Perchloroethylene Leak Detection: Evaluating technical capabilities and usability of vapor leak detectors

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List of Tables

List of Figures

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Introduction

Dry cleaning is the process of cleaning fabrics using an organic solvent rather than water. Some precursors to today's most common dry cleaning solvent, perchloroethylene (PERC), 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 smell. PERC is also an important chemical intermediate or starting material for the creation of other chemicals. Widely used as a metal-degreaser, PERC can also be found in many household products, including water repellants, silicone lubricants, fabric finishers, and brake cleaner.[2] PERC goes by many names, including perchloroethylene, tetrachloroethylene, PCE, tetrachloroethene, perclene, perchlor, or the Chemical Abstracts Service number 127-18-4.[2]

Local Hazardous Waste Management Program in King County

The Local Hazardous Waste Management Program in King County was formed in 1991 in an effort to help reduce the threat posed by hazardous materials, including their production, use, storage, and disposal. LHWMP is a multi-jurisdictional program focusing on the reduction of hazardous waste exposures to the public and environmental.

Figure 1: LHWMP program partners

Figure 1 shows several programs that partner with LHWMP to reduce hazardous waste.

LHWMP operates a voucher incentive program, in which funding is offered to businesses that seek to better manage, dispose of, reduce, or recycle waste. To qualify for the incentive a business must 1) have a license and be located in King County, and 2) be a small quantity generator of hazardous waste. Qualifying businesses are eligible for 50% matching funds of up to $500 for every dollar spent on hazardous materials management and reduction.[3] For example, purchasing a leak detector or switching to alternative solvents qualifies as money spent to reduce and manage hazardous materials.

Perchloroethylene as a Cleaning Solvent

Michael Faraday first synthesized PERC in 1821 but it would not be until the 1940s that it would become the predominant dry cleaning solvent in the United States. PERC was seen as 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. When exposed to sufficient heat, typically not found in dry cleaners however, PERC decomposes into several hazardous gases, such as phosgene and hydrogen chloride.[4]

PERC is highly lipophilic and able to readily break down grease, fat, oil, and wax without causing damage to fabrics. The Kauri Butanol (KB) number is an estimate of a solvent’s degreasing or cleaning ability. A high KB value indicates a stronger cleaning ability than that of a low KB value. Generally, larger KB values are more efficient at removing stains, but may cause damage to delicate garments.[5] Table 1 shows KB values and a cleaning performance summary of dry cleaning solvents including PERC.

Table 1. KB values and cleaning summaries of dry cleaning solvents[5]

Solvent	KB Value	Cleaning Performance
PERC	92	Oil-based stains, most water-based stains, silks, wools, rayons. Not good for delicates.
Stoddard Solvent	32-39	Less aggressive than PERC for oil-based stains. Can handle delicate garments.
Pure Dry	37-40	Less aggressive than PERC for oil-based stains. Can handle delicate garments.
Shell 140	N/A	Less aggressive than PERC for oil-based stains. Can handle delicate garments.
EcoSolv	26-27	Less aggressive than PERC for oil-based stains. Can handle delicate garments.
DF-2000	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 delicates. Not good for heavily soiled garments.
Rynex 3	70	Aggressive, cleans water-soluble and oil-based stains.
GreenEarth	<20	Less aggressive than PERC for oil-based stains. Good for water-based stains, delicates.
CO_2	<10	Good for all stains and most fabrics. Very effective in removing oils, greases, sweats.
Wet Cleaning	N/A	Aggressive, good for both oil and water-based stains. Can handle delicate garments.

PERC is also highly stable, which enables it to be filtered, distilled, and re-used. Low solubility in water allows for a faster separation of moisture from the solvent in a dry cleaning machine’s water separator.[6] 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 pretreating with a spot cleaner, washing, solvent extraction, drying, and finishing treatments including pressing or ironing.

Initial spot treatment is done by hand with a variety of available chemicals. Depending on the type of chemical used, spot treatment can be responsible for the presence of chlorinated hydrocarbons in the waste streams of businesses that do not use PERC as their primary solvent.

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

The drying step currently takes place in the same machine as washing. This “dry-to-dry” technology reduces occupational exposure to PERC when 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 PERC machines are referred to as “generations”. Each generation incorporates attributes the previous did not in an attempt to lower the amount of PERC lost during operation. The 5th Generation PERC machines are the most technologically advanced and allow the least amount of PERC to escape. Table 2 provides a summary of the different generations and the advances that separate them.

Table 2. Summary of PERC 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

For a more detailed explanation of different solvents and the processes they entail, please refer to the California Environmental Protection Agency Air Resources Board's technical assessment of the California dry cleaning industry.[5]

Machine components, such as gaskets and hoses, can become sources of PERC release towards the end of their lifespan. PERC release can expose workers and communities to hazardous levels of PERC, and can 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 Authority (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 exposure.

According to a 2011 EPA estimate, there were approximately 28,000 dry cleaners in the U.S. that used PERC.[7] The industry is gradually transitioning away from PERC to less toxic solvents. This has also contributed to lowering occupational exposures and environmental releases.[8]

However, upgrading technologies can be cost prohibitive, and there is a generally accepted belief in the industry that “nothing cleans like PERC”.

Exposure Routes

Inhalation

Inhalation of vapor is the major exposure route of PERC. Because PERC is readily volatilized at standard temperature and pressure, any leak, spill, or open container can contribute to potential exposure.

In the dry cleaning industry, inhalation can occur during normal operating procedures as well as during machine maintenance, filter changing, cleaning of still bottoms, and spot treatments. Some of the newer machines have mechanisms in place that can engineer out some causes of inhalation exposures. Vapor condensers, for example, remove PERC from the machine air before it is discharged. The most recent machines have doors that will remain locked until the PERC concentration in the machine falls below a threshold level.

Inhalation 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 can vary a great deal depending on the generation of machine as well as the type of fabric cleaned. A NIOSH study showed that two identical swatches of fabric emitted 31.8 and 1.34 mg PERC/kg cloth when cleaned in a refrigerated dry-to-dry machine and a 5th generation machine, respectively.[8]

Fabric type has also been shown to influence the amount of PERC retained in identically sized swatches. After six cycles through a dry cleaning machine wool retained nearly four times the PERC as cotton and twice as much as polyester.[10]

Dermal Contact

Unprotected skin that contacts PERC is another route of exposure. PERC is not rapidly absorbed through dermal contact, although it can be measured in exhaled breath after prolonged skin contact.[11] Maintenance operations such as cleaning lint and button traps, changing solvent filters, and disposal of hazardous waste are potential sources of skin contact. Without the use of proper personal protection equipment (PPE), a worker's skin could be in direct contact with the solvent and therefore at risk for harmful health effects. Health effects due to dermal contact are described in another section. However according to an ATSDR report, circumstances in which PERC is trapped against the skin, little will actually cross into the body.[2]

Ingestion

Ingestion is not typically considered 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] Studies have also shown that PERC can cross the placental membrane and may 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 certain types of deli meats and mayonnaise. One study looking at ambient concentrations of PERC found levels in margarine of up to 50 mg/kg in a business located next to a PERC dry cleaner.[13]

Health Effects

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] Eliminating PERC from adipose tissue is difficult and slow due its stability, high adipose/blood partition coefficient, and the low blood delivery to the 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] PERC has also been shown to adversely affect the liver and kidneys.[13]

Respiratory System

PERC causes irritation of the upper respiratory tract as well as mucous membranes. A survey of dry cleaning workers showed 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] However, the PERC toxicity studies conducted in experimental animals are difficult to extrapolate to humans due to uncertainties involving inter-species, and gender differences in metabolism.[17]

Skin

PERC is an effective degreasing agent and will remove 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.[18]

Reproductive systems

A study of pregnancy outcomes among 419 dry cleaning workers suggested that PERC exposure was associated with spontaneous abortion as well as certain developmental abnormalities.[14,19] Ingesting water contaminated with PERC at Camp Lejeune in North Carolina showed an association between PERC exposure and lower mean birth weight.[12] However, the risk estimates from the available studies are thought to be inaccurate due to small sample sizes. Therefore the association between PERC and reproductive concerns is limited and results are inconclusive.[15]

Carcinogenicity

EPA guidelines for carcinogen risk assessment indicate that PERC is likely to be carcinogenic in humans by all routes of exposure. Epidemiologic studies show a pattern of PERC exposure associated with several types of cancer, including bladder cancer, non-Hodgkin lymphoma and multiple myeloma.[15]

Before the EPA finalized the document, *Toxicological Review of Tetrachloroethylene (Perchloroethylene)(CAS No. 127-18-4) in Support of Summary Information on the Integrated Risk Information System (IRIS)*, it requested the National Research Council (NRC) of the National Academies of Science to conduct an independent assessment. The NRC created a committee to conduct a scientific review including an evaluation of the adequacy of the assessment, data, and methods of supporting the derivation of cancer risk. The committee agreed with the EPA position that PERC is likely to be carcinogenic in humans due to the weight of evidence of bioassays and less from epidemiological evidence.[20]

PERC is classified by the International Agency for Research on Cancer (IARC) as a Group 2A carcinogen.[13] A Group 2A classification indicates that it 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.[21]

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.[22] Animal studies have shown PERC to cause cancer but at concentrations and exposure routes not likely to be encountered by humans.

Because PERC is known to cause cancer in animals and is likely a human carcinogen, minimizing exposure is of great importance.

PERC in the Environment

As a result of its volatility, much of the PERC lost due to leaks, spills, and other uncontrolled releases escapes into the atmosphere. Uncontained liquid PERC can also travel through concrete floors, into the soil, and can eventually contaminate ground and surface water.[2]

Because PERC does not bind well 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 as well as foods having high fat content.[23]

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.[24] 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] Commonly found in Superfund sites across the U.S., PERC was found in at least 771 of the 1,430 National Priority List (NPL) sites identified by the EPA.[2] (The NPL is a list of national priorities among the known or threatened releases of hazardous substances, pollutants, or contaminants. The NPL is used to guide the EPA in determining which sites warrant further investigation.)

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 33rd on the 2011 Substance Priority List.[25]

A 2011 review of the State Cleanup Sites database managed by Washington State Department of Ecology showed that approximately 50 current and former dry cleaning sites were under investigation for environmental contamination concerns in King County.[26]

Regulatory and Advisory Limits

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 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.[27] In 1988, OSHA attempted to decrease the 8-hr TWA for PERC to 25 ppm, but was ultimately unsuccessful. In January 1989 the Final Rule on Air

Contaminants Project was remanded by the U.S. Circuit Court of Appeals leaving the 8-hr TWA at 100 ppm.[28]

The National Institute for Occupational Safety and Health (NIOSH) is responsible for conducting research and making recommendations for the prevention of work-related injury and illness.[29] NIOSH has no recommended exposure limit (REL) for PERC, but does recommend minimizing workplace exposures due to PERC's carcinogenic potential.[4] 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.[4]

The American Conference of Governmental Industrial Hygienists (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 has recommended an 8-hour TWA of 25 ppm and a short duration exposure limit (STEL) of 100 ppm for PERC.[22]

The Division of Occupational Safety and Health (DOSH) within the Department of Labor and Industries 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]

Like federal OSHA regulations, 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. 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. Hazardous waste regulations depend on the monthly amount of hazardous waste either generated or stored on-site. 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 water at 0.005 mg/L or 5 parts per billion (ppb).[33]

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 EPA and PSCAA regulations. Currently the PSCAA requires PERC dry cleaners provide notification before beginning operations, but does not issue permits or enforce the regulations.

Leak Detection Rules

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. It states:

> *The owner or operator of a dry cleaning system shall inspect the system weekly for perceptible leaks while the dry cleaning system is operating. Inspection with a halogenated hydrocarbon detector or PCE gas analyzer also fulfills the requirement for inspection for perceptible leaks. The following components shall be inspected:*

(1) Hose and pipe connections, fittings, couplings, and valves;
(2) Door gaskets and seatings;
(3) Filter gaskets and seatings;
(4) Pumps;
(5) Solvent tanks and containers;
(6) Water separators;
(7) Muck cookers;
(8) Stills;
(9) Exhaust dampers;
(10) Diverter valves; and
(11) All Filter housings

40 CFR Part 63 Subpart M defines a halogenated hydrocarbon detector as "…a portable device capable of detecting vapor concentrations of PCE of 25 parts per million by volume and indicating a concentration of 25 parts per million by volume or greater by emitting an audible or visual signal that varies as the concentration changes."[35]

Sources of Detector Information

Many different agencies provide information regarding who needs to check for leaks and how often. However, there is little information available that goes beyond that. Many sources repeat the same basic information, which does very little to help the decision-making process when looking to purchase a leak detector. The basic information many agencies present typically includes a product picture, the manufacturer, model number, and sensitivity ratings primarily in ounces per year. The entities providing the information generally state that the detectors are only expected to meet guidelines, that it is not an extensive list, that they do not endorse any of the products, and that further research is recommended to find the best leak detector.

The California Air Resources Board (CARB) released a technical assessment of the overall dry cleaning industry in California. The report included detailed analysis of dry cleaning technologies, emission control and ventilation technologies, dry cleaning survey results, health and environmental impacts, efficacy evaluations, and cost estimations.

In the report CARB also conducted an evaluation of ten leak detectors and photoionization detectors (PIDs). In one phase of their evaluation, detectors were tested under laboratory conditions to determine the detection accuracy and response time to PERC standards.[5] Testing was geared towards the quantitation of concentrations and stability of measurements due to specific concentration-based compliance rules. The Airborne Toxic Control Measure for Emissions of Perc from Dry Cleaning Operations only requires a facility to fix leaks greater than 50 ppm.[5] Response times were reported in ranges rather than individual measurements. Consequently, the designation of leak detector suitability does not necessarily provide information that is applicable outside of the CARB jurisdiction. In addition, the analysis was conducted in 2005 and since then several of the detectors have been replaced by newer models. This limits the availability of information available to the current dry cleaning industry.

The Oregon Department of Environmental Quality's Small Business Assistance Program helps dry cleaners become compliant with its enhanced leak detection and repair program (OR DEQ). Grant money from the EPA was used in part to distribute TIF XP-1A leak detectors to dry cleaners who participated in workshops or training sessions.[36] 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 its performance. Reasons why this manufacturer and model of leak detector was chosen were not presented on the webpage.

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.[37] 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.[37]

The Air Pollution Control Division of the Colorado Department of Public Health and Environment provides dry cleaning specific information on its website. The document titled "New Requirements for Leak Detectors and Monitoring Equipment for Perchloroethylene Drycleaning Facilities in Colorado" 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.[38]

Current Study

A recent survey by LHWMP provided valuable insight into the local dry cleaning industry. Surveys were sent to dry cleaning businesses throughout King County. Results of the survey showed that 26 percent of the respondents were owner-operated and had no employees. Eightyfour percent of all respondents self-identified as Korean. Sixty-nine percent of all respondents reported using PERC in their primary dry cleaning machine, and sixty-nine percent of all respondents did not own and use a PERC leak detector.[39]

This current research was conducted in an effort to increase the number of King County dry cleaning facilities that own and regularly use vapor leak detectors. As described above, there is a general lack of readily available, easy to understand information regarding the purchase and use of leak detectors. Without technical guidance, money could easily be spent on detectors which may not be able to meet the needs of the industry.

In order to help facilitate an informed decision on how to wisely spend LHWMP's financial incentive funds, several readily available leak detectors were evaluated using criteria deemed useful to the dry cleaning industry.

Specific aims

- Characterize the technical capabilities of vapor leak detectors.
    - Determine the response time of each leak detector.
    - Determine the lower limit of detection of each leak detector.
- Characterize the usability of selected vapor leak detectors.
    - Are leak sources able to be found?
    - Which detector is the easiest to operate?
- Provide specific recommendation(s) for which of the tested detectors to purchase.
    - Which leak detector(s) will be the best use of voucher incentive money?

Materials and Methods

Eight readily available leak detectors were chosen for inclusion in the testing procedures:

- Kanomax AeroQual Series 200
- Nova Systems BOLO GRN
- Snap-On ACT760A
- Inficon TEK-Mate
- TIF RX-1A
- TIF XL-1A
- TIF XP-1A
- TIF ZX-1

We subsequently learned that TIF had discontinued production of the ZX-1 in favor of the ZX model. Once a ZX model was received, it was included in the remaining procedures, along with the ZX-1. Prior to testing, we determined that the BOLO GRN was malfunctioning and was returned to the manufacturer for repair. A replacement BOLO GRN detector was delivered shortly after the rest of the detectors had completed the first day of testing.

Leak detectors are designed to alert the user when certain chemicals are detected in the atmosphere. Unlike other instruments, such as photo- or flame ionization detectors, leak detectors do not indicate concentrations of a chemical in the atmosphere. Leak detectors indicate only whether or not a chemical is present, which allows the operator to locate the source of the chemical release.

The evaluation of the detectors was conducted in two phases. Phase I involved laboratory testing to determine technical capabilities of each detector. Phase II included hands-on usability testing outside of the laboratory.

Phase I: Materials to Test Technical Capabilities

Several concentrations of PERC vapor were needed to test the technical capabilities of the leak detectors. Figure 2 shows the general layout of the components used in Phase I.

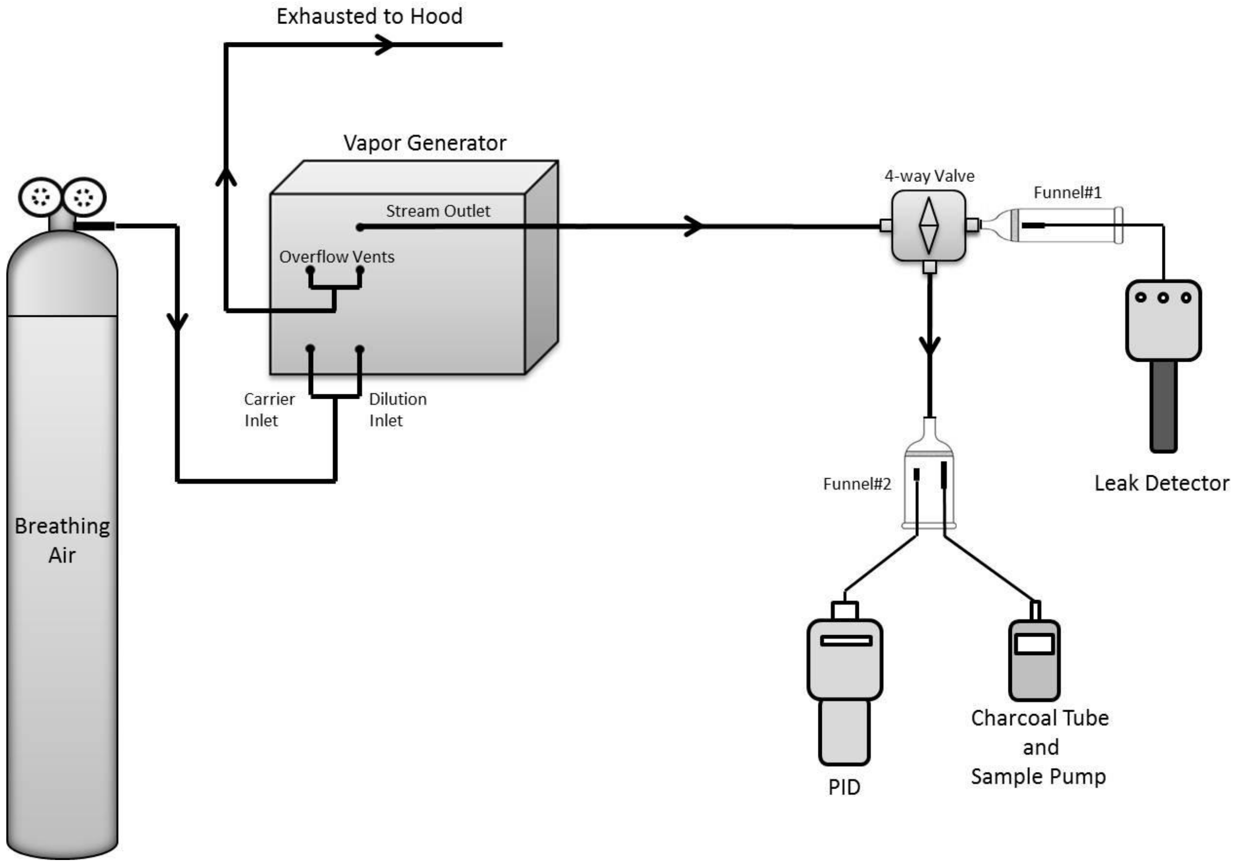

Figure 2: PERC vapor generation system configuration

Vapor Generation

A Dynacalibrator Model 450 (VICI Metronics, Poulsbo, Washington) was provided by the University of Washington Environmental Health Laboratory to generate the PERC concentrations needed for testing. Permeation tubes and diffusion vials can be used in the Dynacalibrator’s permeation chamber. Diffusion vials are capable of generating concentrations ranging from ppb to ppm, whereas permeation tubes are typically limited to ppb concentrations.[40] (For the purposes of this current study, a diffusion vial was used to generate PERC vapor concentrations in the hundreds of ppm range.)

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 can be adjusted using dual flowmeters. Two flowmeters enable the user to create two distinct concentrations by changing the flowrate through the flowmeters. Because the temperature and flow of the carrier stream are unchanged, the flowmeter with the lower flowrate generates the higher concentration. Similarly the flowmeter with the higher flowrate generates the lower concentration.

The carrier stream passes through a temperature-controlled permeation chamber, which houses either a diffusion vial or a permeation tube containing the test chemical. 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. Varying a vial’s bore diameter and diffusion path length influences the diffusion rate at a fixed temperature. As it passes through the permeation chamber, the carrier stream 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 chamber 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. Figure 3 shows the schematic of flow for the Dynacalibrator 450.

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.

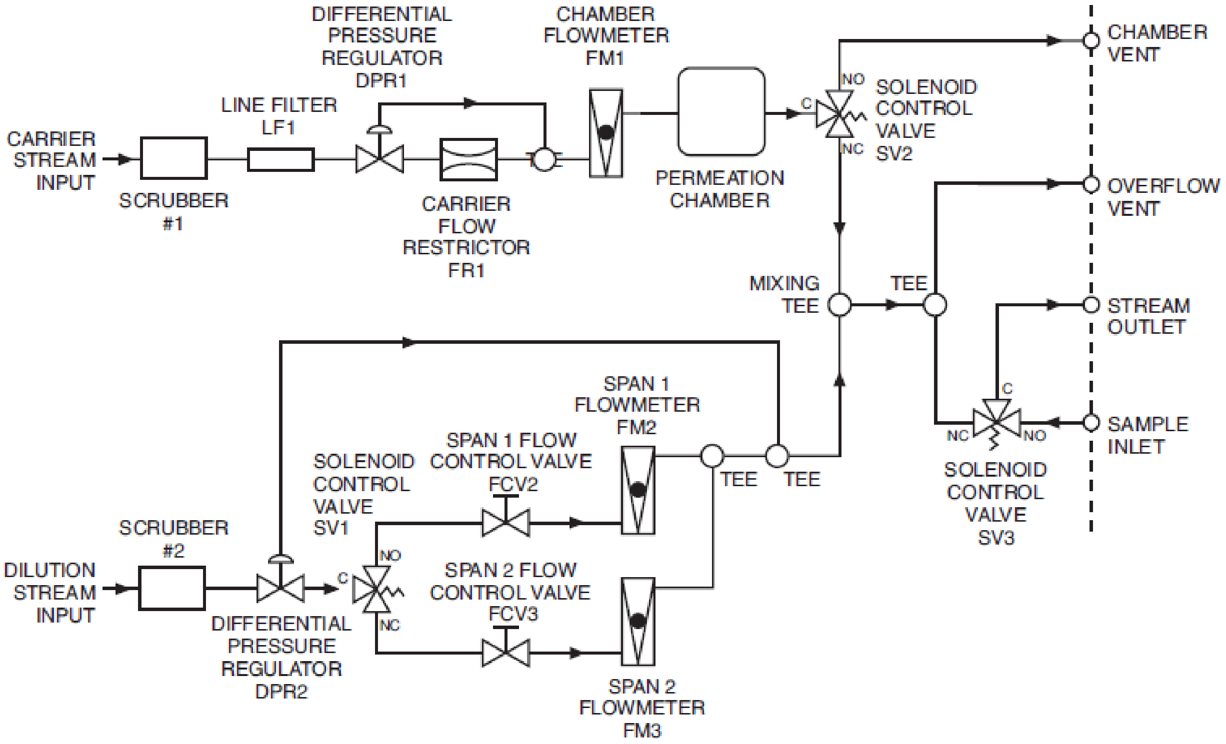

Figure 3: Dynacalibrator model 450 schematic[41]

Diffusion Vial

A model 'D' VICI diffusion vial was used to create the calibration gas. 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 a 5 mm inside capillary diameter. Figure 4 shows a 'D' sized diffusion vial similar to the one used during testing.

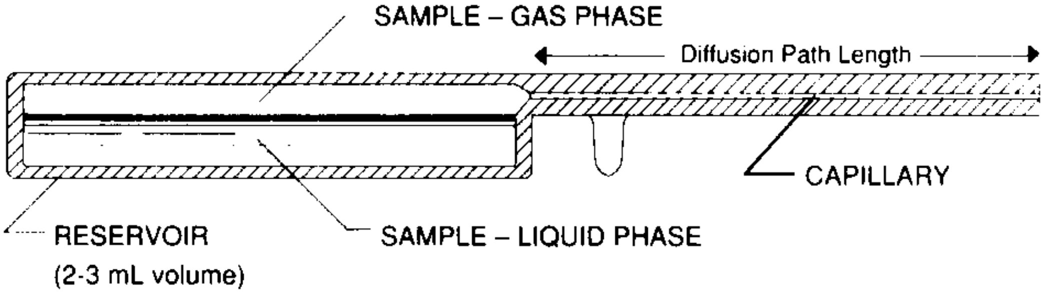

Figure 4: Diagram of 'D' sized diffusion vial with 5.0 mm capillary[40]

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 ft^3) 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 exclusively of PTFE construction.

Tubing/Fittings

Tygon tubing was used to connect the air cylinder to the Dynacalibrator because it is sufficiently flexible and was readily available. 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, or 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 photoionization detector (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 PID'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.[42]

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 onto a computer for further analysis. A pump with an internally regulated flow rate of between 450-550 ml/min limits the effect of the outside airstream flow rate. Calibration of the PID was conducted per manufacturer's instruction using a cylinder of isobutylene calibration gas certified to 100 ppm. Because the PID was calibrated with isobutylene, a correction factor of 0.57 was applied to the PID readings to obtain the PERC concentration.[43]

Charcoal Tubes

SKC® Anasorb® coconut shell charcoal sorbent sample tubes (catalog number 226-01) were used for the sampling procedures. PERC concentrations were sampled and analyzed in order 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.

Sampling Pumps

A Gilian dual-mode, low-flow pump was used to pull 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 give a sampling volume of 0.003 cubic meters (m^3).

Sample Analysis

The University of Washington 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.

Phase I: 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 allowed us to keep the chamber temperature the same while being able to measure two different concentrations. The groupings are listed in Table 3 below.

Table 3. Theoretical PERC concentrations and corresponding Dynacalibrator settings

Group	Theoretical Concentration	Digital Temperature Setting	Chamber Temperature (^oC)	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 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 for a visual cue indicating temperature equilibrium has been reached in the permeation chamber. Data logging with the PID showed that the visual cue was premature by a few minutes.

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 lab for quantitative analysis.

Limit of Detection

Before testing at Span1 and Span2, detectors were exposed consecutively to zero air 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 differently 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 once more recorded. Concentrations were then stepped back down to 25 and 0 ppm with responses recorded at each step.

Phase II: Materials for Usability Testing

Testing Apparatus

In an effort to simulate the search for a vapor leak in a PERC dry cleaning machine, three identical testing units were assembled. Each unit consisted of a sample pump, glass impinger, ¼" tubing, and ¼" fittings. Flexible tubing connected the pump to the impinger, and 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. Figure 5 shows a diagram of one testing unit. Four of the five outlet tubes were blocked, indicated by an “X”, 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.

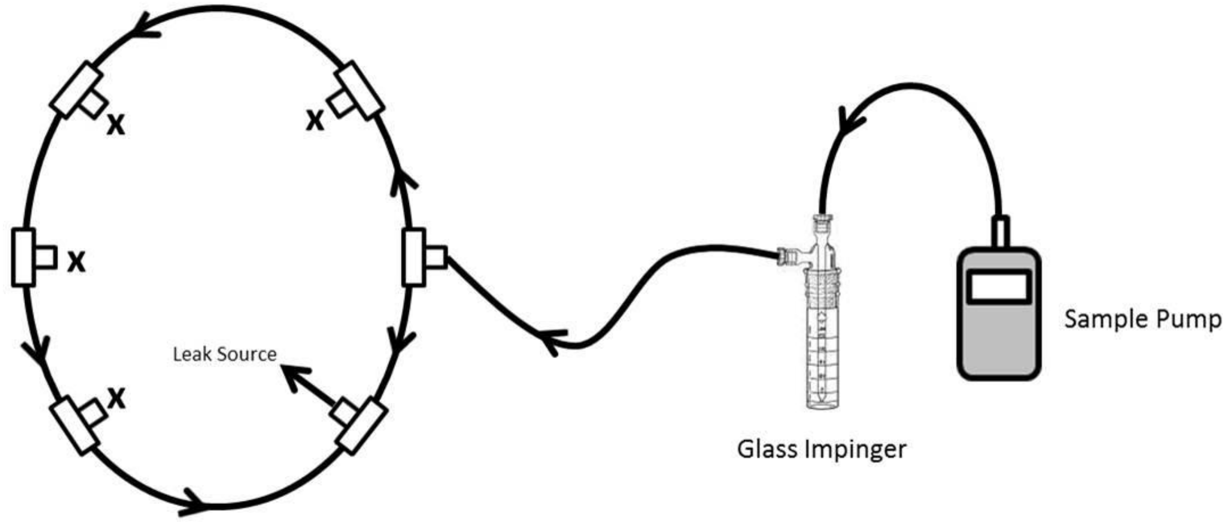

Figure 5: Diagram of single usability test unit

Sampling Pumps

The same low-flow sampling pumps used in Phase I testing procedures were used in the usability testing. 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 the pumps to push air through the impingers and testing units. Pumps were connected to a charging station during testing.

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 chosen. 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.

Phase II: 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. Some subjects had experience using hand-held instruments like vapor leak detectors. Subjects were asked to sign a written consent form before testing, and encouraged to take as much time as they needed and 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. Other features of the detectors that were not applicable to the testing were not demonstrated.

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 and 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 was stopped when the leak was found. The detector was then powered down and returned to its carrying 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 had found the leak source with each detector.

Subjects were then asked to complete a questionnaire asking about their experience. Questions were asked about the visual and audio responses, which detector they disliked the most, and which they liked the most. If deemed necessary, the investigator would ask questions to help clarify subject responses. The questionnaire administered to subjects can be found in the Appendix A.

Results

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 hardcopies, and then entered into a Microsoft Excel 2010^{TM} worksheet for data management.

Table 4 includes basic instrument information provided by the manufacturers and results from preliminary tests, including warm-up time and motion sensitivity. 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 gave an audible or visual response when quickly moved from an overhead position to waist height with a straight arm.

Table 4. Basic 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 hr	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
Inficon TEK-MATE	200	2	100 hrs	Internal Pump	20 sec	Auto	Yes	Yes	No	No
Snap-0n 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

*Costs reflect the price at the Nov 2010 date of purchase and may not be representative of the current purchase price.

[1] indicates manufacturer information

[2] indicates laboratory tested information

Phase I: Limit of Detection Results

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. 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). Because two-thirds of the detectors were able to detect this concentration, additional testing at lower concentrations was conducted. To further evaluate the capabilities of detectors, testing was performed 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. Table 5 shows the results of the LOD testing. Shaded boxes indicate that the specified concentration was detected.

Table 5. Leak detector limit of detection

	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

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 limit of detection. 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.

Phase I: Response Time Results

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. Table 5 shown above, provides the concentrations at which each detector was tested. Response times were measured three times per detector at each detectable concentration. Figure 6 shows detector response time in box-plot form. Raw data collected during response time testing can be found in Appendix B.

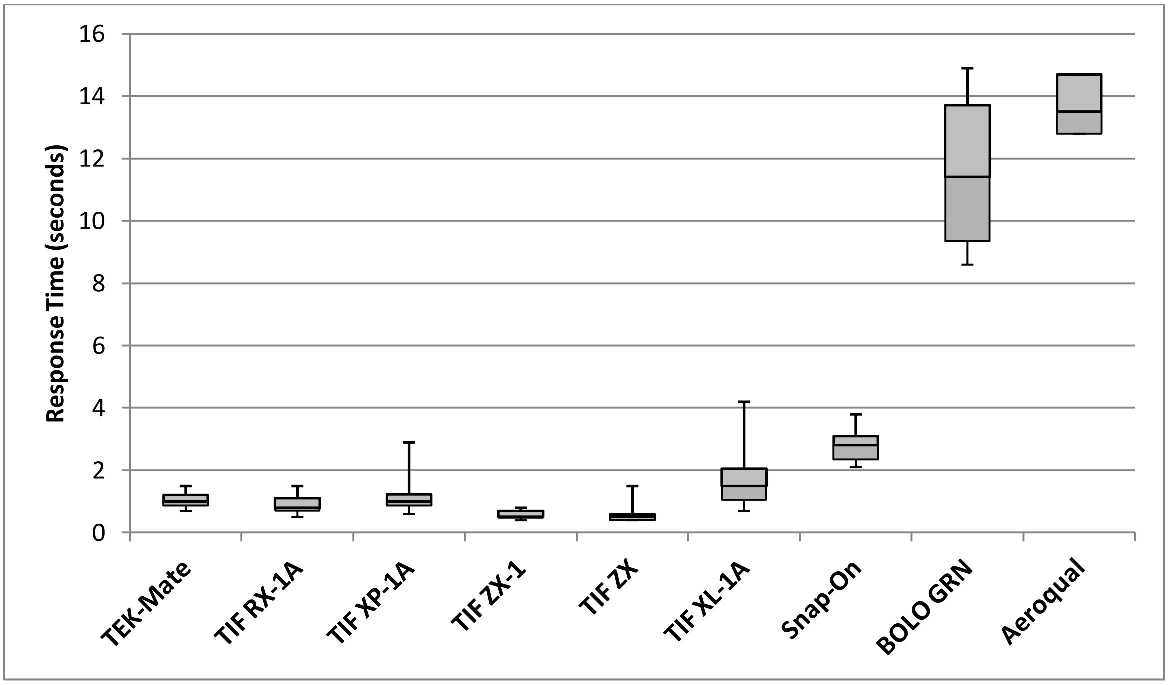

Figure 6. Detector response times

Phase I: Concentration Gradient Results

Results from gradient testing are shown below in Table 6. The Aeroqual, BOLO GRN, and Snap-On did not respond at the test concentrations and were 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.

Table 6. 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

Phase I Analysis

Response time descriptive statistics are presented in Table 7. 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).

Table 7. Detector response time descriptive statistics (seconds)

	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

The TIF ZX, XP-1A, and XL-1A had single response time measurements that skew 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. Figures 7, 8, and 9 show the distribution of response time measurements for the ZX, XP-1A, and XL-1A respectively.

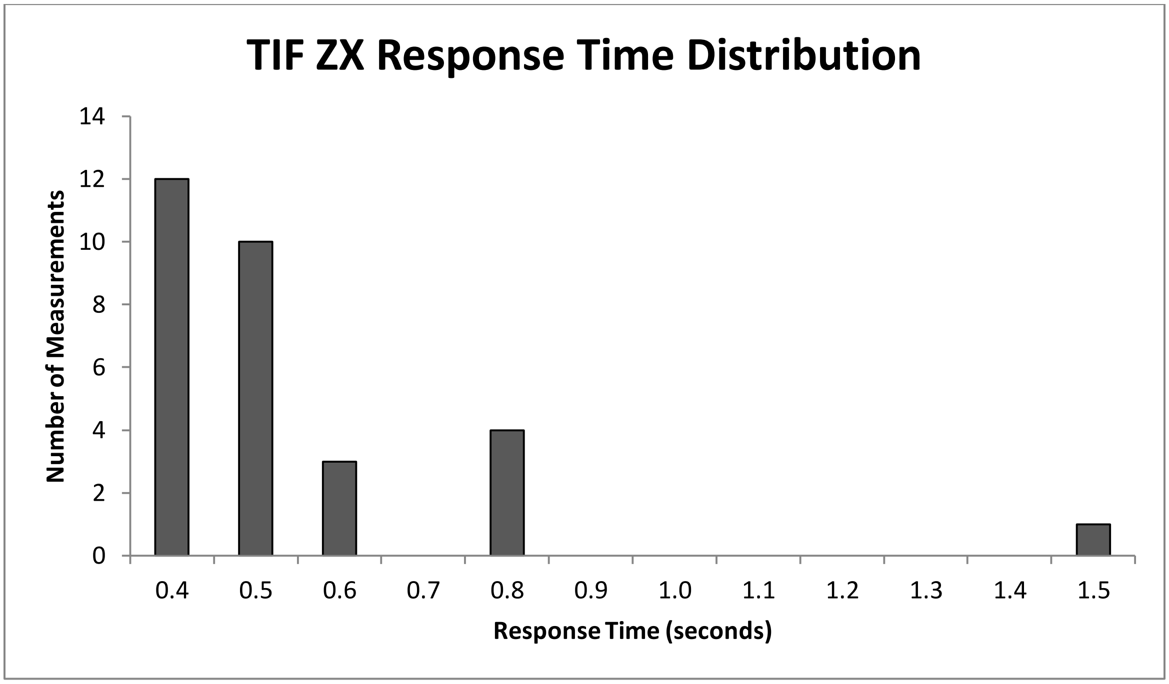

Figure 7: Distribution of response times for the ZX

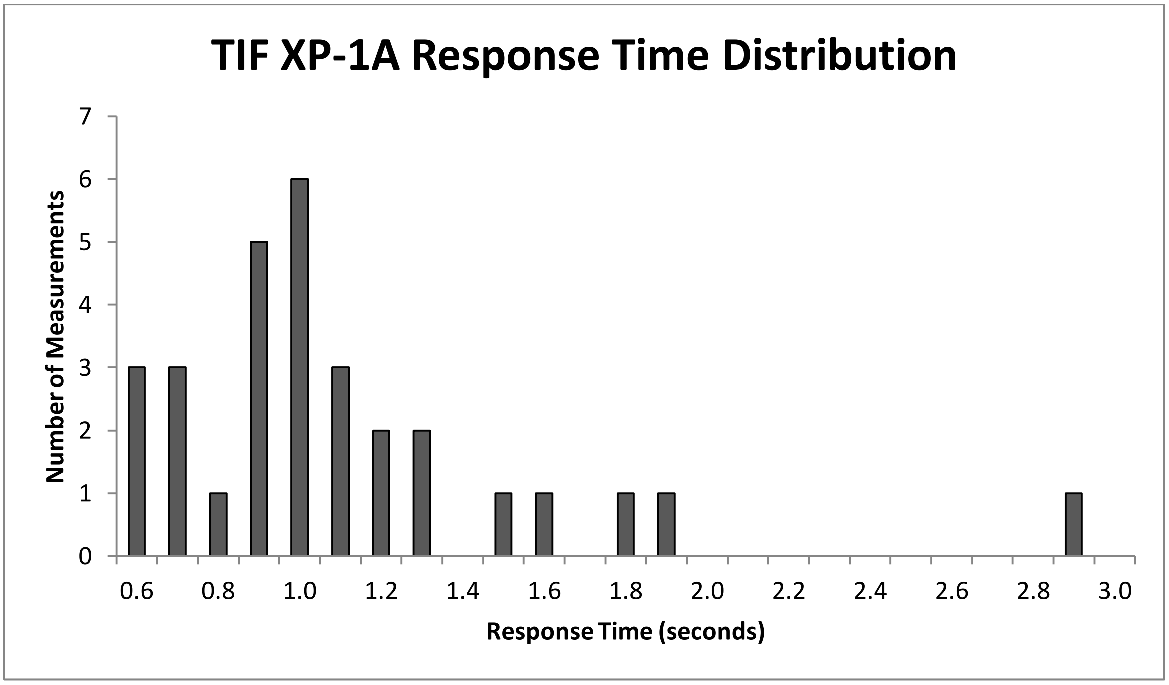

Figure 8: Distribution of response times for the XP-1A

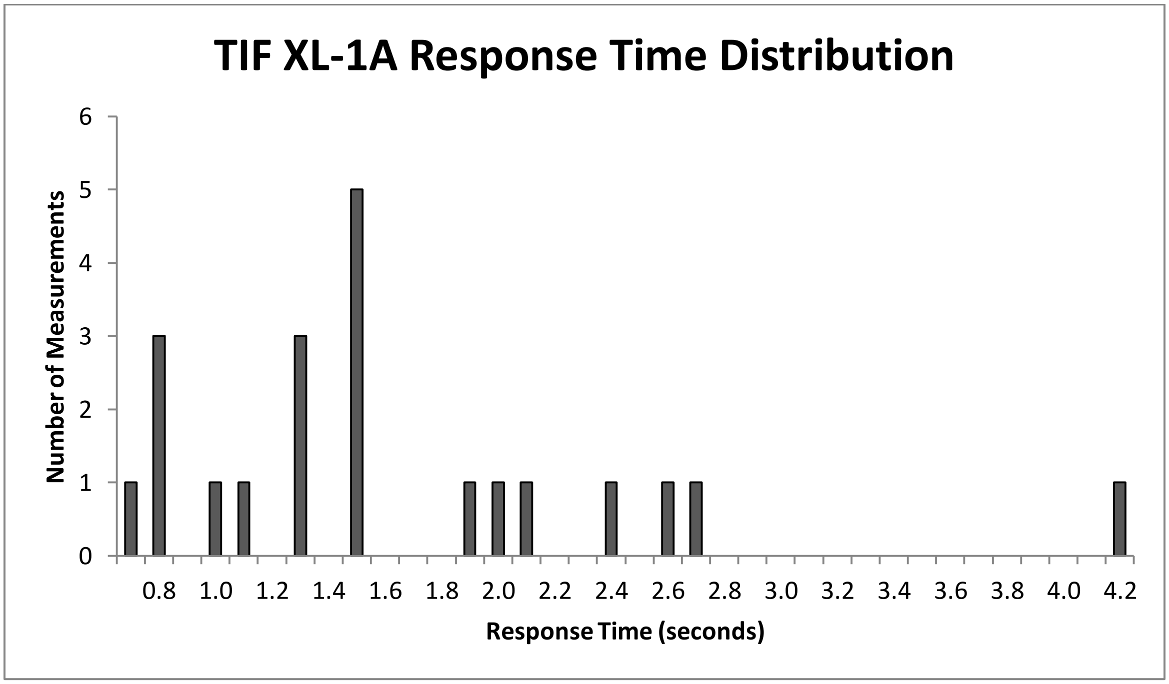

Figure 9: Distribution of response times for the XL-1A

Detector Cost as a Predictor of Limit of Detection

As shown in Figure 10, when all detectors were included in the regression between Cost and LOD, LOD increased as price increased (r = 0.72, p = 0.03). However this result does not accurately reflect the true relationship between the two variables because the LOD for the Aeroqual was artificially high due to specific relative humidity requirements not being met by the exhaust stream. Additionally, the true LOD for the most sensitive detectors could not be measured; consequently, the recorded LOD of 0.2 ppm could also be artificially high.

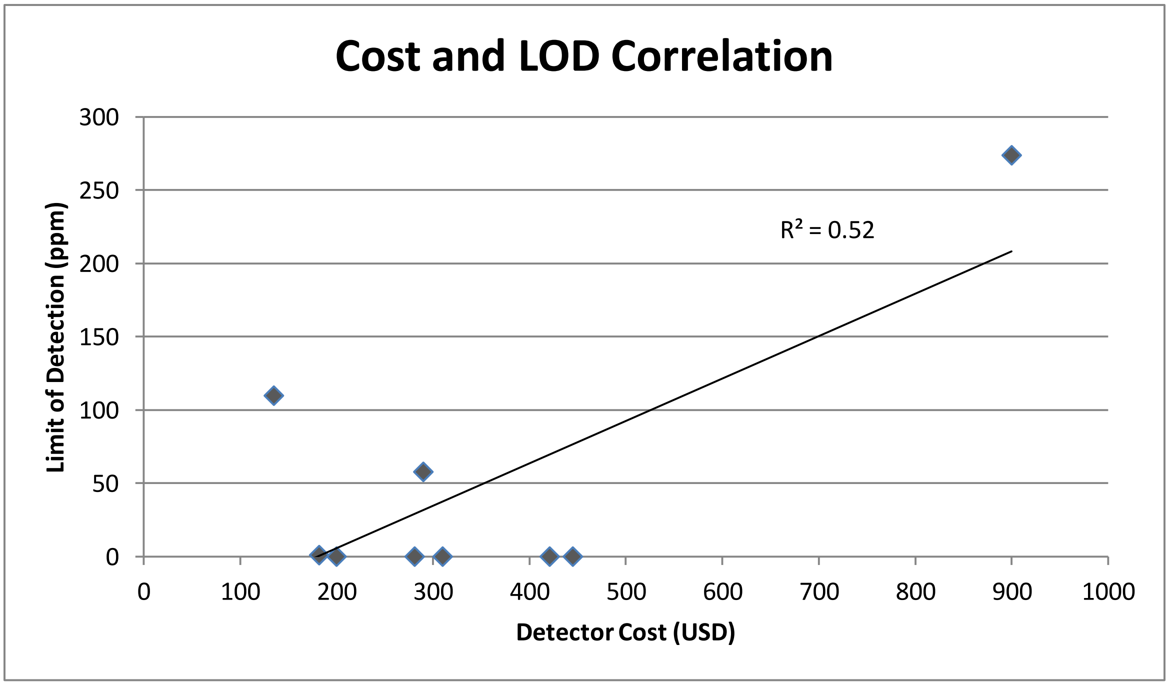

Figure 10: Graphical representation of cost and LOD relationship

Excluding the Aeroqual changed the slope from positive to negative indicating a moderate negative correlation (i.e., LOD decreased with increasing Cost) (r = -0.50, p = 0.20). Excluding both the Aeroqual and BOLO GRN from the regression yielded an almost negligible correlation (r = -0.07, p = 0.88). Therefore, the cost of a detector did not appear to be a good indicator of its LOD.

Detector Cost as a Predictor of Response Time

The regression of Cost and Response Time for all detectors showed a moderate positive correlation, (r = 0.47, p = 0.20). Excluding the Aeroqual and BOLO GRN changed the direction of the association, indicating that as response time decreased Cost increased (r = -0.45, p = 0.31). Including only the TIF detectors yielded a strong negative correlation between Cost and Response Time (r = -0.96, p = 0.01). A significance test using critical values of the correlation coefficient determined this result was significant. Figure 11 shows that when comparing only TIF detectors, more expensive models had faster response times than less expensive models.

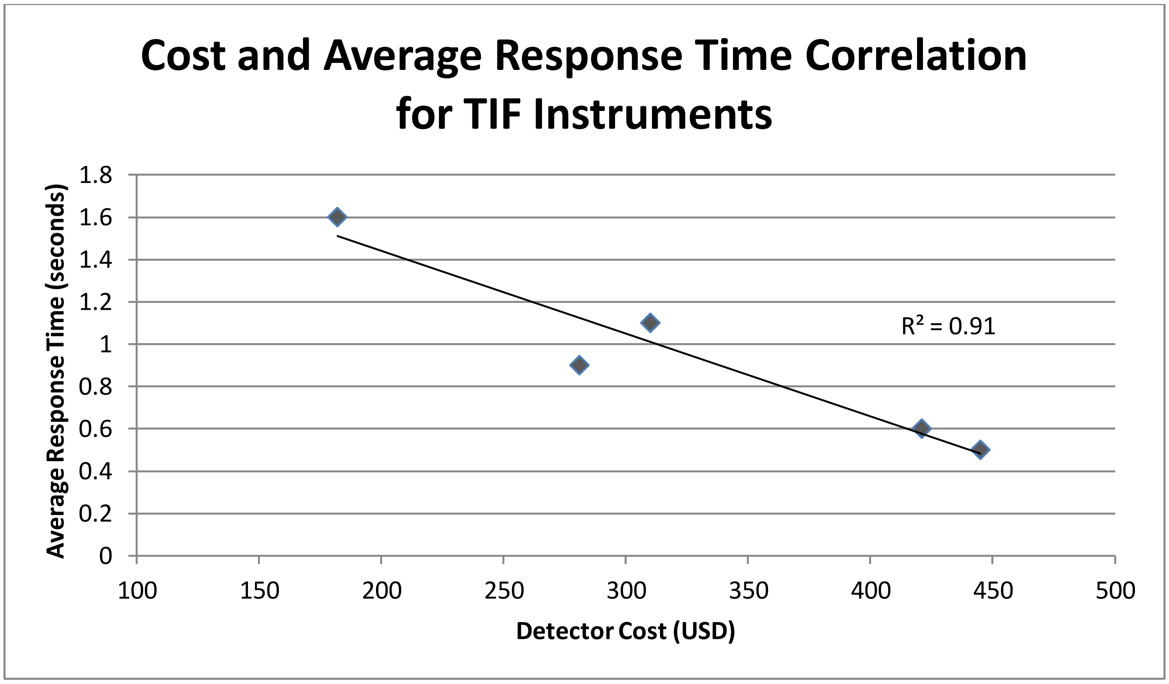

Figure 11: Graphical representation of cost and response rime relationship

Therefore, cost did not appear to be a good indicator of response time when comparing all detectors. However when comparing only TIF detectors, cost appeared to be a strong predictor of response time.

Sensitivity Rating as a Predictor of Limit of Detection

A detector's manufacturer-provided sensitivity rating depends in some cases on the industry or application a detector is intended for. Those intended for detecting automotive air conditioning leaks have their sensitivities listed in ounces per year of R134a. Those intended for use in the dry cleaning industry have their sensitivities listed in either ounces per year of PERC or ppm PERC. Those not intended for a specific industry or application can have their sensitivities listed in ounces per year of ALL Halogens.

The Aeroqual, BOLO GRN, and TEK-Mate had sensitivity ratings in ppm of PERC. Including these detectors in the analysis would require the conversion of sensitivity from ppm units to ounces per year. For this reason the TEK-Mate was not included in the analysis. The Aeroqual and BOLO GRN were excluded from analysis due to their high LODs.

The TEK-Mate however was comparable to the TIF RX-1A and XP-1A detectors in terms of cost, response time, and LOD, so it would presumably behave similarly in sensitivity analysis.

The remaining detectors were grouped according to whether their sensitivities were listed as All Halogens or R134a refrigerant. Those listed with R134a showed a moderate negative correlation to LOD ($r = -0.44$, $p = 0.56$). Detectors sensitive to All Halogens were highly correlated to LOD (r = 0.87, p = 0.33). However there were only three detectors included in the group sensitive to All Halogens and the results were not statistically significant.

Combining the All Halogen and R134a sensitivity groups showed a moderate negative correlation between detector sensitivity rating and corresponding LOD (r = -0.48, p = 0.33).

Manufacturers stated sensitivity did not appear to be a good indicator of LOD among detectors grouped by intended application, or with the same units of sensitivity. It is unclear whether detectors are differentially sensitive to certain chemicals according to intended application. However a technical support representative for one manufacturer suggested there was no technical difference.

Sensitivity Rating as a Predictor of Response Time

Detectors were again grouped according to their chemical sensitivity. Detectors with sensitivity ratings to All Halogens showed a moderate correlation with response time (r = 0.69, p = 0.51). Detectors with sensitivity ratings to R134a were almost negligibly correlated with response time (r = -0.21, p = 0.79).

Excluding the Snap-On detector from the R134a analysis changed the sign of the Pearson coefficient and returned a very high positive correlation between sensitivity and response time (r = 0.99, p = 0.02). However, there were only three detectors included in the group. Additionally the ZX and ZX-1 are virtually identical detectors since the ZX is the newest version of the ZX-1.

Detector Response Time as a Predictor of Limit of Detection

Testing whether or not a detector's response time was an accurate predictor of LOD returned a very high positive correlation between the two (r = 0.93, p = 0.0002). A significance test using critical values of the correlation coefficient determined this result was significant. Figure 13 shows that as response time increases with increasing LOD. Therefore, a detector's response time appears to be correlated with its LOD.

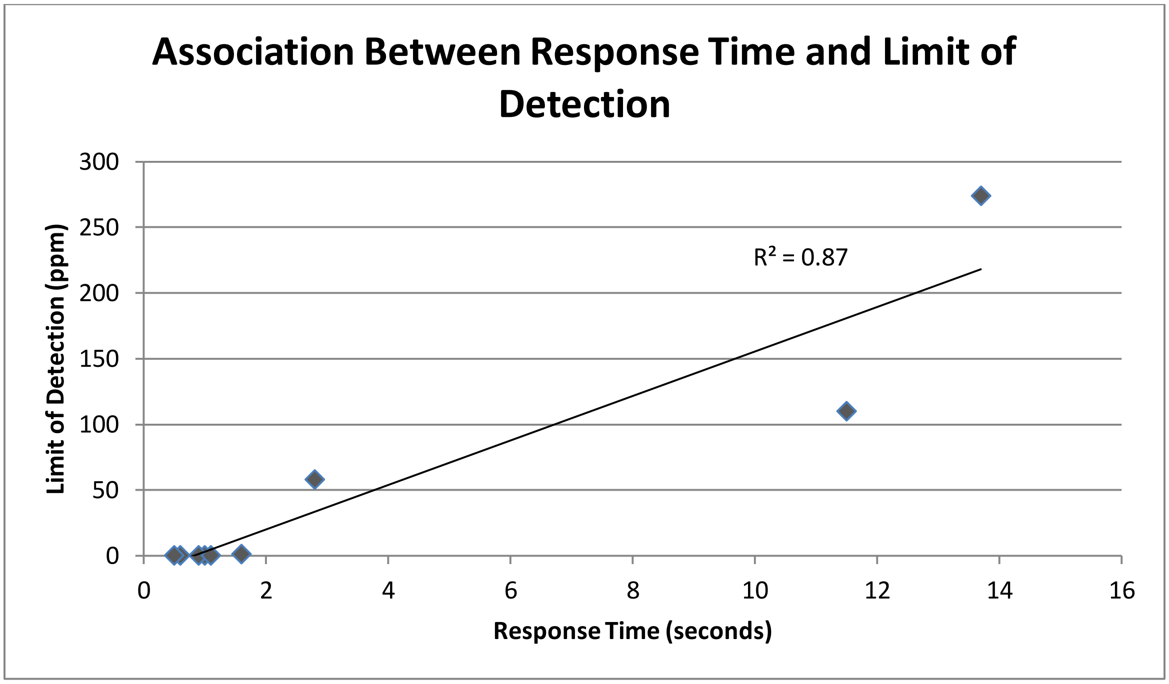

Figure 12: Graphical representation of response time and LOD relationship

Concentration Gradient Testing

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

The ZX, ZX-1, and XP-1A use multi-color LED light displays and changed colors through green, orange, and red, respectively, when PERC was introduced. The RX-1A had red only lights which would increase in number from 0 to 6. The TEK-Mate had two single color lights, 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 light of the XL-1A indicated only that the detector was powered on.

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 detector’s 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 after completing the initial procedures showed that resetting at

25 ppm prior to switching to 50 ppm resulted in a gradual increase through visual and audio responses. This is consistent with the way leak detectors are actually operated.

Procedures included in gradient testing under controlled conditions were not able to demonstrate a detector's concentration gradient recognition ability. However field testing in a King Co. dry cleaner demonstrated one detector's ability to quickly locate a leak source. The Aeroqual, TIF ZX-1, and MiniRae 2000 PID were taken to a dry cleaning facility with a distinct PERC odor. Using the Reset function several times, the ZX-1 located the leak source, which was rubber hose connecting the PERC storage tank to the machine. The PID read 9,999 ppm at the source, which was the upper limit of the digital display. Because the PID was calibrated to isobutylene gas, a correction factor was applied to scale the measurement to PERC. After applying the 0.57 correction factor the actual PERC concentration was at least 5,699 ppm.

Laboratory Analysis of Charcoal Tube Samples

The University of Washington Environmental Health Laboratory analyzed 19 charcoal tubes including field and lab blanks. Table 8 shows the ID number, measured concentration, and date of collection for each charcoal tube. Results were not corrected for spike recovery efficiency, which was approximately 92%. 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 are as follows: 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: Timed Trials

During the usability testing, the selected detectors were used to locate a leak source on the testing apparatus. After observing the leak detection testing and an initial analysis of the results, it became clear that the detection times were heavily influenced by variables not associated with detector usability. Influences on detection time included where each subject began searching on the test apparatus and direction of travel around the circular apparatus. Recording the time taken to find the leak source was discontinued after the seventh subject and the data are not reported.

Phase II: Questionnaire

Upon completion of the leak detection trials, subjects were asked to complete a questionnaire. Subject participation in the questionnaire was 100%. Some subjects provided more than one answer to a question. Consequently, 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 respondents 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 thought the ZX felt the best to hold during testing. The RX-1A and XP-1A were similarly ranked with approximately 19% and 13% respectively. One subject had no preference. Table 9 shows the distribution of responses.

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 thought the LED displays were very helpful, 40% thought it neither helped nor hindered detection, and 7% thought it was not helpful. Table 10 shows the distribution of responses.

Table 10. Was the light display helpful?

Response	Number	Percent
Very Helpful	5	33
	2	13
	6	40
	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, 50% thought the XP-1A had the most easily understood light display. Table 11 shows the distribution of responses.

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 thought the audible alarms were not helpful, 73% thought they were very helpful. Table 12 shows the distribution of responses.

Table 22. 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 fairly evenly distributed between the RX-1A, ZX, and XP-1A with 30%, 40%, and 30% respectively. Tables 13 and 14 show the respective distribution of responses.

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 thought the RX-1A had the easiest controls to use, followed closely by the XP-1A with 31%. Table 15 shows the distribution of responses.

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 thought the ZX's controls were the hardest to use. Table 16 shows the distribution of responses.

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 percent was not 100%. Table 17 shows the distribution of responses.

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. Table 18 shows the distribution of responses.

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

Phase II Analysis

To simulate scenarios that could occur in dry cleaning businesses, operator’s manuals were not made available to subjects prior to testing. Instead, a brief tutorial was provided, which included how to power-on/off and a demonstration of how each detector would respond to the leak.

Approximately 84% of King County dry cleaner owner/operators identified themselves as Korean.[39] However no manufacturer offers a Korean language manual. An owner/operator that may not be fluent in any of the languages a manual is written in will find it to be of little use. In addition, the individual using a detector may not receive a detailed training session before using it.

The subject's decision to pick one of the three test units to start with, and then which of the five outlets on each test unit to start searching had a large effect on detection times. Table 19 presents the detection times of each detector. Because one subject failed to detect the leak with the ZX, n=6 for this detector while n=7 for the others.

Table 19. Leak source detection times for each detector (seconds)

	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)
RX-1A	7	17.7	6.9	18.2	2.5	5.1	7.6	29.1	45.7	43.2
XP-1A	7	8.4	2.0	5.2	2.6	3.7	9.2	11.9	16.1	13.5
ZX	6	10.2	3.2	7.8	3.0	5.5	7.3	12.8	24.0	21.0

The questionnaire indicated that subjects generally did not have a clear preference amongst the three detectors. Only three questions indicated clear preferences:

- The ZX felt the best to hold,
- The ZX had the hardest controls to use, and
- Instrument response sounds were helpful in finding the leaks

Chi-Square tests were performed for responses to each question. Questions 3 and 6 had p-values of 0.006 and 0.00002 respectively, indicating a significant difference between the observed and expected response frequencies, which is unlikely due to chance. The remaining questions had p-values greater than 0.05 and therefore their results were not significantly different than those due to chance. Similar responses would be seen for all but two questions had the subjects randomly filled out the questionnaire.

Written responses on the questionnaire helped determine what subjects did and did not like about each detector. Tables 20, 21, 22, and 23 present the subjects written comments from the four questions that asked for reasons why a particular answer was given. Not every subject provided written comments.

Table 20. Written comments from Question 8

Q8: Which Instrument's Controls Were the Easiest to Use?	Written Comments from Questionnaire
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 21. Written comments from Question 9

Q9: Which Instrument's Controls Were the Hardest to use?	Written Comments from Questionnaire
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"

The ZX controls use symbols instead of words which some subjects found difficult to understand. The XP-1A has more buttons to choose from which some subjects also found difficult to understand.

Table 22. Written comments from Question 10

Q10: Overall, Which Detector Did You Like the MOST?	Written 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”

Detector characteristics that subjects liked included how it felt to hold/use, and clarity of the sound/light display. It was noticed during testing that a detector’s speaker could become obstructed depending on hand size and grip position.

Table 23. Written comments from Question 11	
Q11: Overall, Which Detector Did You Like the LEAST?	**Written 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."

Characteristics the subjects did not like included long warm-up time, unclear button meaning, and too many button options.

Analysis of the technical capabilities measured in Phase I and usability from Phase II was performed to help answer questions one might find useful when recommending a leak detector for a dry cleaning business. For example it might be useful to know whether the amount of money spent on the detector would have an impact on the user's ability to actually find a leak source. There is no benefit to saving money on a detector if it does not allow the user to find a leak. Alternatively, a relatively inexpensive detector may have the technical capabilities and usability properties of a more expensive model.

Discussion

The overall goal of this research was to help LHWMP select a detector that would enable King County dry cleaning businesses to comply with local, State, and Federal leak detection requirements. The specific aims were to characterize the technical capabilities and usability of vapor leak detectors, and to provide specific recommendations about which detector to purchase. Testing showed that the quickest and most sensitive detectors were able to identify very low concentrations of PERC in less than one second, and that with minimal training, subjects could successfully operate detectors and use them to locate leak sources.

Characterization of Technical Capabilities

Of all 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.

Limit of Detection testing resulted in a tie between five detectors for the lowest LOD. Each was able to detect PERC at concentrations beyond the capability of the PID.

Characterization of Usability

Leak source detection procedures showed that each of the detectors was able to 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 what qualities were liked and disliked during leak detection testing. The detector with the most buttons was viewed as too complicated and overwhelming to some. Symbols on the controls instead of words led to confusion for subjects unfamiliar with international symbols. Audible response was viewed more helpful finding a leak than the visual response. However it was mentioned several times that volume control other than muting would be a preferred option.

The ZX received the most positive and negative comments out of the three detectors. Subjects liked how it felt to hold and its speed, but disliked the 20 second warm-up period and symbols instead of words on the controls. Overall the ZX was both the most and least liked detector. In each case however two responses separated the detectors with the most and least responses.

Recommendations

Several detectors demonstrated the ability to quickly detect low concentrations of PERC. Usability testing showed that these abilities can enable users to locate a leak source with minimal training.

Core features that a detector should have are an internal pump and a manual reset or auto-zero function. The internal pump draws air into the probe and over the sensor. Manual reset or auto-zero enables the detector to ignore ambient concentrations of PERC in order to detect larger concentrations. Available options beyond these should be up to the discretion of the user. However a flexible probe is highly recommended in order to access the difficult to reach places of a dry cleaning machine.

Recommendations to leak detector manufacturers about how to better serve the dry cleaning industry in King Co. would include those identified during technical capability and usability testing, as well as from previous research on the health and safety needs of the industry.

A detector best suited for the King Co. dry cleaning industry should have an internal pump, manual reset button or auto-zero function, long flexible probe, quick warm-up period, handle designed for proper ergonomic position of hand, weight distribution to eliminate the feeling of being top-heavy, speaker for audible response positioned where it cannot be obstructed by hands or fingers, and limit number of sensitivity settings.

Additionally, manufacturers could better serve the industry by providing information in demographically relevant languages. A majority of the survey respondents self-reported as Korean, yet none of the operator’s manuals have Korean translations. Providing stickers or decals in demographically relevant languages that can be placed over the English language control panel could also help ensure detectors are being used correctly.

Limitations of the Research

Number of Response Time Data Points per Concentration

Three measurements were recorded at each concentration that elicited a response from a detector. Therefore the most sensitive detectors had 30 measurements to calculate an average response time because they were able to respond to all PERC concentrations. The least sensitive had three measurements because it only elicited a response at one concentration. While the overall average response time could have included 30 measurements, only three measurements were recorded at individual concentrations. Increasing the number of measurements recorded at each concentration could provide a more accurate estimation of each detector's true response time.

Relative Humidity Requirements of Certain Detectors

At the outset of the study, the effect of humidity on detector response was considered to be an important parameter. The original intent was to introduce water vapor to the exhaust stream, downstream of the 4-way valve. The humidity was generated by passing air through a rotameter into a glass impinger containing 150 mL of de-ionized water. Using a NIST Traceable® hygrometer, RH was measured at 100% across all flow rates between 0.011 and 1.93 L/min as measured on a low-flow rotameter.

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. All detectors also responded to exhaled breath when the probe was held close to the mouth. The hygrometer measured 100% RH for the exhaled breath.

LOD Measurement Accuracy

Experimental design contributed to concerns about the accuracy of LOD test results. Testing detectors at specific PERC concentrations ignores the other possible concentrations between those points. For example, if a detector responded at 100 ppm but not at 50 ppm, it is only correct to state that the true LOD exists somewhere between those concentrations. However as the range between test concentrations decreases, the accuracy of the measured LOD should increase.

A more accurate LOD could have been identified for each detector if the procedures had included adjusting the concentration until a response was no longer given. Concentration changes could be achieved by either increasing or decreasing the flow rate of air through the Dynacalibrator. However this process would only benefit those detectors with LODs at concentrations the PID was able to measure.

Lower Limit of PID above the LOD of most sensitive detectors

The lower LOD of the PID was higher than that of several detectors. Consequently, the true LOD of the most sensitive detectors was somewhere below 0.2 ppm PERC. However, this concentration is below all recognized odor thresholds, and is well below 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. Figure 14 shows PERC concentrations for each charcoal tube as well as the average of PID readings taken before and after sampling.

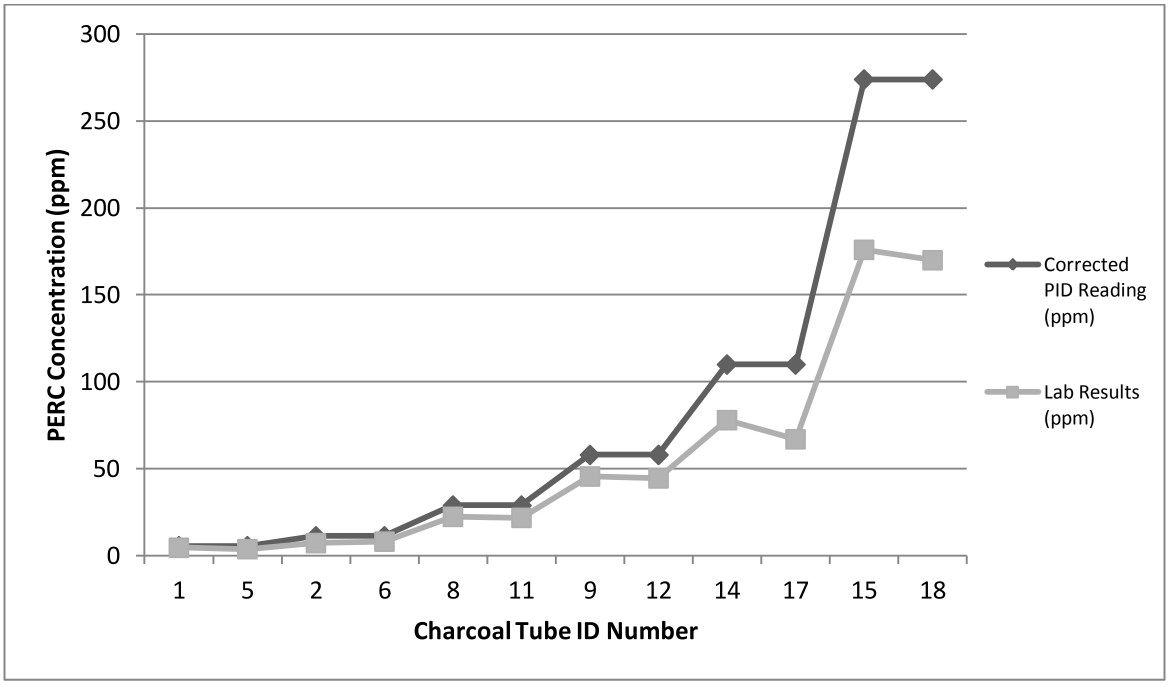

Figure 13: PERC concentration measured by charcoal tubes and PID

Figure 15 shows the matched PID and charcoal tube measurements at each test concentration. 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).

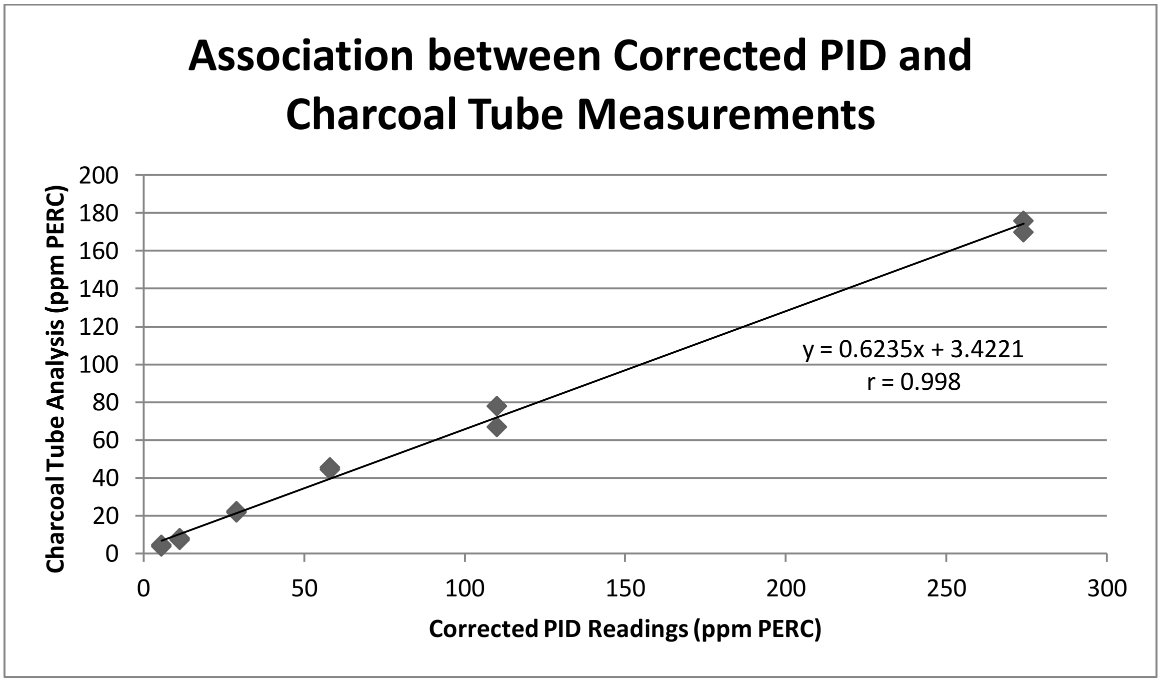

Figure 14: Plot of matched PID and charcoal tube concentrations

The 0.62 slope of the regression line in Figure 15 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 was not able to 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 large 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. 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 showed that in doing so, a detector's visual response traveled through green, orange, and red LED displays gradually. Without a reset or auto-zero a detector would produce a full red light display almost instantly when exposed to the first concentration. When exposed to the second concentration there was no change in display because the detector was already displaying its maximum response.

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. Figure 16 shows the average response times for detectors that responded at each concentration. Initially a one-way ANOVA was performed for each detector to check 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.

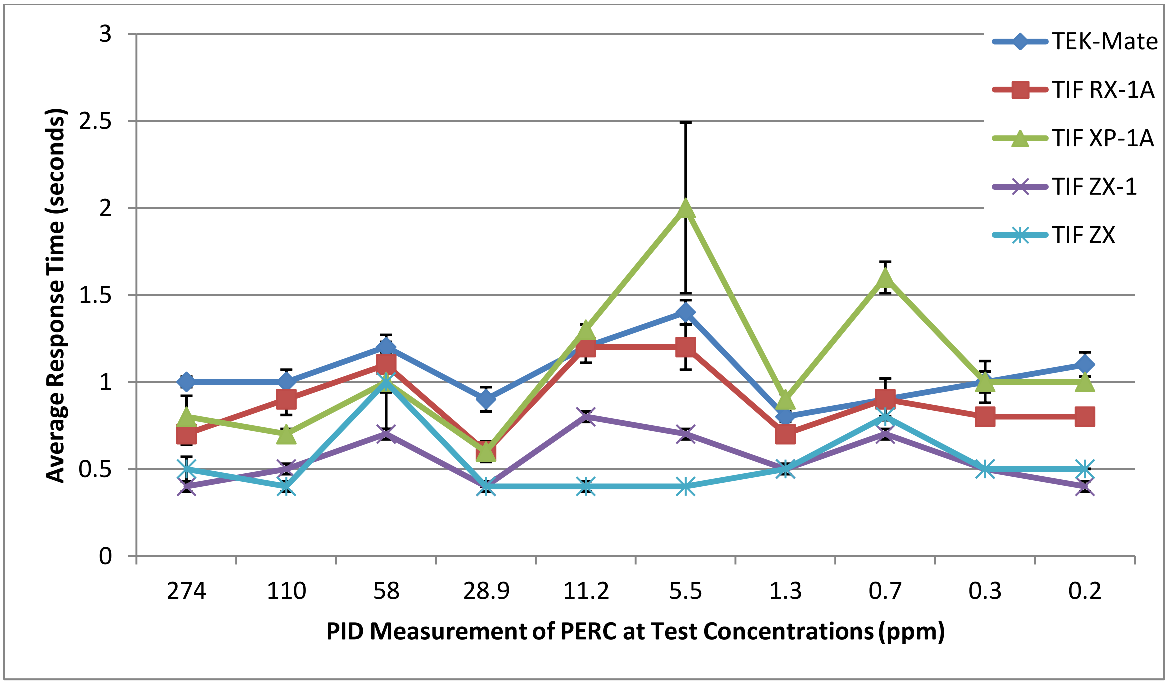

Figure 15: Average response time with standard errors of the mean measured at each concentration

Visual analysis of Figure 16 shows that there is a tendency for response time to vary at different concentrations and by detector. The general lack of parallel lines indicated the possibility of an interaction. 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 can be found 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 x 10^{-17}), detector ($F_{4, 100}$=74.4, p=4 x 10^{-29}), and interaction effects ($F_{36, 100}$=4.2, p=9.16 x 10^{-9}).

The detectors in Figure 16 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 10 apart, which could be an artifact of input division during analog to digital conversion.

Human error 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 responds provided several opportunities for the introduction of error. Human reaction time is on average around 200 millisecond or 0.2 seconds, which is roughly half of the fastest detector's response time.

Usability testing not conducted with dry cleaners

Usability testing was originally going to be performed by attendees of a dry cleaning association meeting. This would have provided valuable insight into the opinions of the target market. Difficulties in scheduling however forced a change in participants.

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

Usability testing apparatus not representative of real dry cleaning machines

The testing apparatus created for usability testing was suitable for watching 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. Demonstrating on active dry cleaning machines was suggested as the best method to demonstrate a detectors ability to locate a leak source.

Difficulties associated with this approach include scheduling visits during business hours, overcoming potential language barriers, and possible apprehension of inviting a government agency into a business.

Future Opportunities

An unforeseen result from the research came about on the last day of usability testing. The last subject to participate was a Korean State employee who had experience working with the dry cleaning industry. One of the subject’s industry contacts was the President of a local dry cleaning supply company, who was present during testing.

After testing, the subject and supply company President discussed the strengths and weaknesses of the apparatus and procedures. The biggest weakness identified from the conversation was that testing was not conducted with a dry cleaning machine under “real world” conditions.

The industry contact offered to coordinate visits to approximately 10 of his clients’ businesses over the course of several days. Similar test procedures would be followed, except that the leak sources would be fully functioning PERC dry cleaning machines, rather than simplified test apparatus.

The opportunity to partner with the dry cleaning community in this way will help LHWMP better communicate with this typically underserved industry. Providing hands-on, personal assistance in cooperation with credible industry members can increase the awareness, acceptance, and use of hand held leak detectors.

References

1. Doherty RE. A history of the production and use of carbon tetrachloride, tetrachloroethylene, trichloroethylene and 1,1,1-trichloroethane in the united states: Part 1—Historical background; carbon tetrachloride and tetrachloroethylene. *Environmental Forensics*. 2000;1(2):69-81. doi: DOI: 10.1006/enfo.2000.0010.

2. Agency for Toxic Substances and Disease Registry [ATSDR]. ATSDR - toxicological profile: Tetrachloroethylene (PERC). http://www.atsdr.cdc.gov/ToxProfiles/TP.asp?id=265&tid=48. Updated 1997. Accessed January 4th, 2011.

3. Local Hazardous Waste Management Program in King County [LHWMP]. Voucher incentive program. http://www.lhwmp.org/home/BHW/voucher.aspx. Updated May 27. Accessed September 28, 2011.

4. CDC - NIOSH pocket guide to chemical hazards - tetrachloroethylene. http://www.cdc.gov/niosh/npg/npgd0599.html. Accessed March 15, 2011.

5. California Air Resources Board [CARB]. Final california dry cleaning industry technical assessment report. http://www.arb.ca.gov/toxics/dryclean/finaldrycleantechreport.pdf. Updated 2006. Accessed May 20, 2011.

6. Tirsell DC. Dry cleaning. *Ullmann's Encyclopedia of Industrial Chemistry*. 2000.

7. United States Environmental Protection Agency (US EPA). Basic information about perchloroethylene. http://www.epa.gov/drycleaningrule/basic.html. Accessed 02/20, 2013.

8. NIOSH, ed. *Control of health and safety hazards in commercial drycleaners: Chemical exposures, fire hazards, and ergonomic risk factors.* ; 1997; No. 97-150.

9. ATSDR. Case studies in environmental medicine; tetrachloroethylene toxicity. *Agency for Toxic Substances and Disease Registry*. 2008.

10. Sherlach KS, Gorka AP, Dantzler A, Roepe PD. Quantification of perchloroethylene (PCE) residues in dry cleaned fabrics. *Environmental Toxicology and Chemistry*. 2011:n/a-n/a. doi: 10.1002/etc.665.

11. CCOHS. Canadian centre for occupational health and safety, health effects of tetrachloroethylene. http://www.ccohs.ca/oshanswers/chemicals/chem_profiles/tetrachloroethylene/health_tetra.html. Updated 1999. Accessed 6/27, 2012.

12. Johnson BL. A review of the effects of hazardous waste on reproductive health. *Am J Obstet Gynecol*. 1999;181(1):S12.

13. World Health Organization [WHO]. Tetrachloroethylene. *Air Quality Guidelines, Second Edition*. 2000:Chapter 5.13.

14. California Air Resources Board [CARB]. Technical support document part B: Proposed identification of perchloroethylene as a toxic air contaminant. . 1991.

15. United States Environmental Protection Agency (US EPA). Toxicological review of tetrachloroethylene (perchloroethylene). . 2012;EPA/635/R-08/011F.

16. Cai SX, Huang MY, Chen Z, et al. Subjective symptom increase among dry-cleaning workers exposed to tetrachloroethylene vapor. *Ind Health*. 1991;29:111--121.

17. Lash LH, Parker JC. Hepatic and renal toxicities associated with perchloroethylene. *Pharmacol Rev*. 2001;53(2):177-208.

18. Scientific Committee on Occupational Exposure Limits. Recommendation of the scientific committee on occupational exposure limits for tetrachloroethylene (perchloroethylene). . 2009.

19. Kyyrönen P, Taskinen H, Lindbohm M, Hemminki K, Heinonen O. Spontaneous abortions and congenital malformations among women exposed to tetrachloroethylene in dry cleaning. *Journal of Epidemiology and Community Health*. 1989;43(4):346--351.

20. National Research Council [NRC]. Review of the environmental protection agency’s draft IRIS assessment of tetrachloroethylene. . 2010.

21. World Health Organization [WHO]. WHO guidelines for indoor air quality: Selected pollutants; tetrachloroethylene. . 2010:415--454.

22. American Conference of Governmental Industrial Hygienists. *2010 TLVs and BEIs : Based on the documentation of the threshold limit values for chemical substances and physical agents & biological exposure indices.* Cincinnati, Ohio: ACGIH Signature Publications; 2010.

23. Brown Dzubow R, Makris S, Siegel Scott C, Barone S,Jr. Early lifestage exposure and potential developmental susceptibility to tetrachloroethylene. *Birth Defects Res B Dev Reprod Toxicol*. 2010;89(1):50-65. doi: 10.1002/bdrb.20222.

24. Waste and cleanup risk assessment glossary. http://www.epa.gov/oswer/riskassessment/glossary.htm. Accessed 07/18, 2012.

25. Agency for Toxic Substances & Disease Registry. The priority list of hazardous substances that will be the subject of toxicological profiles. http://www.atsdr.cdc.gov/SPL/index.html2011.

26. Facility/site database -- WA state dept. of ecology. http://www.ecy.wa.gov/fs/. Accessed January 1, 2011.

27. United States Department of Labor, Occupational Safety and Health Administration [OSHA]. Occupational safety and health standards, TABLE Z-2: Toxic and hazardous substances 29CFR part 1910 subpart Z. . 2006;1910.1000. Accessed 06/27/2012.

28. CDC - NIOSH. 1988 OSHA PEL project documentation, perchloroethyle. http://www.cdc.gov/niosh/pel88/127-18.html. Accessed 06/28, 2012.

29. Fact sheet - NIOSH, publication number 2009-120. http://www.cdc.gov/niosh/docs/2009-120/pdfs/2009-120.pdf. Updated 2009. Accessed 06/28, 2012.

30. About washington state department of labor and industries. http://www.lni.wa.gov/main/aboutlni/. Accessed 06/28, 2012.

31. WA State Dept of Labor and Industries. Airborne contaminants- WAC 296-841. . ;2011(March 15). Accessed 3/15/2011.

32. United States Environmental Protection Agency (US EPA). Plain english guide for perc dry cleaners, A step-by-step approach to understanding federal environmental regulations. . 1996;EPA 305-B-96002.

33. United States Environmental Protection Agency (US EPA). Basic information about tetrachloroethylene in drinking water. http://water.epa.gov/drink/contaminants/basicinformation/tetrachloroethylene.cfm. Accessed 6/30, 2012.

34. Puget Sound Clean Air Agency. 2010 air quality data summary. . 2012.

35. Occupational Safety and Health Administration [OSHA]. National perchloroethylene air emission standards for dry cleaning facilities. . 2006;40CFR63.321.

36. Oregon Department of Environmental Quality. Taking the uncertainty out of perchloroethylene leak detection. http://www.deq.state.or.us/aq/BAP/success.htm. Accessed 6/30, 2012.

37. Spokane Regional Clean Air Agency. Compliance Assistance Program. Dry cleaning & air quality requirements in spokane county. . 2010.

38. Colorado Department of Public Health and Environment. New requirements for leak detectors and monitoring equipment for perchloroethylene drycleaning facilities in colorado. http://www.colorado.gov/cs/Satellite?blobcol=urldata&blobheadername1=Content-Disposition&blobheadername2=Content-Type&blobheadervalue1=inline%3B+filename%3D%22Requirements+for+Leak+Detectors+and+Monitoring+Equipment.pdf%22&blobheadervalue2=application%2Fpdf&blobkey=id&blobtable=MungoBlobs&blobwhere=1251808803413&ssbinary=true. Accessed 6/30, 2012.

39. Whittaker SG, Johanson CA. A profile of the dry cleaning industry in king county, washington. . 2011;LHWMP 0048.

40. Worthington B, Rey AR. Generation of dynamic standard test atmospheres for aromatic compounds by using the diffusion vial method. *American Industrial Hygiene Association Journal*. 1991;52(11):464-468.

41. Valco Instruments Co. Inc. Dynacalibrator model 450 instruction manual. . 2012.

42. RAE Systems. RAE systems PID training outline. application note AP-000. http://www.raesystems.com/sites/default/files/downloads/AP-000_PID_Training_Outline.pdf. Accessed 6/29, 2012.

43. RAE Systems. Technical note TN-106: Correction factors, ionization energies*, and calibration characteristics. http://www.raesystems.com/sites/default/files/downloads/FeedsEnclosure-TN-106_Correction_Factors.pdf. Updated 08/2010. Accessed 08/15, 2012.

Appendices

Appendix A: usability questionnaire

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	

Appendix B: detector response times (seconds)

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				

Appendix C: two-way ANOVA

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

C1.0						
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

C.5						
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

C.3						
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

C.15						
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

Total						
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						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Concentrations	4.492267	9	0.499141	17.91175	2.42E-17	1.974829
Between	8.298267	4	2.074567	74.44617	4E-29	2.462615

Detectors						
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 x 10^{-17}), detector ($F_{4, 100}$=74.4, p=4 x 10^{-29}), and interaction effects ($F_{36, 100}$=4.2, p=9.16 x 10^{-9}).