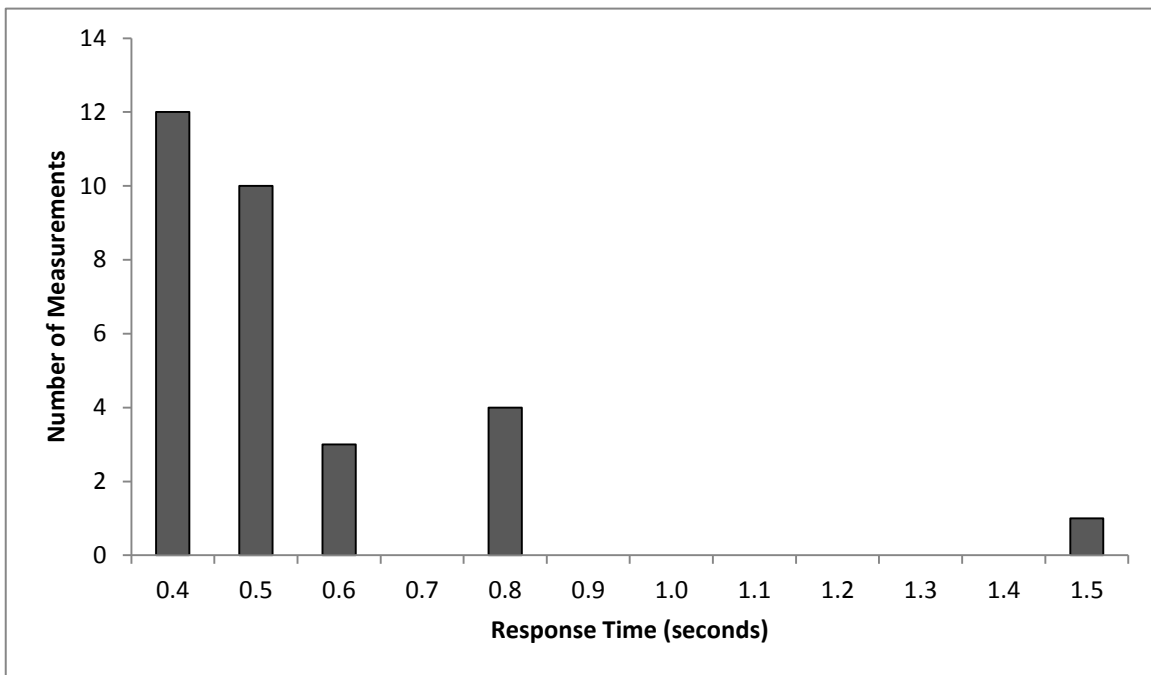


Figure 7. Distribution of response times for the ZX model

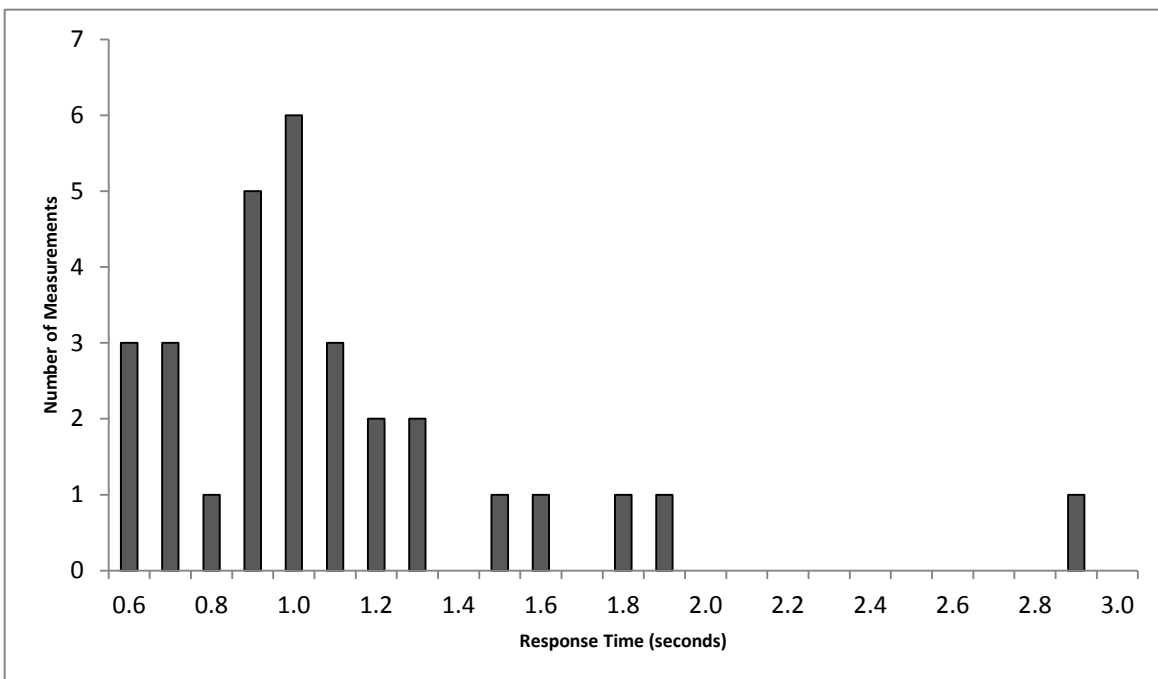


Figure 8. Distribution of response times for the XP-1A model

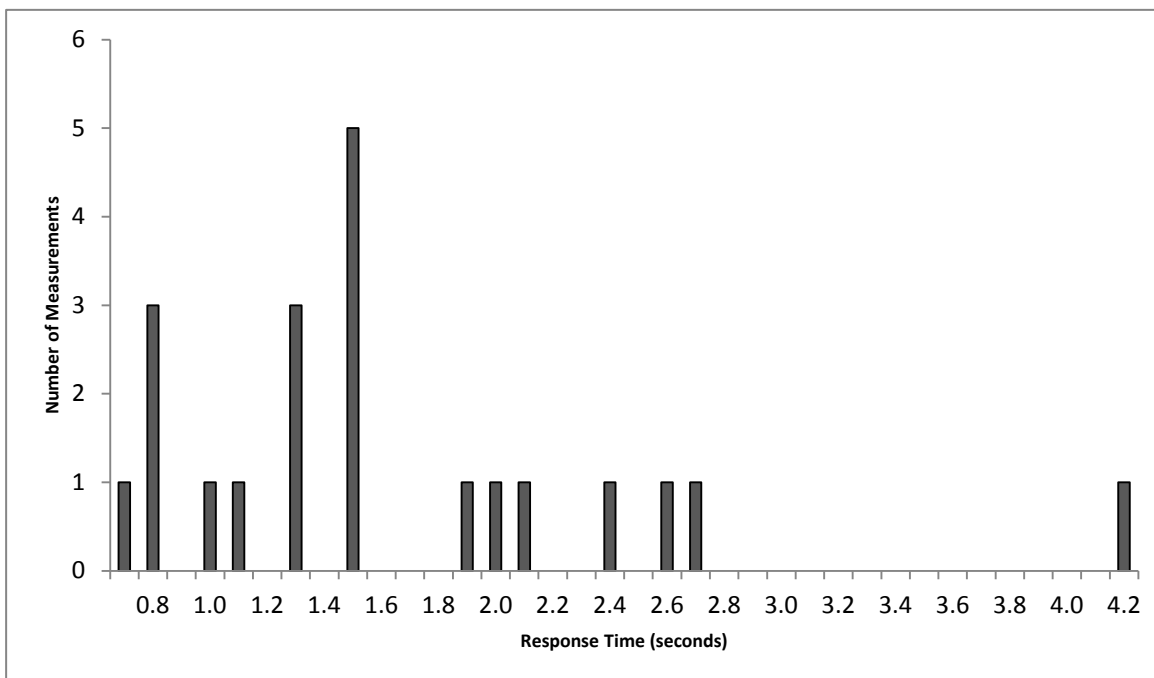


Figure 9. Distribution of response times for the XL-1A model

Concentration gradient

Results from gradient testing are presented in Table 7. The Aeroqual, BOLO GRN, and Snap-On did not respond at the test concentrations and are omitted from the table. The TIF XL-1A does not have a visual display and therefore is noted as “N/A” under the Visual column. If detector response changed when exposed to the two test concentrations, it was assigned a “Yes”. If detector response remained unchanged when exposed to the two test concentrations it was assigned a “No”. If visual response was unable to be differentiated it was assigned an “Inconclusive” in the Visual column.

Because no distinct changes in audible alarms were detected when switching between concentrations, sound alone was not an accurate measure of changing concentration. The audible alarm of the XL-1A changed when PERC concentration increased from 0 to 25 ppm, but remained unchanged from 25 to 50 ppm.

The ZX, ZX-1, and XP-1A employ multi-color light-emitting diode (LED) displays that transitioned in color through green, orange, and red when PERC was introduced. The RX-1A had only a series of red LEDs, which would increase in number from 0 to 6. The TEK-Mate had two single color LEDs, representing separate sensitivity settings, which would rapidly blink until reaching the full display at which time the light would stop blinking and remain lit. The single red LED of the XL-1A indicated only that the detector was powered on.

Table 7. Concentration gradient detection from 25 to 50 ppm		
Detector	Gradient Recognition	
	Visual	Audible
TEK-Mate	No	No
TIF RX-1A	Inconclusive	No
TIF XL-1A	N/A	No
TIF XP-1A	Inconclusive	No
TIF ZX-1	Inconclusive	No
TIF ZX	Inconclusive	No

The step-up in concentration from 0 to 25 ppm resulted in an almost instantaneous maximum visual response. The visual display remained unchanged when the PERC concentration was increased from 25 to 50 ppm. This rapid initial response to PERC and subsequent unchanged response to a larger concentration prevented the accurate demonstration of a detectors' ability to detect concentration gradients.

The experimental design used in this study was a probable source of error when evaluating concentration gradients. First, unlike test conditions, which changed from 0 to 25 to 50 ppm instantaneously, the PERC concentrations associated with dry cleaning machine leaks increase more continuously as the distance to the source decreases. Procedures that employ continuous increases in concentration would likely yield results that more accurately demonstrate the detectors' ability to recognize variations in PERC concentration.

Second, the detectors were not reset or allowed to auto-zero before switching to the higher concentration. Further analysis demonstrated that resetting at 25 ppm prior to switching to 50 ppm resulted in a gradual increase through visual and audio responses. This procedure is consistent with the way in which leak detectors are used in the field.

Although the detectors were unable to recognize a concentration gradient using these testing procedures, field testing at a local dry cleaner demonstrated the TIF ZX-1's ability to quickly locate a leak source. Using the Reset function several times, the ZX-1 identified the leak source, which was a rubber hose that connected the PERC storage tank to the machine.

Laboratory analysis of charcoal tube samples

The University of Washington's Environmental Health Laboratory analyzed 19 charcoal tubes, including field and lab blanks. The ID number, measured concentration, and date

of collection for each charcoal tube are presented in Table 8. The analytical results were not corrected for spike recovery efficiency, which was approximately 92%. However, the results were corrected for matrix blank values. Tube 3 was collected while the Dynacalibrator was in the Zero position. Tubes 16 and 19 were field blanks.

The laboratory's quality assurance parameters were: R^2 Calibration = 1.0000, Reporting Limit = 2 µg, Spike Recovery Efficiency = 92%.

Table 8. Target concentration, lab result, corrected PID result, identification, and collection date for charcoal tube samples				
Target (ppm)	Lab Result (ppm)	Corrected PID Ave. (ppm)	Tube ID	Date Collected
0	<0.08	0	3	2/12/2012
5	4.6	5.5	1	2/12/2012
5	3.8	5.5	5	2/12/2012
10	7.27	11.2	2	2/12/2012
10	8.13	11.2	6	2/12/2012
25	22.4	28.9	8	3/16/2012
25	21.8	28.9	11	3/16/2012
50	45.6	58	9	3/16/2012
50	44.5	58	12	3/16/2012
100	78	110	14	3/18/2012
100	67	110	17	3/18/2012
250	176	274	15	3/18/2012
250	170	274	18	3/18/2012
Field Blank	<0.08	NA	16	3/16/2012
Field Blank	<0.08	NA	19	3/16/2012
Lab Blank	Blank	NA	4	3/19/2012
Lab Blank	Blank	NA	7	3/19/2012
Lab Blank	Blank	NA	10	3/19/2012
Lab Blank	Blank	NA	13	3/19/2012

Phase II: Usability testing

Selection of detectors for usability testing

A critical review of the technical capabilities of the nine detectors evaluated in Phase I revealed that the response times and LODs for the following instruments were adequate: the INFINICON Tek-Mate, the TIF ZX, the TIF ZX-1, the TIF RX-1A, and the TIF XP-1A. However, the TIF ZX-1 was excluded from further evaluation because it was no longer available. The Tek-Mate was also excluded because it is not possible to manually reset the detector. Consequently, the following detectors were subjected to Phase II usability testing: the TIF ZX, the TIF RX-1A, and the TIF XP-1A. Images of these detectors are presented in Figure 10.



Figure 10. Detectors selected for usability testing

Timed trials

Upon observing subjects conducting the leak detection testing, it became clear that the detection times were heavily influenced by variables not associated with detector usability. Influences on detection time included the location at which the subjects began searching on the test apparatus and their direction of travel around the apparatus. Consequently, recording the time taken to find the leak source was discontinued after the seventh subject and the data are not reported.

Questionnaire

Subjects were asked to complete a questionnaire upon completion of the leak detection trials. Subject participation in the questionnaire was 100%. Because some subjects provided more than one answer to a question, the total number of responses occasionally exceeded the total number of study subjects.

Question 1: Do you have any prior experience with using hand-held real-time instruments, like vapor detectors?

Two-thirds of subjects indicated they had no prior experience using hand-held scientific instruments.

Question 2: If yes, describe experience.

One subject responded “PIDs” which was the only response to the question.

Question 3: Which felt the best to hold?

Sixty-three percent reported that the ZX felt the best to hold during testing. The RX-1A and XP-1A were similarly ranked with 19% and 13% respectively. One subject had no preference (see Table 9).

Table 9. Detector that felt the best to hold		
Detector	Number	Percent
RX-1A	3	19
ZX	10	63
XP-1A	2	13
No Preference	1	6
Total	16	100

Question 4: Was the light display helpful in finding the leaks?

Thirty-three percent of the respondents reported that the LED displays were very helpful, 40% suggested that the LED displays neither helped nor hindered detection, and one subject suggested that the LEDs were not helpful (see Table 10).

Table 10. Was the light display helpful?		
Response	Number	Percent
Very Helpful	5	33
	2	13
	6	40
	1	7
	1	7
Not Helpful	1	7
Total	15	100

Question 5: Which light display was the easiest to understand?

No preference between light displays was recorded by 38% of subjects. Of those with a preference, 31% suggested that LED display on the XP-1A was the easiest to understand (see Table 11).

Table 11. Detector with easiest light display to understand		
Detector	Number	Percent
RX-1A	2	13
ZX	3	19
XP-1A	5	31
No Preference	6	38
Total	16	100

Question 6: Were the sounds helpful in finding the leaks?

While one subject suggested that the audible alarms were not helpful, 73% reported that they were very helpful (see Table 12).

Table 12. Were instrument sounds helpful in finding the leak?		
Response	Number	Percent
Very Helpful	11	73
	1	7
	2	13
	0	0
Not Helpful	1	7
Total	15	100

Question 7: Which instrument had response sounds that were easiest to understand?

Six subjects had no preference. Those with a preference were evenly distributed between the RX-1A, ZX, and XP-1A with 30%, 40%, and 30% respectively (see Tables 13 and 14).

Table 13. Detector with easiest response sounds to understand		
Detector	Number	Percent
RX-1A	3	19
ZX	4	25
XP-1A	3	19
No Preference	6	38
Total	16	100

Table 14. Detector with easiest response sounds to understand (among those with a preference)		
Detector	Number	Percent
RX-1A	3	30
ZX	4	40
XP-1A	3	30
Total	10	100

Question 8: Which controls were the easiest to use?

Thirty-eight percent of subjects reported that the RX-1A had the easiest controls to use, followed closely by the XP-1A with 31% (see Table 15).

Table 15. Detector with easiest controls to use		
Detector	Number	Percent
RX-1A	6	38
ZX	3	19
XP-1A	5	31
No Preference	2	13
Total	16	100

Question 9: Which controls were the hardest to use?

Forty percent of respondents had no preference. Of those with a preference, two-thirds reported that the ZX's controls were the hardest to use (see Table 16).

Table 16. Detector with hardest controls to use		
Detector	Number	Percent
RX-1A	1	7
ZX	6	40
XP-1A	2	13
No Preference	6	40
Total	15	100

Question 10: Overall, which detector did you like the MOST?

The ZX was preferred by 41% of subjects, while 29% preferred the RX-1A and XP-1A respectively. Due to rounding the total percentage is not 100% (see Table 17).

Table 17. Detector that was liked the most		
Detector	Number	Percent
RX-1A	5	29
ZX	7	41
XP-1A	5	29
No Preference	0	0
Total	17	99

Question 11: Overall, which detector did you like the LEAST?

Forty percent liked the ZX the least, 33% liked the XP-1A the least, and 27% liked the RX-1A the least (see Table 18).

Table 18. Detector that was liked the least		
Detector	Number	Percent
RX-1A	4	27
ZX	6	40
XP-1A	5	33
No Preference	0	0
Total	15	100

Narrative responses on the questionnaire are summarized in Tables 19-22.

Table 19. Which instrument's controls were the easiest to use? (Q.8)	
Detector	Comments
ZX	"simple design"
RX-1A	"on/off in red/green easy to find"
	"easiest for casual user"
XP-1A	"color indicator for on/off as well as written cues (as opposed to just symbols)"
	"clearly labeled sensitivity buttons, clearly marked on/off switch though English Language required"
	"labeled, large font, uses words, not symbols, more buttons"

Table 20. Which instrument's controls were the hardest to use? (Q.9)	
Detector	Comments
ZX	"icons aren't meaningful"
	"Symbols had to be deciphered"
	"symbols only, need to read directions to figure out what they are for."
RX-1A	NO COMMENTS
XP-1A	"Too many options for someone to make a mistake"
	"more options"

Table 21. Overall, which detector did you like the MOST? (Q.10)	
Detector	Comments from Questionnaire
ZX	“Easy to use + understand”
	“feel in my hand’
	“Simple to use, Has good sensitivity”
	“comfort and ease of use”
	“Was the lightest &most comfortable, warm up time not an issue”
	“Ease of handling”
	“easy to hold”
RX-1A	“Easy to use + understand”
	“easy to pick up & use, effective”
	“controls”
	“simple design to follow directions”
	“The response sound was strong”
XP-1A	“ease of use, comfortable grip, has battery test button”
	“Clear sound response without annoying sounds”
	“after taking time to investigate the features further, I like the direct features of this one – I can understand the controls better in terms of how I can vary the sensitivity and sounds”
	“No warm up time. Easy to access + understand sensitivity Function. Good button feel. Battery tester is a good + useful feature”
	“light display- red (not ready) green- ready- orange/red-detect. Better balance than RX-1A”

Table 22. Overall, which detector did you like the LEAST? (Q.11)

Detector	Comments from Questionnaire
ZX	"Warm up time, was more challenging to determine warm up was over + it was ready to be used."
	"didn't seem to work well"
	"controls require more guessing and you can't figure out what responds to what and how I'm actually changing the settings."
	"symbols not really self-evident"
	"waiting time to activate it."
	"Warm up time, hard to understand button functions"
RX-1A	"too noisy"
	"Top heavy- Hard to hold. Light display is all red- thought was not ready, when it was, button labels a mix of symbols, colors and text. Text too small."
	"on/off switch slightly confusing"
	"needs a mute button"
XP-1A	"...but the lights + sound at beginning were a wee bit confusing."
	"more functions for someone to make a mistake. Although more information can be got from it."
	"The response sound was weak."
	"too many options for the average user"
	"Bulky to hold and the touch pad wasn't as clear as the others."

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DISCUSSION

The overall goal of this study was to inform the selection of leak detectors that would enable dry cleaning businesses to comply with local, state, and federal requirements. The specific aims were to characterize the technical capabilities and usability of vapor leak detectors.

Technical capabilities

Of all the variables tested, only response time testing resulted in a clear ranking of detectors. The detector with the fastest response time was the TIF ZX, with a mean of 0.5 seconds. The predecessor to the ZX, the ZX-1, had a mean response time of 0.6 seconds.

LOD testing resulted in a tie between five detectors. All five of these instruments were capable of detecting PERC at concentrations beyond the capability of the PID.

Overall, three detectors manufactured by TIF Instruments, Inc. were determined to warrant further testing for usability: the ZX, RX-1A, and the XP-1A.

Usability

All the tested detectors could locate a leak source on the testing apparatus. The time needed to find a leak was heavily influenced by a subject's starting point in relation to where the leak was located, and method of searching the apparatus with the probe.

Questionnaire responses indicated that the detector with the most buttons was considered by some to be too complicated. Symbols on the controls instead of words led to confusion for subjects unfamiliar with international symbols. Audible response was considered more helpful when finding a leak than the visual response. However, several subjects mentioned that having a volume control, rather than just a mute button, would be preferable.

The ZX received the most positive and negative comments of the three tested detectors. Subjects liked how it felt to hold and its speed, but disliked the 20 second warm-up period and the symbols rather than words on the controls. Overall, the ZX was both the most- and least- liked detector.

Limitations of the study

Although this study provided valuable insights into the technical capabilities and usability of readily available leak detectors, the following limitations should be considered when evaluating the results.

Number of response time data points per concentration

Three response time measurements were recorded at every PERC concentration that elicited a response from a detector. Because the most sensitive detectors responded to

every tested PERC concentration, their average response times were based on 30 measurements. However, because the least sensitive detector elicited a response at only one concentration, only three measurements were used to calculate the response time. Consequently, a more accurate determination of response time could have been achieved by increasing the number of measurements recorded at each concentration, particularly for the less sensitive instruments.

Relative humidity requirements

The effect of humidity on detector response was considered to be an important parameter at the outset of the study. The original intent was to introduce water vapor to the exhaust stream, downstream of the 4-way valve. However, maintaining a constant RH throughout the various procedures was deemed impractical. For example, when the Dynacalibrator setting changed between Zero, Span1, and Span2, the flow rate of the RH system would require adjustment to maintain a constant RH.

Additionally, because the PID and several detectors respond to water vapor, this response could confound evaluation of their sensitivity to PERC.

Limit of Detection measurement accuracy

Testing the detectors at incremental PERC concentrations failed to consider other possible concentrations that lie between those increments. For example, if a detector responded at 100 ppm, but not at 50 ppm, it can only be stated that the true LOD exists somewhere between those concentrations.

A more accurate LOD could have been identified for each detector if the concentration had been adjusted continuously until there was no longer a response.

Lower limit of Photoionization Detector above the Limit of Detection of the most sensitive detectors

The LOD of the PID was higher than that of several detectors. Consequently, the true LOD of the most sensitive detectors was determined to be less than 0.2 ppm PERC. However, this concentration is considerably lower than any occupational exposure limits.

Discrepancy between PID and charcoal tube concentrations

The concentrations of PERC detected in the charcoal tube samples were lower than the expected concentrations measured with the PID. The PERC concentrations for each charcoal tube and the average of PID readings taken before and after sampling are presented in Figure 11.

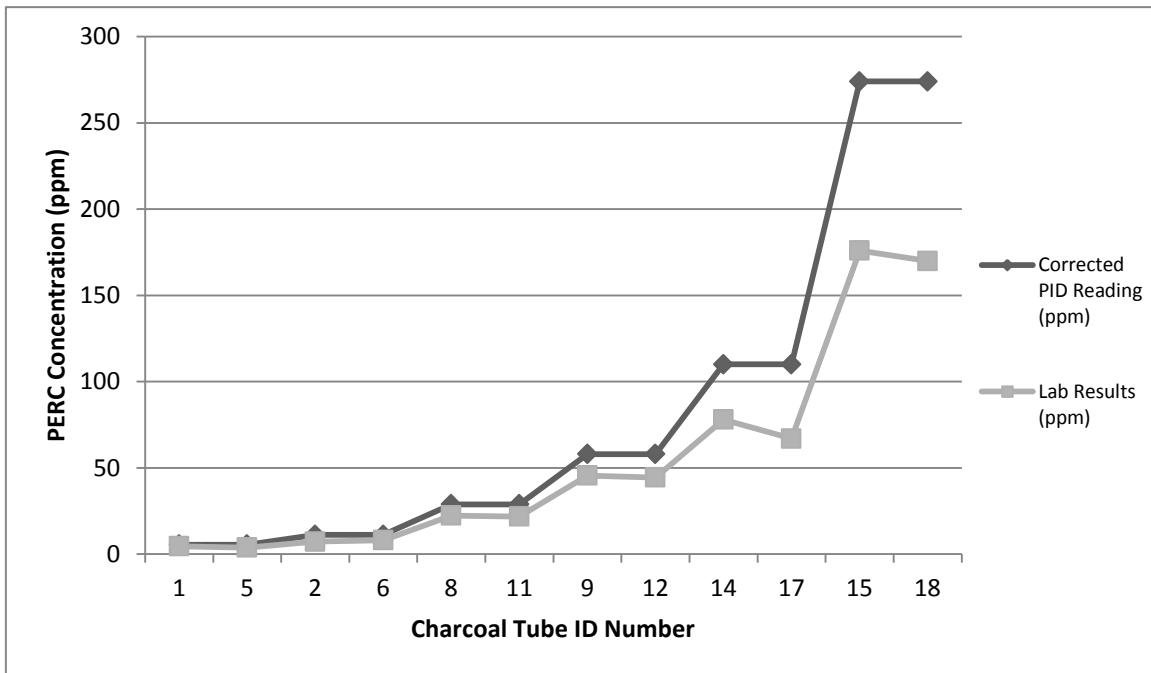


Figure 11. PERC concentration measured by charcoal tubes and PID

The matched PID and charcoal tube measurements at each test concentration are presented in Figure 12. The PID measurements with the 0.57 correction factor applied are highly correlated with the concentrations reported by charcoal tube analysis ($r = 0.998$, $p < 0.001$).

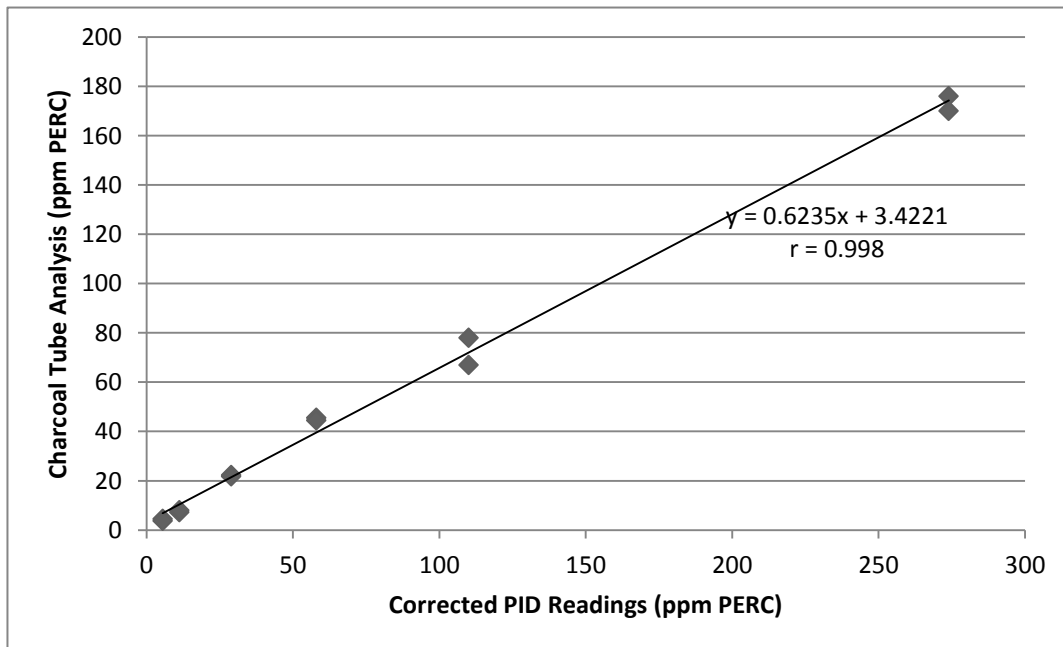


Figure 12. Relationship between matched PID and charcoal tube concentrations

The 0.62 slope of the regression line in Figure 10 does not agree with the 0.57 response factor used to correct the PID readings. The linearity of the calibration curve for the 0.57

response factor could not be acquired, but may influence the relationship between the two factors.

Results from charcoal tube sampling may have been influenced the configuration of funnel #2. Air could have been pulled into the funnel opening when the exhaust stream flow rate was low. This would be more likely to occur at high PERC concentrations due to low flow rate requirements of the dilution stream. A funnel cap over the open end, which includes a port for a charcoal tube and a long section of tube as an exhaust, would help prevent outside air from diluting the sample.

Other contributing factors to the measurement differences could reflect issues with the charcoal tube analysis. For example, solvent desorption of PERC from the activated charcoal may not necessarily have been 100%, and the laboratory has an extraction efficiency of 92%.

Gradient testing

The results from gradient testing did not accurately demonstrate a detector's ability to detect concentration gradients. During normal operation, a user typically resets the detector several times in order to detect higher concentrations and find a leak. However, test procedures did not include reset or auto-zero steps. To replicate this operation, the procedures should include a manual reset at the lower concentration before switching to the higher concentration. Post-experiment practice tests demonstrated using the manual reset caused a detector's visual response to travel through green, orange, and red LEDs. Without a reset or auto-zero, a detector would instantly produce a full red LED display when exposed to the first concentration.

Effects on average response time

Plotting the average response time for detectors at each test concentration indicated that further analysis of the data was needed. The average response times for detectors that responded at each concentration is presented in Figure 13. Initially a one-way ANOVA was performed for each detector to determine whether there were significant differences in response time across concentrations. All detectors except the BOLO GRN and Snap-on had results showing that response times recorded at one or more concentration differed significantly from response times recorded for at least one other concentration.

As shown in Figure 13, response time appears to vary at different concentrations and by detector. The lack of parallel lines indicates the possibility of an interaction effect. A two-way ANOVA with replication was performed to test for the significance of an effect of concentration on response time, significance of an effect of the detector on response time, and significance of an interaction between concentration and detector. Results from the two-way ANOVA are presented in Appendix C.

The two-way ANOVA revealed significant main effects for RT pertaining to the concentration ($F_{9, 100}=17.9$, $p=2.4 \times 10^{-17}$), detector ($F_{4, 100}=74.4$, $p=4 \times 10^{-29}$), and interaction effects ($F_{36, 100}=4.2$, $p=9.16 \times 10^{-9}$).

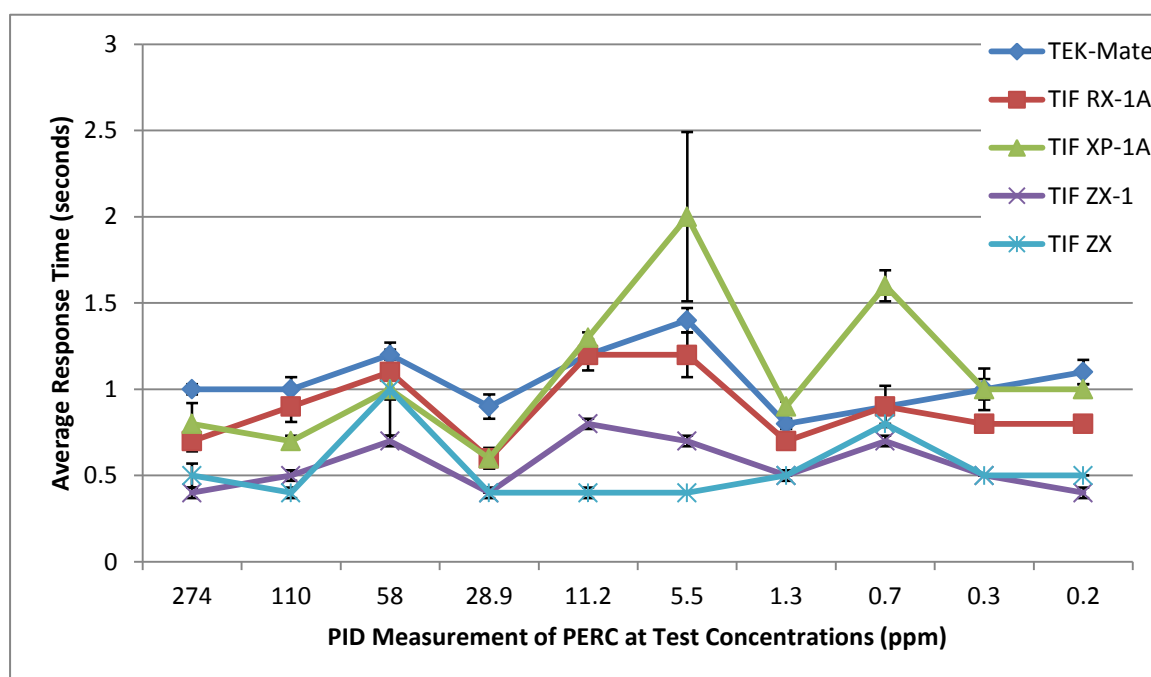


Figure 13. Average response time with standard errors of the mean at each concentration

The detectors included in Figure 11 use analog-to-digital converters to convert analog input from the probe into digital values that can be read by a microprocessor. Part of the conversion process involves dividing analog voltage or current into smaller ranges. This process may contribute to the peaks in response time seen at specific concentrations. Peaks in response time at around 50, 5, and 0.5 ppm are roughly a factor of ten apart, which could be an artifact of input division during analog to digital conversion.

Human error while operating the stopwatch could also influence the measured detector response time. Simultaneously turning the 4-way valve and starting the stopwatch, then stopping the stopwatch when a detector responded provided several opportunities for the introduction of error. Human reaction time is approximately 0.2 seconds, which is approximately half of the fastest detector's response time.

Other potentially suitable leak detectors not evaluated

As described previously, instruments were selected for evaluation based on information provided by other programs, conversations with study authors, and reviewing product catalogs. It is possible that we failed to identify detectors at the outset of this study that may have performed at least as well as the three TIF instruments that underwent usability evaluation.

Usability testing not conducted with dry cleaners

Usability testing was originally to be performed by attendees of a dry cleaning association meeting. This approach would have provided valuable insights into the opinions of the target population. However, difficulties in scheduling forced a change in participants.

Subjects included in Phase II testing were recruited from several state, county, and local agencies. One-third of participants reported having prior experience with hand-held real-time instruments. However, this proportion of these subjects with prior experience is likely higher than the population of dry cleaning workers.

Usability testing apparatus not representative of real dry cleaning machines

The testing apparatus used for the usability testing was suitable for observing how subjects use a detector and identifying individual preferences. However, a Korean equipment supplier suggested that this test would not likely convince Korean dry cleaners that a leak could be found on an actual dry cleaning machine. This individual suggested that the instrument should be demonstrated on an active dry cleaning machine.

Difficulties associated with this approach include scheduling visits during business hours, identifying a dry cleaning machine that is leaking PERC during a site visit, overcoming potential language barriers, and possible apprehension of inviting a government agency into a business.

Conclusions

Despite the study limitations described above, we conclude that the three detectors manufactured by TIF Instruments, Inc. (RX-1A, ZX, and XP-1A) appear to be good candidates for adoption by the dry cleaning industry, although other instruments with the following characteristics would also likely be suitable:

- Limit of detection for PERC of ≤ 1 ppm,
- Response time of ≤ 2 seconds
- An internal pump to draw air over the sensor,
- A manual reset button to allow identification of relatively high PERC concentrations,
- A long flexible probe to reach obscured components of dry cleaning machines,
- A handle designed for a comfortable grip,
- A speaker for audible response, positioned where it cannot be obstructed by hands or fingers, and
- Visual display of relative concentration, with the option to mute the audible response.

Manufacturers should provide user manuals in appropriate languages, including Korean. Manufacturers could also provide stickers or decals in appropriate languages, which could be placed on the appropriate buttons.

Future opportunities

LHWMP enjoys excellent working relationships with local dry cleaning business associations, and vendors to the industry, in addition to many individual dry cleaning business owners. Consequently, the next stage of this project will be to demonstrate the use of these leak detectors in a variety of venues, ranging from individual shops to business association meetings. LHWMP can also help offset the cost of these detectors by either issuing grants to cover the entire purchase price or vouchers to cover 50 percent of the cost. This strategy has recently been welcomed by members of the local Korean Dry Cleaners Association. The opportunity to partner with the dry cleaning community in this way will help LHWMP better communicate and provide service to this typically underserved community. Providing hands-on, personal assistance in cooperation with credible industry members will likely increase the awareness, acceptance, and use of hand-held leak detectors.

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APPENDIX A

USABILITY QUESTIONNAIRE

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Leak Detector Usability Questionnaire

Subject #: _____



RX-1A



ZX



XP-1A

Do you have any prior experience with using hand-held real-time instruments, like vapor detectors?

____ Yes

____ No

If "yes", please describe your experience:

Which felt the best to hold? (Circle one)

RX-1A

ZX

XP-1A

No Preference

Was the light display helpful in finding the leaks? (Pick one)

Very Helpful						Not Helpful at All
	1	2	3	4	5	

Which light display was the easiest to understand? (Circle one)

RX-1A ZX XP-1A No Preference

Were the sounds helpful in finding the leaks? (Pick one)

Very Helpful						Not Helpful at All
	1	2	3	4	5	

Which had response sounds that were easiest to understand? (Circle one)

RX-1A ZX XP-1A No Preference

Which controls were the easiest to use? (Circle one) Why?

RX-1A ZX XP-1A No Preference

Which controls were the hardest to use? (Circle one) Why?

RX-1A ZX XP-1A No Preference

Overall, which detector did you like the MOST?

Circle One	What did you like about it?
RX-1A	
ZX	
XP-1A	

Overall, which detector did you like the LEAST?

Circle One

What did you NOT like about it?

RX-1A	
ZX	
XP-1A	

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APPENDIX B

DETECTOR RESPONSE TIMES

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Reading Number	TEK-Mate	TIF RX-1A	TIF XP-1A	TIF ZX-1	TIF ZX	TIF XL-1A	Snap-On	BOLO GRN	Aeroqual
1	0.9	0.8	1.0	0.4	0.4	0.7	3.1	10.0	14.7
2	1.0	0.6	0.6	0.5	0.6	1.1	2.1	9.6	12.8
3	1.0	0.7	0.9	0.4	0.6	1.0	2.3	12.8	13.5
4	0.9	0.7	0.7	0.4	0.4	1.3	2.5	8.6	
5	1.1	1.0	0.8	0.5	0.5	1.5	2.8	14.9	
6	1.1	0.9	0.7	0.5	0.4	1.5	3.1	13.3	
7	1.1	1.1	1.0	0.8	0.6	1.3	2.4		
8	1.2	1.2	0.9	0.7	0.8	1.3	3.8		
9	1.2	1.1	1.1	0.7	1.5	1.5	2.8		
10	1.0	0.6	0.6	0.5	0.4	0.8			
11	0.8	0.7	0.6	0.4	0.4	0.8			
12	1.0	0.5	0.7	0.4	0.4	0.8			
13	1.2	1.2	1.3	0.7	0.5	1.5			
14	1.2	1.1	1.2	0.8	0.4	2.1			
15	1.2	1.4	1.3	0.8	0.4	2.0			
16	1.5	1.1	2.9	0.6	0.4	4.2			
17	1.5	1.1	1.2	0.7	0.4	2.4			
18	1.3	1.5	1.9	0.7	0.4	2.7			
19	0.8	0.7	1.0	0.5	0.4	1.9			
20	0.7	0.8	0.9	0.5	0.5	2.6			
21	0.8	0.7	0.9	0.5	0.5	1.5			
22	1.1	1.0	1.8	0.7	0.8				
23	0.7	0.9	1.5	0.7	0.8				
24	0.8	0.9	1.6	0.8	0.8				
25	1.2	0.8	1.1	0.5	0.5				
26	0.8	0.8	1.0	0.5	0.5				
27	0.9	0.7	0.9	0.5	0.5				
28	1.2	0.8	1.1	0.5	0.5				
29	1.0	0.8	1.0	0.4	0.5				
30	1.0	0.7	1.0	0.4	0.5				

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APPENDIX C

TWO-WAY ANALYSIS OF VARIANCE (ANOVA)

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Anova: Two-Factor With Replication						
SUMMARY	TEK-Mate	TIF RX-1A	TIF XP-1A	TIF ZX-1	TIF ZX	Total
C6						
Count	3	3	3	3	3	15
Sum	2.9	2.1	2.5	1.3	1.6	10.4
Average	1.0	0.7	0.8	0.4	0.5	0.7
Variance	0.00333	0.01000	0.04333	0.00333	0.01333	0.051

C5						
Count	3	3	3	3	3	15
Sum	3.1	2.6	2.2	1.4	1.3	10.6
Average	1.0	0.9	0.7	0.5	0.4	0.7
Variance	0.01333	0.02333	0.00333	0.00333	0.00333	0.064

C4						
Count	3	3	3	3	3	15
Sum	3.5	3.4	3	2.2	2.9	15
Average	1.2	1.1	1.0	0.7	1.0	1.0
Variance	0.00333	0.00333	0.01000	0.00333	0.22333	0.060

C3						
Count	3	3	3	3	3	15
Sum	2.8	1.8	1.9	1.3	1.2	9
Average	0.9	0.6	0.6	0.4	0.4	0.6
Variance	0.01333	0.01000	0.00333	0.00333	0.00000	0.043

C2						
Count	3	3	3	3	3	15
Sum	3.6	3.7	3.8	2.3	1.3	14.7
Average	1.2	1.2	1.3	0.8	0.4	1.0
Variance	0.00000	0.02333	0.00333	0.00333	0.00333	0.120

C1						
Count	3	3	3	3	3	15
Sum	4.3	3.7	6	2	1.2	17.2
Average	1.4	1.2	2.0	0.7	0.4	1.1
Variance	0.01333	0.05333	0.73000	0.00333	0.00000	0.458

<i>C1.0</i>						
Count	3	3	3	3	3	15
Sum	2.3	2.2	2.8	1.5	1.4	10.2
Average	0.8	0.7	0.9	0.5	0.5	0.7
Variance	0.00333	0.00333	0.00333	0.00000	0.00333	0.035

<i>C.5</i>						
Count	3	3	3	3	3	15
Sum	2.6	2.8	4.9	2.2	2.4	14.9
Average	0.9	0.9	1.6	0.7	0.8	1.0
Variance	0.04333	0.00333	0.02333	0.00333	0.00000	0.125

<i>C.3</i>						
Count	3	3	3	3	3	15
Sum	2.9	2.3	3	1.5	1.5	11.2
Average	1.0	0.8	1.0	0.5	0.5	0.7
Variance	0.04333	0.00333	0.01000	0.00000	0.00000	0.058

<i>C.15</i>						
Count	3	3	3	3	3	15
Sum	3.2	2.3	3.1	1.3	1.5	11.4
Average	1.1	0.8	1.0	0.4	0.5	0.8
Variance	0.01333	0.00333	0.00333	0.00333	0.00000	0.077

<i>Total</i>						
Count	30	30	30	30	30	
Sum	31.2	26.9	33.2	17	16.3	
Average	1.0	0.9	1.1	0.6	0.5	
Variance	0.04386	0.05826	0.22271	0.02023	0.05013	

ANOVA						
<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Concentrations	4.492267	9	0.499141	17.91175	2.42E-17	1.974829
Between Detectors	8.298267	4	2.074567	74.44617	4E-29	2.462615
Interaction	4.181733	36	0.116159	4.168394	9.16E-09	1.535138
Within	2.786667	100	0.027867			
Total	19.75893	149				

The ANOVA revealed significant main effects for RT pertaining to the concentration ($F_{9,100}=17.9$, $p=2.4 \times 10^{-17}$), detector ($F_{4,100}=74.4$, $p=4 \times 10^{-29}$), and interaction effects ($F_{36,100}=4.2$, $p=9.16 \times 10^{-9}$).