End of Service Life Indicator

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Table of Contents

A. List of Terms and Abbreviations

AFC International	Accessories for Chromatography International
BCP	Bromocresol Purple
BRY	Brilliant Yellow
BV	Blue Violet
°C	Celsius degrees
CIE	International Commission on Illumination
CRC	Chemical Rubber Company
CO_2	Carbon Dioxide
DCM	Dichloromethane
ESLI	End of Service Life Indicator
HAZMAT	HAZardous MATerials
HCl	Hydrogen Chloride
HCN	Hydrogen Cyanide
IS&T	Imaging Science and Technology
Ind	Indicator
IPA	Isopropyl Alcohol
i-PrOH	Isopropanol
FIC	Flow Indicator Control
g	grams; gas
γ-Al_2O_3	gamma aluminum oxide
GC	Gas Chromatography
HSO_3^-	Bisulfite ion
in	Inch
$KMnO_4$	Potassium Permanganate
L	Level of black and white
LiCl	Lithium chloride
m^2	Square meters
mM	milli-moles
Mn	Manganese
Mn(III)	Manganese 3^+ ion
Mn(IV)	Manganese 4^+ ion
Mn(VII)	Manganese 7^+ ion
MnO_2	Manganese (IV) oxide
MnO_4^-	Permanganate ion
MSA	Mine Safety Appliances
Na	Sodium
$NaHCO_3$	Sodium Bicarbonate
$NaMnO_4$	Sodium Permanganate
NaOH	Sodium hydroxide
NH_3	Ammonia
NH_4^+	Ammonium ion
NIH	National Institutes of Health
NIP	Non-Impact Printing
NIOSH	National Institute for Occupational Safety and Health
NIST	National Institute of Standards and Technology
NPPTL	National Personal Protection Technology Laboratory
O	Oxygen atom
OH^-	Hydroxide ion

OSHA	Occupational Safety and Health Administration
PEL; P.E.L.	Permissible Exposure Limit
PI	Principal Investigator
P&ID	Process and Instrumentation Diagram
pH	Power of Hydrogen
pK_a	Power of Acid Equilibrium Constant
ppm	parts per million
PVC	Polyvinyl Chloride
R	Response
RH; R.H.	Relative Humidity
R-O	Red-Orange
R-Y	Red-Yellow
Ref	Reference strip
S	Solenoid Valve
SBIR	Small Business Innovation Research
SCBA	Self-Contained Breathing Apparatus
SO_2	Sulfur Dioxide
SRI	Company name; formerly Stanford Research Instruments
TDA Research, Inc.	Company name; formerly Technology Development Associates
TIC	Toxic Industrial Chemical
TOC	Toxic Organic Compound
TWA	Time Weighted Average
VOC	Volatile Organic Compound
wt%	Weight Percent
Y-B	Yellow-Blue
Y-BV	Yellow-Blue Violet
YIC	y-axis Event Indicator Controller
Y-R	Yellow-Red

B. Abstract (500 words or less)

Gas masks and respirators employing activated carbon, with or without additives, to remove a wide variety of air-borne toxic substances, have been in use for well over 100 years. In this Small Business Innovation Research Phase I project, the goal was to develop and test indicators that changed color as the protective carbon reached its end-of-service life, but with about 20% of its service life remaining in order for the user to evacuate the area and replace the cartridge with a fresh carbon air filter. Three types of colorimetric indicator were tested in Phase I and are under further development in Phase II. One indicator is for detection of organic compounds and changes color when exposed to a variety of toxic organic chemicals. This indicator was tested extensively against 400 parts per million by volume isopropyl alcohol (the upper permitted exposure level), in various level of relative humidity (5, 50 and 90% relative humidity), at room temperature (20°C), as recommended by staff at the National Personal Protection Technology Laboratory. This indicator changes color as it oxidizes organic substances and works well with other easily-oxidized alcohols such as methanol and ethanol. It was also tested against the aromatic hydrocarbon, toluene, and worked well. In Phase II, many additional toxic organic compounds of interest in occupational health will be tested. A second indicator changes color upon exposure to acid gases and was tested against sulfur dioxide, also in 5, 50 and 90% relative humidity at 20°C and worked well. Phase II will test this acid indicator against hydrogen chloride and other acid gases of concern to worker health. A third indicator is designed to change color upon exposure to basic gases and was tested in Phase I against ammonia, and worked well in 5, 50 and 90% relative humidity at 20°C. Ammonia has been of growing concern for the estimated 700,000 workers in agriculture, who are increasingly exposed to toxic levels of ammonia released from concentrated animal feeding lots. Exposure to toxic levels of ammonia can lead to a variety of respiratory illness as well as to blindness. In Phase I, color changes were rigorously quantified by standardized procedures of the International Commission on Illumination. Additional tests were run for all three indicators at -10°C and +40°C (just above body temperature of +37°C), and all performed well. A prototype respirator was designed, built and tested with the three types of colorimetric indicator, each placed next to a reference color band with fixed color for comparison. In Phase II, formulations of the colorimetric indicators are to be optimized to achieve extended shelf life of approximately three years and to minimize premature color changes due to storage, photodecomposition, and exposure to the carbon dioxide (an acid gas) of the atmosphere and other substances off-gassing from the activated carbons and respirator wall materials.

C. Section 1 (2-page limit)

Introduction

The overall goal of the Phase I project was to identify indicators that change color upon exposure to toxic organic chemicals, acid gases and basic gases. These were to be non-specific, and change color within respirators upon exposure to a wide variety of toxic substances when their concentrations exceeded permissible exposure limits that are typically in the parts per million by volume range. The color changes would signal the respirator users that the respirator was approaching its end-of-service life, with about 20% of its lifetime remaining, so as to give adequate warning and time to evacuate the toxic environment and change the respirator cartridge. Furthermore it was necessary that the indicators possess adequate storage life so as not to change color for approximately three years during storage (as typical for respirator cartridges) and not to change color upon exposure to benign substances in the atmosphere such as normal levels of carbon dioxide. Three color-changing indicators were identified: permanganate for toxic organic substances, bromocresol purple (an organic dye) for acid vapors such as sulfur dioxide, and brilliant yellow (another organic dye) for basic gases and especially ammonia. The latter is of increasing concern for the over 700,000 agricultural workers now exposed to high levels of ammonia at concentrated animal feedlots. Ammonia readily dissolves in the moist tissues of the lungs and eyes and can lead to a wide variety of respiratory disease and blindness.

Significant (Key) Findings

Sodium Permanganate found to be Superior to Potassium Permanganate for the Toxic Organic Substance Indicator. Although potassium permanganate has been used for many years as a color indicator and changes color from a deep purple to a tan-brown when it oxidizes organic compounds, it has a number of issues. Potassium permanganate has limited solubility in water, causing it to precipitate and plug pores of its supports. This blocks access of the organic substances to the permanganate. Sodium permanganate was found to be far more soluble in water and could be more readily dispersed upon high-surface area supports such as gamma alumina. It was realized that water is critical for the oxidation reactions of permanganate due to formation of the highly reactive hydroxide radicals, ·OH. The sodium permanganate was found to be a superior deliquescent substance, attracting the necessary moisture from the air, and allowing oxidation of a wide variety of organic substances. Sodium permanganate was deemed superior to other permanganates such as those of lithium, calcium and barium.

Nano-porous Gamma Aluminum Oxide Found to be a Superior Support for Sodium Permanganate. Many high-surface area materials were considered as supports for the sodium permanganate. A special type of gamma alumina, often used as a catalysts support, was found to be especially effect for sodium permanganate. The optimum alumina has high surface area and also a pore-sixe that readily accommodates the sodium permanganate. The gamma alumina is also deliquescent and aids adsorption of the necessary moisture from the air. The hydrophilic nature of the support also readily adsorbs hydrophilic organic substances and especially alcohols including methanol, ethanol and isopropanol. Moreover, the selected type of aluminum also has a high concentration of Lewis and Brønsted acid site that readily adsorb non-polar, hydrophobic organic molecules such as toluene. Thus this alumina support allows adsorption of both hydrophilic and hydrophobic organic compounds, allowing their oxidation by permanganate, and is critical for non-specific colorimetric indicators that must change color when exposed to a very wide variety of organic substances.

Addition of Sodium Bicarbonate Makes System Slightly Alkaline, Increasing Activity, Shelf Life and Stability against Carbon Dioxide. Addition of sodium bicarbonate, $NaHCO_3$, (common baking powder) to the alumina support was used to increase alkalinity to pH > 7, and thus concentration of hydroxide ions, OH^-, desired in the permanganate oxidation reactions. Systems with slightly alkaline pH (pH > 7) are also known to increase permanganate shelf life indefinitely, when stored in the dark to avoid photochemical reactions. The bicarbonate ion, also acts as an excellent buffer, retaining the desired pH and limiting reaction with atmospheric CO_2, an acidic gas.

Bromocresol Purple Identified as an Acid–Gas Indicator; Brilliant Yellow as the Basic Gas Indicator. Although many dyes change color with change of pH, bromocresol purple and brilliant yellow change color in a pH range that avoids interference by the acid gas, CO_2, which forms H_2CO_3 in aqueous solution. Many other organic dyes would change color upon exposure to atmospheric CO_2. It was also realized that water is critical for function of the dyes. The deliquescent substance, LiCl, was added to the dye support to attract moisture from the air allowing transfer of protons, H^+, as H_3O^+, which bind to the dye and change its color.

Translation of Findings. Indicators were identified in Phase I that changed color in a prototype respirator under laboratory conditions when tested in 5%, 50% and 95% relative humidity and at minus 10°C, 20°C and 40°C with a variety of toxic gases used at concentrations just above their permitted exposure levels. These color indicators look promising for further development in Phase II and tests with a wider variety of toxic substances. Upon further testing, the color indicators could be placed within transparent windows of respirators, giving wearers adequate warning that their masks are reaching their end of service life.

Outcomes/Impacts. The Phase I tests look promising in that the color indicators have the potential to be mass-produced at reasonable cost and placed within existing respirators and gas masks and change color in time to give wearers adequate warning to evacuate the toxic area and to change the respirator cartridge before it is fully saturated and before the toxic substance can reach the wearer at toxic levels. Due to time and budget constraints, the Phase I color indicators were tested against a limited number of toxic agents. However, the results appeared sufficiently promising as to predict that the permanganate would be effective against a much wider variety of easily-oxidizable organic substances, and should be further tested in Phase II with many organic substance of concern in occupational health. Likewise, the acid and base gas indicators showed promise that they would change color upon exposure to many acidic and basic substances, which could be demonstrated in Phase II.

D. Section 2

Project Period

September 1, 2009 to August 31, 2010

D.1 Listing of Key Personnel

Name	Position	Dates	Hours
Girish Srinivas	P.I.	09/2009 – 08/2010	94
Brady J. Clapsaddle	Scientist	09/2009 – 08/2010	181
Michael V. Mundschau	Senior Scientist	07/2010 – 08/2010	
Steven C. Gebhard	Senior Engineer	09/2009 – 08/2010	30
Andrew D. Galloway	Materials Engineer	09/2009 – 08/2010	468
Michael J. Looker	Technician	09/2009 – 04/2010	85

D.2 Summary of Specific Aims

As stated in the Phase 1 proposal, the specific aims of this project were:

Aim 1: Build a test apparatus that permits us to generate precise and verifiable concentrations of contaminant gasses (e.g. TOCs (Toxic Organic Compounds), acid gases, etc.) for testing the ESLI (End-of-Service-Life Indicator).

Aim 2: Prepare substrate-supported indicator strips for indicator color-change sensitivity tests.

Aim 3: Test the colorimetric indicator sensitivity using at least three contaminant vapors at different concentrations, temperatures, and relative humidity levels.

Aim 4: In collaboration with our industrial partner, Mines Safety Appliances (MSA), construct and test a prototype device.

Aim 5: In collaboration with MSA, perform an engineering analysis to estimate the costs of manufacturing commercial ESLIs for carbon gas mask cartridges.

D.3 Phase I Results

D.3.1 Executive Summary

TDA Research, Inc. (TDA) and Mines Safety Appliances (MSA) have collaborated to develop and test a colorimetric End of Service Life Indicator (ESLI) for activated carbon cartridges used on personal respirators such as MSA's Comfo Classic® (Figure 1; MSA 2008). The goal of the Phase I project was to develop and test an ESLI in a full-scale prototype of an activated carbon respirator filter cartridge so that tests could be performed with the ESLI incorporated into an actual product canister. Activated carbon-filled respirator cartridges have been used as adsorptive filters in gas masks since the early 1900s (Mantell 1951), but a persistent drawback is that there is no simple way to know if the chemical protection capability of a respirator cartridge has been compromised (Favas 2005). What is needed is a simple device that indicates that the respirator cartridge is either used up or unsuitable for use. The ESLI will be built into the respirator cartridge as part of the original manufacturing process (it is not an addon component), and in fact must be incorporated during manufacturing in order to obtain NIOSH certification.

Integrating a device into the activated carbon filter that changes color just prior to exhausting the capacity of the activated carbon is one way to indicate that no capacity remains for removing hazardous vapors from the atmosphere. Several non-hazardous, chemical colorimetric indicators currently exist that undergo a high-contrast color change when exposed to a large variety of toxic industrial chemical (TIC) vapors, including volatile organic chemicals (VOCs), acid gases, and basic gases. By integrating these indicator chemicals into an array, a visual ESLI can be constructed that allows the user of the gas mask to unambiguously determine if the capacity of an activated carbon respirator cartridge is approaching saturation. In TDA's design, the ESLI is a thin band that is located toward the exit of the cartridge. A layer of activated carbon between the ESLI and the cartridge exit gives the wearer time to leave the hazardous location and replace the cartridge with a new one once the ESLI indicates the cartridge is approaching expiration. The part of the housing where the ESLI is located is made from a clear plastic such as polycarbonate. In this configuration, as the carbon reaches its adsorptive capacity and vapors begin to break through (this is well before the bed is totally saturated) the vapors react with the indicators, producing color changes that indicate that the cartridge must be replaced.

In the Phase I project, with the help of its collaborator MSA, TDA has successfully designed, fabricated, and demonstrated this ESLI prototype incorporated into an activated carbon-filled respirator cartridge. As part of the ESLI prototype design and development, TDA selected appropriate colorimetric indicators for colorimetric detection of the three major classes of TICs, VOCs, acid vapors, and basic vapors. Following the loading of these indicators onto compatible support (substrate) materials, the indicators' sensitivity and color change magnitudes were evaluated using the CIE (International Commission on Illumination) Lab quantitative color system (CIE, 1986) and various contaminant gas concentrations under a variety of environmental conditions in which temperature and relative humidity were varied. Based on these results, TDA selected three colorimetric indicators for incorporation into its ESLI prototype – bromocresol purple (acid gas indicator), brilliant yellow (basic gas indicator), and sodium permanganate (VOC indicator). The choice of these three indicators in the prototype ESLI enables the ESLI to indicate that saturation of the gas mask carbon bed has been reached for any of the three major classes of TIC vapors; for operation of this ESLI, if a color change of any of the three indicators is observed to change, the gas mask activated carbon cartridge must be replaced. Following prototype fabrication, the prototype was demonstrated to respond to carbon bed saturation for all three vapor classes, as well as mixtures of vapor containing either VOC and acids, or VOCs and bases. During the testing and demonstration of the ESLI prototype, no mechanical failures of the device were observed and bed saturation was consistently indicated.

The successful fabrication and testing of TDA's ESLI prototype demonstrates the effectiveness of an inexpensive, colorimetric ESLI for indicating the expiration of activated carbon respirator cartridges. TDA's concept for developing a simple, inexpensive, colorimetric ESLI for use in carbon cartridge gas mask filters can be used as a basis for optimizing the design and constructing a manufacturing prototype in Phase II.

D.4 Detailed Discussion of Phase I Results

D.4.1 Background

There are hundreds of toxic industrial chemicals (TICs) that have vapor pressures high enough to pose an inhalation hazard to workers. First responders and chemical workers must be able to function in environments where chemical hazards are present. Industrial workers need protection against hazardous chemicals used in the workplace and HAZMAT personnel need respiratory protection when dealing with chemical spills, methamphetamine labs, and other cleanup operations. In the event of exposure to chemical vapors/gases from an industrial or environmental accident, respiratory protection is particularly important. Two types of protection are typically used: supplied air and adsorptive filters. Supplied fresh air is the most effective type of protection and is exemplified by the self-contained breathing apparatus (SCBA). Unfortunately, using a SCBA requires carrying a relatively heavy tank of compressed air that lasts generally 30 minutes or less. Hoses instead of a tank can supply fresh air, but this requires a compressor that is located in a contaminant-free area and limits the user's mobility to the hose length. As a result, supplied air systems severely limit either mobility or use time.

Gas adsorption by activated carbon is the basis of the gas mask that was first developed in the early 1900s; the basic design has not changed much since then (Mantell 1951). The modern gas mask has a vapor tight polymer face piece that is equipped with windows and a cartridge containing activated carbon that filters the inhaled air. Most modern masks have a check valve so that exhaled air passes out of the valve rather than back through the activated carbon cartridge to make breathing easier (Figure 1). As air is inhaled through the activated carbon in the cartridge, hazardous contaminants physically adsorb on the carbon surface, and because activated carbons can have surface areas of 1000 m^2/g or greater, reasonably large amounts of contaminants can be removed with a single cartridge.

The main problem with current carbon cartridges is that there is no simple way to determine if the protective capacity of a respirator cartridge has been used up; to date, no simple technology has been developed that allows the user to determine if the chemical protection capability of a respirator cartridge has been reduced by exposure during storage, or by saturation with gases while it is in use (Favas 2005). For storage, manufacturers simply mandate a shelf life of three years, after which the cartridge is to be replaced. When in use, the carbon cartridge lifetime is much shorter (hours to days) and is estimated based on the air concentration of contaminants in the work environment. In either case, the use of gas masks containing carbon filter cartridges is subject to strict change-out schedules to ensure that their gas mask cartridges are not used-up and unsafe. If the user exceeds this strict change-out schedule, the first sign of a spent cartridge is usually odor, which is dangerous and unreliable at best (peoples sense of smell is notoriously variable). The incorporation of an end of service life indicator (ESLI) that will indicate the actual lifetime of a cartridge will allow consumers of gas masks to obtain the maximum use out of a cartridge without compromising safety and without the need for costly overstocking of spare cartridges.

Figure 1. MSA carbon cartridge respirators.

There are two main factors that determine when an activated carbon respirator cartridge needs to be replaced: 1) whether the carbon has been contaminated during storage, and 2) whether the capacity of the cartridge has been reached during use. Any substance that adsorbs on the activated carbon (during use or storage) will reduce the capacity of the carbon for removing hazardous vapors. One potential source of contamination is organic vapors found in the work place during storage (i.e. solvents, equipment exhaust, etc.). For this reason, a new cartridge must be sealed from air exposure while being stored, and without an ESLI, must be replaced every 3 years (even if the integrity of the seal is good; MSA 2008). Between uses the respirators (with cartridges installed) are stored in special bags (Figure 2; AFC International, 2008) to prevent exposure to atmospheric contamination. Unfortunately, since there is no way to know if the bag is completely sealed and leak-proof, the cartridges must still be replaced every 3 years as a standard precaution.

Figure 2. Respirator and storage bag .

Current ESLI Technologies. End of Service Life Indicators (ESLIs) can be broadly categorized as either active or passive. Active devices use electronic chemical sensors (*e.g.,* semiconductors), thermistors, light absorption, fluorescence, etc. to detect the presence of contaminants breaking through the main carbon bed in the gas mask canister. One advantage of electronic devices is that they can be extremely sensitive, however, electronic devices are also complex, prone to failure, require carrying a power supply, and are expensive to manufacture (Favas 2005). While active devices may be suitable for highly specialized applications, they are not inexpensive, simple solutions that can be used for routine applications, and thus have never been widely used.

Passive ESLIs do not require power or electronics and are typically based on colorimetric chemistry or the release of odorants that are displaced by the contaminants being adsorbed (Favas 2005). As an example of the latter approach, one design described by Favas uses a small device located inside the charcoal canister that contains carbon saturated with isoamyl acetate (banana oil). When the hazardous industrial chemical is more strongly adsorbed than isoamyl acetate, the latter is displaced. By placing the isoamyl acetate device near the exit of the carbon bed, the user will smell bananas when the cartridge is almost spent. The main problems with this approach are different olfactory sensitivities from person to person and the necessity for the contaminant to adsorb strongly enough to the carbon that it can displace the isoamyl acetate at contaminant concentrations that are not hazardous. If the contaminant does not adsorb much more strongly than the isoamyl acetate, the contaminant can breakthrough before the user smells bananas. As a result NIOSH does not consider this a viable approach for ESLIs.

Colorimetry. Colorimetric indicators use the change in the color of chemical compounds when they react with contaminants to tell the user when the contaminants are present. Colorimetry is commonly used in gas detection and quantification due to its sensitivity and the ease of "detection" by the user. The human eye can detect over 256,000 variations in color (Color Matters, 2008), thus a color change indicating the presence of a gas can be easily detected by the human eye. As a result, for most colorimetric gas indicators, very small levels (ppb) of gas are enough to effect a noticeable color change to the user (Rutkowski, 2008). In addition, colorimetric assays, since they are well characterized and need no electronics, are extremely cheap to incorporate into safety devices. This is a key requirement since safety devices are sold to a very cost-conscious market.

Colorimetric indicators can be grouped into two classes – non-specific and specific. Using acidic gases as an example, a non-specific indicator used for detecting acid gases would detect all acid gases (such as SO_2, HCN and HCl), but would not indicate to the user which gas it was detecting, only that an acid gas was detected. A specific indicator would not necessarily indicate that all gases in a class of vapors are present, but would be able to tell the user what <u>specific</u> gas was present. A specific indicator, again using acidic gases as an example, would indicate the presence of SO_2 <u>or</u> HCN, but would <u>not</u> respond to both or other acid gases. Finally, some specific indicators may be able to detect multiple gases, but would distinguish between them by presenting different color changes (i.e. HCN may cause a color change from red to orange and SO_2 may cause a color change from red to yellow).

Table 1. Acid-base indicators (Dean 1999).

Indicator	Chemical name	pH range	pK_a	λ_{max}, nm	Color change
Cresol red (acid range)	*o*-Cresolsulfonephthalein	0.2–1.8			R-Y
Cresol purple (acid range)	*m*-Cresolsulfonephthalein	1.2–2.8	1.51	533, —	R-Y
Thymol blue (acid range)	Thymolsulfonephthalein	1.2–2.8	1.65	544, 430	R-Y
Tropeolin OO	Diphenylamino-*p*-benzene sodium sulfonate	1.3–3.2	2.0	527, —	R-Y
2,6-Dinitrophenol	2,6-Dinitrophenol	2.4–4.0	3.69		C-Y
2,4-Dinitrophenol	2,4-Dinitrophenol	2.5–4.3	3.90		C-Y
Methyl yellow	Dimethylaminoazobenzene	2.9–4.0	3.3	508, —	R-Y
Methyl orange	Dimethylaminoazobenzene sodium sulfonate	3.1–4.4	3.40	522, 464	R-O
Bromophenol blue	Tetrabromophenolsulfone-phthalein	3.0–4.6	3.85	436, 592	Y-BV
Bromocresol green	Tetrabromo-*m*-cresol-sulfonephthalein	4.0–5.6	4.68	444, 617	Y-B
Methyl red	*o*-Carboxybenzeneazo-dimethylaniline	4.4–6.2	4.95	530, 427	R-Y
Chlorophenol red	Dichlorophenolsulfone-phthalein	5.4–6.8	6.0	—, 573	Y-R
Bromocresol purple	Dibromo-*o*-cresolsulfone-phthalein	5.2–6.8	6.3	433, 591	Y-P
Bromophenol red	Dibromophenolsulfone-phthalein	5.2–6.8		—, 574	Y-R
p-Nitrophenol	*p*-Nitrophenol	5.3–7.6	7.15	320, 405	C-Y
Bromothymol blue	Dibromothymolsulfone-phthalein	6.2–7.6	7.1	433, 617	Y-B
Neutral red	Aminodimethylaminotolu-phenazonium chloride	6.8–8.0	7.4		R-Y
Phenol red	Phenolsulfonephthalein	6.4–8.0	7.9	433, 558	Y-R
m-Nitrophenol	*m*-Nitrophenol	6.4–8.8	8.3	—, 570	C-Y

The most common non-specific indicator is potassium permanganate ($KMnO_4$), which changes from pink/purple to tan/brown. The permanganate ion (MnO_4^-) is a strong oxidizer that changes color from purple (or pink when dilute) to tan when the Mn(VII) in the permanganate ion is reduced to a combination of lower valence compounds (i.e. Mn(II), Mn(III) and Mn(IV)). As a result of its oxidizing strength, the permanganate ion will oxidize most organics, including hydrocarbon vapors (i.e. aromatics, olefins, aldehydes, alcohols, ketones, ethers, saturated hydrocarbons, etc.), and the color change of the permanganate ion indicates that the oxidation reaction has occurred. To date $KMnO_4$ has been used as an indicator for exposure to vinyl chloride (a carcinogenic monomer for PVC plastic), acetone, methanol, ethanol, acrylonitrile, and stable hydrocarbons in water, to name <u>only</u> a few (Eian, 1982; Favas, 2005; Intertek, 2008; Rannamae, 2001). The fact that all these organic vapors are indicated by $KMnO_4$ shows that this indicator is general (i.e., non-specific) for detection of a large number of other hydrocarbon-containing toxic compounds, such as halogenated solvents (i.e. chloroform), polymer precursors, and even traditionally unreactive saturated hydrocarbons.

The easiest TICs to detect are acid (e.g. SO_2, HCl) and basic gases (e.g. NH_3), which change the color of pH indicators. A variety of acid/base indicators are available, as shown in Table 1. Acid/base indicators are non-specific in that they do not identify the composition of the acid or base, but merely change colors when one or the other is present, and many will detect any acid or base vapor. Acid/base indicators are typically organic dyes that contain aromatic structures (Table 1). The delocalized nature of the aromatic structures permits many of these dyes to absorb light in the visible region of the electromagnetic spectrum. The dyes work as acid/base indictors when the colors (electronic energy levels) are different for the acidic and basic forms of the dyes. In fact, one of the better methods to use for detecting these gases is to prepare the opposite version of the acid-base indicator (rather than using the neutral molecule). When acid gas reaches the base-form indicator, the color changes to that of the neutral/acid form; similarly the acid form of the indicator is used to detect ammonia, amines and other basic vapors. By proper choice of indicator (i.e. choosing the right pK_a), atmospheric CO_2 (ca. 300 ppm) will not cause false positives.

TDA's Approach. TDA Research Inc. (TDA), along with its industrial partner Mine Safety Appliances (MSA) North America, proposed to develop a simple, inexpensive ESLI that would give a quick visual indication of whether an activated carbon respirator cartridge will soon be spent. TDA's ESLI is intended to be an integral part of the activated carbon respirator cartridge and can be easily incorporated during the manufacture of the cartridge. The ESLI uses a series of colorimetric indicator bands that contain chemical indicators supported on compatible substrates that are placed in the cartridge such that a "reserve bed" of carbon remains behind the ESLI to allow time for the cartridge to be replaced upon expiration. As contaminated air is inhaled through the respirator cartridge, eventually contaminants will start to break through the carbon bed. When the resulting vapor-front reaches the ESLI, the appropriate indicating layer will change color to signal the arrival of the vapors towards the back of the cartridge carbon bed. Because the user needs some warning that the cartridge needs to be changed out, there is a small "reserve" carbon bed located downstream of the ELSI. *It is important to note that while a mask may contain multiple indicators, once any single indicator has changed color, the entire cartridge should be replaced; the mask's integrity is compromised following the breakthrough of any one single contaminant. Also, because the ESLI is used for a simple replace/don't-replace decision, there is no need to interpret subtle color changes for any of the indicators of the ESLI, since each indicator undergoes a high-contrast color change.*

In the Phase I project, TDA's goal was to choose colorimetric gas indicators and develop a simple, colorimetric device that demonstrated simultaneous detection of multiple classes of chemical vapors and not just a single, specific gas. The versatile design of the TDA ESLI prototype (Figure 3) is able to accommodate multiple indicators as required for different types of carbon cartridges and classes of TICs. In fact, even if a mask is intended for use against acid gases, its capacity can be used-up by organic gas adsorption, therefore, ESLIs that detect multiple classes of TICs are a good idea in any mask. For these purposes, TDA has chosen to use non-specific indicators for its ESLI prototype. By using non-specific indicators, TDA has developed an ESLI that could be used for gas masks that protect against single gases; however, the innovation in TDA's ESLI is that it will detect all-important classes of TICs. Therefore non-specific indicators are needed to ensure that the majority (if not all) of the TICs in a given class (i.e. organic, acid, base) are detected without using a large number of indicators. We are not building a sensor to tell the user what is in the air around them; we are building a safety device to let them know they need to replace their gas mask cartridge. What matters once the capacity of the carbon bed has been reached is that some vapors are about to break through, not what vapors are about to break through. The function of the ESLI is to protect the user against exposure to ANY potentially harmful gases that are in danger of breaching the gas mask filter, not to tell them WHAT gases are present.

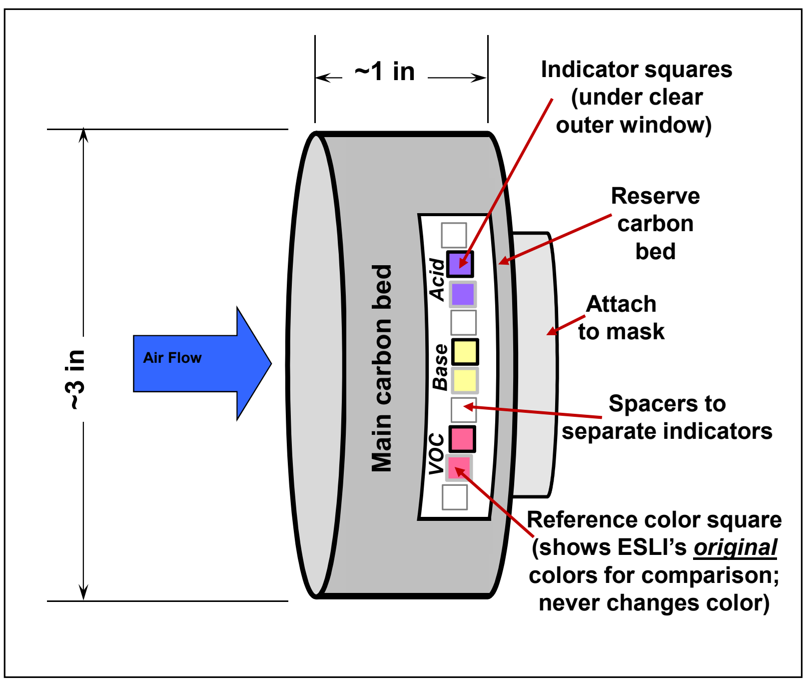


Figure 3. TDA End of Service Life Indicator (ESLI) integrated in to a respirator cartridge.

TDA used both permanganate and acid/base indicators (bromocresol purple and brilliant yellow, respectively) to demonstrate its gas mask ESLI concept. The chosen indicators were loaded onto appropriate support materials and subsequently exposed to various contaminant gases in order to evaluate their use as indicators for the proposed gas mask ESLI. Following identification of appropriate colorimetric indicators and support materials, TDA constructed several prototype ESLIs and incorporated them into activated carbon-based gas-mask cartridges. For demonstration purposes, TDA's collaborator, Mines Safety Appliances (MSA), supplied transparent gas mask cartridges for the incorporation of our colorimetric ESLI prototype; in this manner, TDA was able to tests its prototype in a real gas mask in which the visually detectable color changes could be observed upon exposure of the prototype carbon cartridge to contaminant gases.

Figure 3 shows a schematic diagram of TDA's prototype ESLI design for gas masks cartridges. The ESLI prototype contains multiple bands of indicating chemical for the multiple vapor contaminants (acid, base, organic vapors) that the respirator cartridge is designed to protect against. A non-changing, reference color band is located adjacent to each indicator showing the indicators' original color. The reference color band allows the user to unambiguously verify whether a color change has occurred; it is far easier for a user to notice that the indicator is different from the adjacent strip than to remember the "unexposed" indicator color and then try to determine if the color has changed. Once a color change is observed *in any of the indicators*, the cartridge has no remaining service life and needs to be replaced. The presence of the "reserve" carbon bed behind the ESLI gives the user time to replace the cartridge. Additionally, the ESLI will also alert the user if the cartridge has been contaminated during storage. Normally, cartridges are sealed during storage across their front face at the point where it attaches to the mask and these seals are removed just prior to use. *If the ESLI changes color prior to use (e.g. if there were a leak in the seal that protects the cartridge during storage), the user will know ahead of time if the cartridge's capacity has been unintentionally compromised, and will have the opportunity to discard it (and use a fresh cartridge).* This will save customers of respirator cartridges considerable money since they will not have to replace their entire inventory of cartridges every three years.

TDA's ELSI is intended to be an integral part of the activated carbon respirator cartridge and can be easily incorporated during the manufacture of the cartridge. In fact, any ELSI must be an integral part of the cartridge in order to obtain NIOSH certification (Rutkowski, 2008). TDA's ESLI would be simple and inexpensive and would provide a direct visual indication of the state (safe or expired) of the carbon canister on a respirator. This simple cartridge ESLI configuration, as confirmed in our conversations with MSA, could be easily incorporated into the canister manufacturing production line.

TDA's overall goal for the Phase I project was to develop a simple device that would simultaneously detect multiple classes of chemical vapors and not just a single, specific gas as is often the case in ESLI research. Thus, TDA's approach to a gas mask ESLI is both innovative and novel. The versatile design of the TDA ESLI (Figure 3) accommodated a large number of indicators as required for different types of cartridges (i.e. solvent vapors, acid gases, etc.) and caneasily be adapted to gas-masks that protect against both single or multiple toxic gases. In TDA's design, a single array of 3-4 non-specific indicators can protect a user of a gas mask from multiple classes of TICs. As a result, a novel, compact, passive device has been developed that can simultaneously detect large numbers of TIC vapors and prevent exposure to these chemicals.

For the development and demonstration of TDA's gas mask ESLI, The Phase I work plan consisted of five technical tasks.

1. Build a test apparatus that permits us to generate precise and verifiable concentrations of contaminant gasses (e.g. TOCs, acid gases, etc.) for testing the ESLI.
2. Prepare indicator strips for indicator color-change sensitivity tests.
3. Test the colorimetric indicator sensitivity at different concentrations, temperatures, and relative humidity levels.
4. In collaboration with our industrial partner, Mines Safety Appliances (MSA), construct and test a prototype device.
5. In collaboration with MSA, perform an engineering analysis to estimate the costs of manufacturing commercial ESLIs for carbon gas mask cartridges.

TDA has successfully completed all of the Phase I tasks. Completing these tasks has demonstrated that TDA's concept for developing a simple, inexpensive, colorimetric ESLI for use in carbon cartridge gas mask filters can be used as a basis for optimizing the design and constructing a manufacturing prototype in Phase II. In Phase II, TDA and MSA will optimize the ESLI and integrate it into an actual respirator carbon cartridge.

D.4.2 Phase I Results

The overall goal of the Phase I project was to identify and test colorimetric indicators that could be incorporated into an ESLI prototype for testing using realistic levels of test vapors in order to demonstrate a proof-of-concept ESLI that can be integrated into commercial activated carbon gas mask canisters. The prototype ESLI was designed to detect the three common types of toxic vapors: volatile organic chemicals (e.g. solvents), acid gases (e.g. HCl, SO_2) and basic gases (e.g. ammonia).

To accomplish this goal in the Phase I effort, where the main goal is to demonstrate the validity of our approach, we divided the project into five technical tasks. In Task 1, we built an indicator/prototype test apparatus. In Task 2, we prepared and optimized indicator test strips for testing in subsequent tasks. In Task 3, we performed indicator sensitivity testing using appropriate vapors at different concentrations, temperatures, and relative humidity. In Task 4, in collaboration with our industrial partner MSA, we constructed and tested a prototype device. Finally in Task 5, again in collaboration with MSA, we performed an engineering analysis to

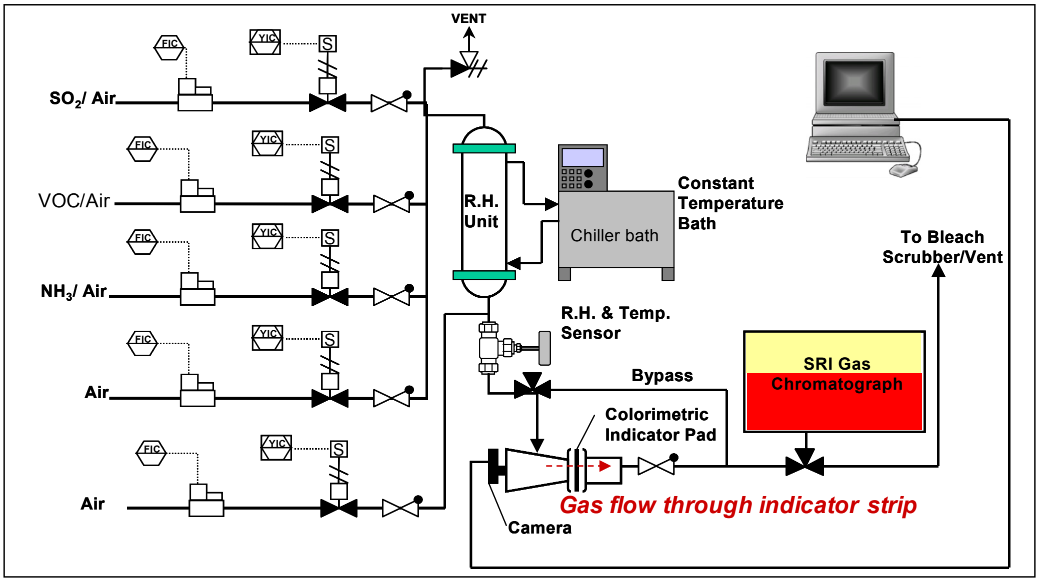


Figure 4. Process diagram for contaminant testing apparatus.

estimate the cost of manufacturing commercial units.

TDA has successfully completed all of the proposed Phase I work. The results of the Phase I effort are summarized in the sections below.

D.4.2.1 Task 1: Construction of the Challenge Contaminant Test Apparatus

The goal of Task 1 was to build a test apparatus that could be used to obtain the data needed to determine indicator sensitivity as well as design and test the Phase I prototype ESLI. The apparatus is able to deliver precisely known flow rates of air with precisely known concentrations of contaminants and is able to monitor the low levels of these contaminants in the test bed.

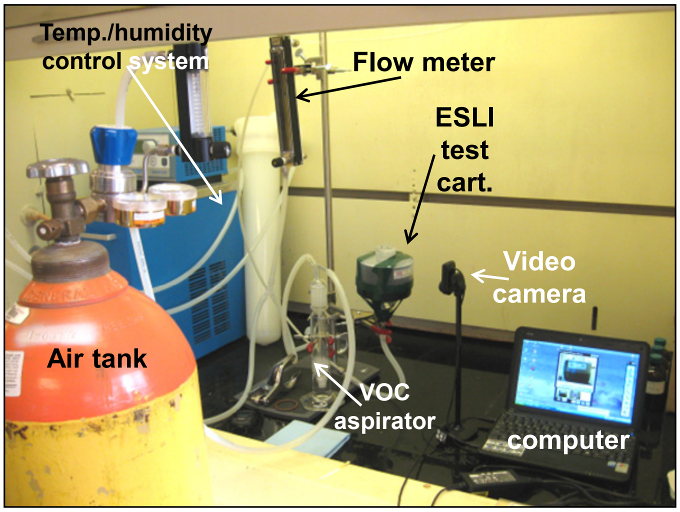


Figure 5. The vapor test apparatus showing testing of one of TDA's ESLI prototype test cartridges. For indicator testing, the prototype would be replaced with the customized test chamber (Figure 6).

Figure 4 is a simplified process and instrumentation diagram (P&ID) for the apparatus. In addition to controlling test vapor concentrations, the apparatus is also capable of producing and controlling different relative humidity levels in the test chamber, as well as different testing temperatures. The test apparatus works by using flow meters to precisely mix air streams containing the test vapors, humidified air, and dry air in appropriate ratios so that the desired concentration of test vapor and humidity can be achieved; this final air stream then flows through a constant temperature bath in order to achieve the desired testing temperature of the gas. A picture of the assembled vapor testing apparatus is shown in Figure 5.

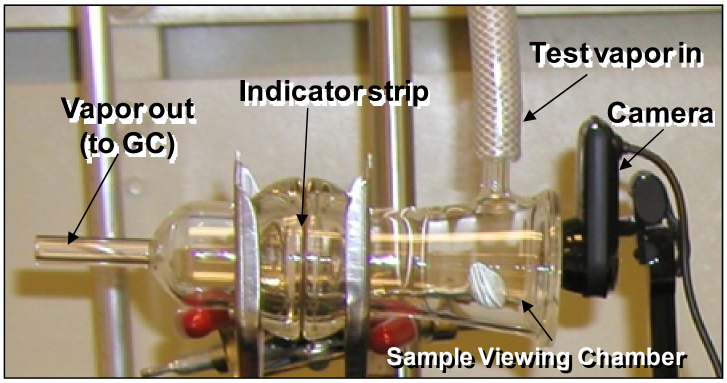


Figure 6. Custom-built transparent test chamber for indicator testing.

The final gas mixture then flows through a custom built test chamber. The transparent test chamber (Figure 6) consists of an indicator test strip holder that can be monitored using a digital camera that records the color change of the indicator strip in real time as the desired contaminant gas vapor flows over the test strip. If necessary, the gas exiting the test chamber can then be analyzed by gas chromatography (GC) to verify contaminant vapor concentration.

Using this test apparatus, following identification of indicators and preparation of appropriate indicator tests strips, evaluation of both TDA's indicator strip compositions (*i.e.*, indicator on a support) and the ESLI prototype was performed using this apparatus.

D.4.2.2 Task 2: Preparation of Indicator Test Strips

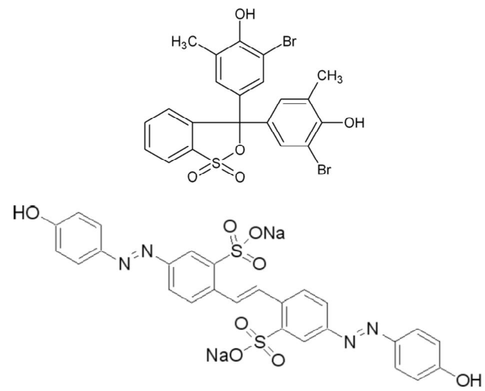


Figure 7. Chemical structures of the bromocresol purple (top) and brilliant yellow (bottom) acid and base colorimetric indicators, respectively.

Prior to testing the sensitivity of an indicator's color change using TDA's challenge contaminant apparatus, test strips containing the indicator were prepared. In Task 2, TDA prepared test strips for evaluation of indicator sensitivity by loading an appropriate support with the indicator. This task consisted of both choosing appropriate indicators for the three classes of test vapors (acid, base, VOC) as well as selecting and preparing a support material that was compatible with each indicator. The colorimetric indicators for the three types of contaminant vapors chosen for testing and our ESLI prototype were bromocresol purple (acid indicator; 5,5′-Dibromo-*o*-cresolsulfonphthalein), brilliant yellow (base indicator; 2,2'(1,2-Ethenediyl)bis[5-[(4-hydroxyphenyl) azo]benzenesulfonic acid]), and sodium permanganate (VOC indicator; $NaMnO_4$).

Once indicator and support materials were identified, considerable work was performed on optimization of the test strip composition and preparation. Prior to testing an indicator strip for color change against contaminant vapors, development of the indicator strip composition was rigorously studied and developed in order to prepare a test strip composition that was both stable to handling and storage, but still provided a relatively quick color change upon exposure to contaminant vapors; tuning the indicators' sensitivity to strike a balance between stability and activity is crucial for the development of an ESLI for respirator cartridges. Optimization of the indicator strips in this manner was challenging due to the fact that stabilization of an indicator would often prevent the indicator from providing the required quick color change. Thus, though the color changing chemistry of indicators is a mature technology, the innovation in TDA's approach lies in stabilizing the indicators on their respective support materials while still producing color changes quickly once exposed to contaminant vapors. Though not fully optimized in the Phase I project, TDA's indicator strips have been developed to the point that they can survive the necessary handling and storage required for TDA to fabricate both the indicator strips and prototype ESLI, as well as provide quick color changes once exposed to the contaminant vapors during indicator and prototype testing.

During the preparation of indicator strips for TDA's ESLI, we have identified several critical variables for the preparation of a stable but robust indicator strip. For the indicator strips prepared, support composition, pre-treatment of support materials, indicator composition, indicator loading levels, and indicator strip water content were the variables identified that had the greatest impact on the robustness and stability of the indicators chosen. Though not all variables are applicable to every indicator, in all cases, a subset of these variables were optimized in order to develop the three indicator (acid, base, VOC) test strip compositions required for the proof-of-concept demonstration during the Phase I testing. Though a complete description of the development of each indicator strip is not possible, a summary of the indicator formulations chosen and the important variables for the optimization of the indicator strips is summarized below.

Figure 8. Color change of bromocresol purple upon exposure to acid (SO_2) vapors.

Acid Indicator Strips. The final acid indicator strip consisted of bromocresol purple (BCP) supported on cellulose 20-25 μm diameter pore filter paper (Whatman®, 2010). A picture of the color change (purple to gray) of the indicator strip upon exposure to acid vapors (SO_2) is shown in Figure 8. The initial indicator chosen for the acid vapors was bromocresol green, however, upon initial testing, it was found that this indicator did was not sensitive enough for use in our ESLI; bromocresol green is not observed to change colors until a pH of 3.8 is reached, whereas BCP gave a vivid color change over the entire acidic pH range (*i.e.*, pH <6.8).

In choosing a support for the BCP indicator, we initially chose a non-woven, polypropylene fiber mat; this polypropylene mat was chosen due to its high porosity and gas permeability. Though the indicator was easily loaded onto the non-woven support and various loading levels, the indicator color change did not occur on this support when exposed to acid vapors unless it was first sprayed with water. It is believed that the hydrophobic polypropylene support prevented the hydrophyilic acid vapors from adsorbing to the loaded polypropylene indicator strip in order to react with the colorimetric indicator. As a result, we explored alternative acid indicator support materials, such as paper supports. The support chosen was Whatman #4 cellulose filter paper, which had ideal absorbency for indicator impregnation and gas permeability for exposure to vapors.

In developing the acid indicator strip formulation, the initial strips, prepared by soaking the cellulose paper in aqueous solutions of BCP, changed color relatively quickly upon impregnation of the paper due to the acidic nature of the paper in its untreated form. As a result, stabilization of the indicator on the paper was accomplished by adding sodium hydroxide (NaOH) to the bromocresol purple formulation. Sodium hydroxide has previously been noted to stabilize bromocresol purple (and other acid indicators) on paper substrates (Livermore, 2001); additionally, the use of excess NaOH serves to neutralize the acidic sites present on the paper substrate. In addition, as noted above for the BCP impregnated polypropylene support, a source of water was necessary in the indicator in order to speed up the color change. Since this water source needed to be present in the indicator strip as a solid, lithium chloride (LiCl), a deliquescent salt, was added to the acid indicator formulation to provide a source of surface-bound water for the BCP/acid color change reaction (Hanna, 1964). The combination of NaOH and LiCl in the final acid indicator strip provided a stable indicator strip that reacted quickly with acid vapors.

Following experiments to optimize the BCP/NaOH/LiCl indicator formulation, an indicator impregnation solution of 0.2 mM BCP, 8 mM NaOH, and 10 mM LiCl in 75% acetone–25% water was chosen for preparing paper substrates with a vivid indicator color that changed colors quickly upon exposure to acid vapors. It should be noted that optimization of the amount of NaOH used to stabilize the BCP is critical, as too much NaOH will result in a very slow color change, while not enough will result in an indicator strip that expires before it can be used (*i.e.*, stability vs. activity). Similarly, without the proper amount of LiCl in the formulation, the color change of the indicator is slow to respond in the presence of acid vapors. Once prepared, the acid indicator strips were stored in sealed plastic bags to protect against loss of sample moisture.

Base Indicator Strips. Preparation of the base indicator strips was very similar in nature to that described above for the acid indicators. The final base indicator strip consisted of brilliant yellow (BRY) also supported on cellulose filter paper. Brilliant yellow was chosen for our colorimetric indicator due to its sensitivity to basic vapors; BRY changes colors at pHs >6.7-8.0, thus a color change results over the entire spectrum of basic pHs (pH 7-14). A picture of the color change (yellow to red) of the base indicator strip upon exposure to basic vapors (NH_3) is shown in Figure 9.

Base indicator strips were also initially prepared on non-woven, polypropylene fibrous supports; however, for the same reason noted above for acid indicators, polypropylene supports did not produce color changes upon exposure to basic vapors. As a result, the same cellulose filter paper chosen for the acid indicator substrate was shown to work for the BRY base indicator. Unlike the acid indicators, since BRY is initially in its acidic form prior to reacting with a base to produce the color change, the presence of acidic sites on the paper substrate was not a problem for this indicator. The addition of LiCl to the base indicator formulation, however, was necessary, as the presence of surface bound water was also shown to be a necessary component for quick color changes of the supported BRY indicator. As a result, several solutions containing BRY and LiCl were tested to find the optimal paper impregnation formulation for preparation of the base indicator strips.

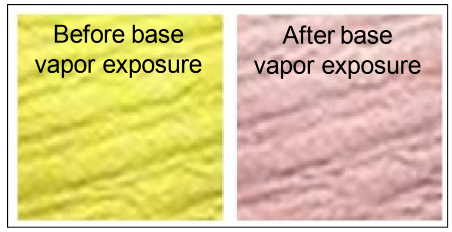


Figure 9. Color change of brilliant yellow upon exposure to base (NH_3) vapors.

Base indicator strips were ultimately prepared using a 75% acetone-25% water solution of 0.2 mM BRY and 10 mM LiCl. Optimization of this formulation consisted mostly of optimization of the water content in the indicator strip, which was controlled by the amount of LiCl that was added to the indicator formulation. As with the acid indicator, optimization of the amount of LiCl was important to the indicator formulation since too little resulted in a slow color change and too much made the strip too sensitive.

<u>*Volatile Organic Chemical (VOC) Indicator Strips.*</u> Of the three indicator formulations prepared for this Phase I work, the sodium permanganate ($NaMnO_4$) on γ-Al_2O_3 VOC indicator (color change pink/purple to brown; Figure 10) was the most difficult to optimize for stability and response. First, substrates that are organic in nature (*e.g.*, polymers, paper) or contain organics (binders, etc.) are easily oxidized by permanganate salts and thus cannot be used since they react immediately with permanganate upon loading of the substrate. Secondly, the color change produced by oxidation of organics by permanganate requires the presence of water to react (Gamson, 1962; Menger, 1979; Osborne, 1989; Lee, 1993). A large number of organic VOCs, however, are hydrophobic, resulting in a slow color change reaction due to the incompatibility of the water and organics. Thus, for the VOC indicator strips, it took quite some effort to find the right balance of water content on a non-reactive substrate to create the optimal balance of stability and sensitivity for the VOC indicators.

TDA explored the use of several substrates for its permanganate indicator; including non-woven polypropylene, filter paper, silicon oxide (SiO_2) and gamma aluminum oxide (γ-Al_2O_3). Ultimately, gamma-alumina (γ-Al_2O_3) was the only substrate that did not react with the permanganate anion immediately following impregnation; the compatibility of γ-Al_2O_3 with permanganate has been routinely noted in the literature (Roberts, 1976; McAllister, 1979; Lee, 1993). Following the selection of γ-Al_2O_3 as a support, we also incorporated sodium bicarbonate ($NaHCO_3$) to both neutralize γ-Al_2O_3 acid surface sites and stabilize the permanganate anion; permanganate is known to decompose under acidic conditions and can be stabilized in the presence of a solid base such as $NaHCO_3$ (Kuehner, 1954; England, 1999).

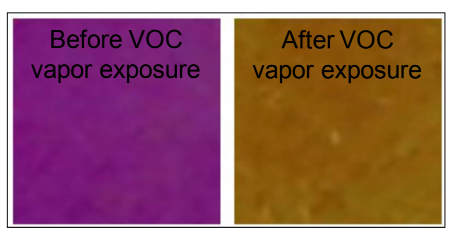


Figure 10. Color change of $NaMnO_4$ upon exposure to VOC (acetone) vapors.

Following the choice of γ-Al_2O_3 for use as a stable permanganate substrate, we worked on optimizing the color change chemistry, which required optimization of the indicator strip water content. TDA found it could best control the surface water content of its permanganate indicator by using the sodium salt ($NaMnO_4$) as opposed to the more common potassium salt ($KMnO_4$). Due to the increased solubility and deliquescent nature of $NaMnO_4$ as compared to $KMnO_4$ (Na-salt ~10x more soluble in water), we were able to lower the overall water content of our VOC indicator strip (Lonnes, 1976; Menger, 1981; CRC, 2006). As a result, our VOC strip was more compatible with hydrophobic organic VOCs, yet the formation of a crystalline permanganate salt in the absence of water (observed for $KMnO_4$) that makes the indicator unreactive was avoided (Lincoln, 1965).

The final, optimized VOC indicator strip formulation of $NaHCO_3$ stabilized $NaMnO_4$ on γ-Al_2O_3 disks had a water content of 8-12 wt%. When stored in a closed container (glass jar), the $NaMnO_4$ impregnated γ-Al_2O_3 was observed to be stable for >3 months with no observable color change.

D.4.2.3 Task 3: Indicator Sensitivity Measurements

The goal of Task 3 was to determine the sensitivities of the three indicator formulations upon exposure to appropriate vapors. The sensitivity of the ESLI depends on the intensity and contrast of the color change produced by a given contaminant concentration integrated over time. Thus, we conducted a series of experiments where we measured the intensity of the color change as a function of contaminant concentration at or below the test contaminant's PEL. For solvents and other toxic industrial chemicals (TICs), the chemical indicator needs to produce a visible color change at the OSHA TWA or PEL for the different classes of compounds. Once the PEL concentration has been reached for any class of compounds, it is time to change the cartridge. *One advantage of our design is that if any indicator shows that the cartridge is spent for that contaminant, the cartridge must be changed out; even if the cartridge has capacity remaining for other contaminants in the atmosphere.*

Figure 11. The difference in yellow color between the central square and any of the surrounding squares represents a *ΔEab** of 10.

Sensitivity of each indicator prepared in Task 2 was evaluated by measuring the magnitude of its color change under a variety of environmental conditions. Color change intensities (*ΔEab**) were quantitatively measured using the CIE L*a*b* color system (For a complete description of the CIE L*a*b* color system, the reader is referred to Appendix I of this report). The CIE L*a*b* color system describes all colors visible to the human eye in a three dimensional color space in which the three axes represent varying levels of black and white (L* axis), green and magenta (a*), and blue and yellow (b*) (CIE, 1986; Ohno, 2000). As a result of the 3-D graphical color system, a color change can be quantified by simply evaluating the magnitude of a line drawn between two graphical points that represent the colors before and after an indicator color change. Thus, by using a handheld colorimeter to measure the indicator color (in CIE L*a*b* color space) before and after exposure to test vapors, the color change of the indicator can be quantified by calculating the length of a line drawn between the before and after color-points using Equation 1; for the 3D CIE L*a*b* color system, Equation 1 is used for calculating a color change magnitude. For ease of reference as well as a visual reference of color change magnitude, are shown in Figure 11;

Equation 1.
$$\Delta E_{ab}^{*} = \sqrt{(\Delta L^{*})^2 + (\Delta a^{*})^2 + (\Delta b^{*})^2}$$

color changes as low as ΔEab^*=2.3 can be detected by the human eye (Fraser, 2004), however, we have found that $\Delta Eab^* \geq 10$ (Figure 11) are more easily seen and we therefore used this value as the lower limit for a detectable color change in our studies.

For these tests, the color of each indicator strip was first measured prior to exposer to an appropriate test vapor (acid gas, base gas, or VOC) at 10%, 50% and 90% of the gases PEL for 15 minutes; at that time, the test was ended, the color measured spectrophotometrically and the color change was calculated. Additionally, environmental conditions of temperature and relative humidity were also varied in order to determine the effect of such variables on the color change of the indicator. At each vapor concentration, 3 different temperatures and relative humidities were also evaluated, resulting in a total of 27 tests for each indicator strip (81 total tests for the three indicators). Under each test condition, the indicator color change was measured before and after exposure to the test vapors and a color change (ΔEab^*) was calculated.

The test gases chosen for evaluating the sensitivity of the indicator test strips represented each of the three main classes of toxic vapors and consisted of sulfur dioxide ($SO_2(g)$; acid vapor), ammonia ($NH_3(g)$; basic vapor), and *iso*-propyl alcohol (IPA; VOC). These test vapors were chosen based on testing input from our commercial collaborator, MSA, and Mr. Jay Snyder, lead scientist at NPPTL (National Personal Protection Technology Laboratory). Both SO_2 and NH_3 are common industrial gases requiring gas mask protection when working in environments where these gases are present. The choice of IPA

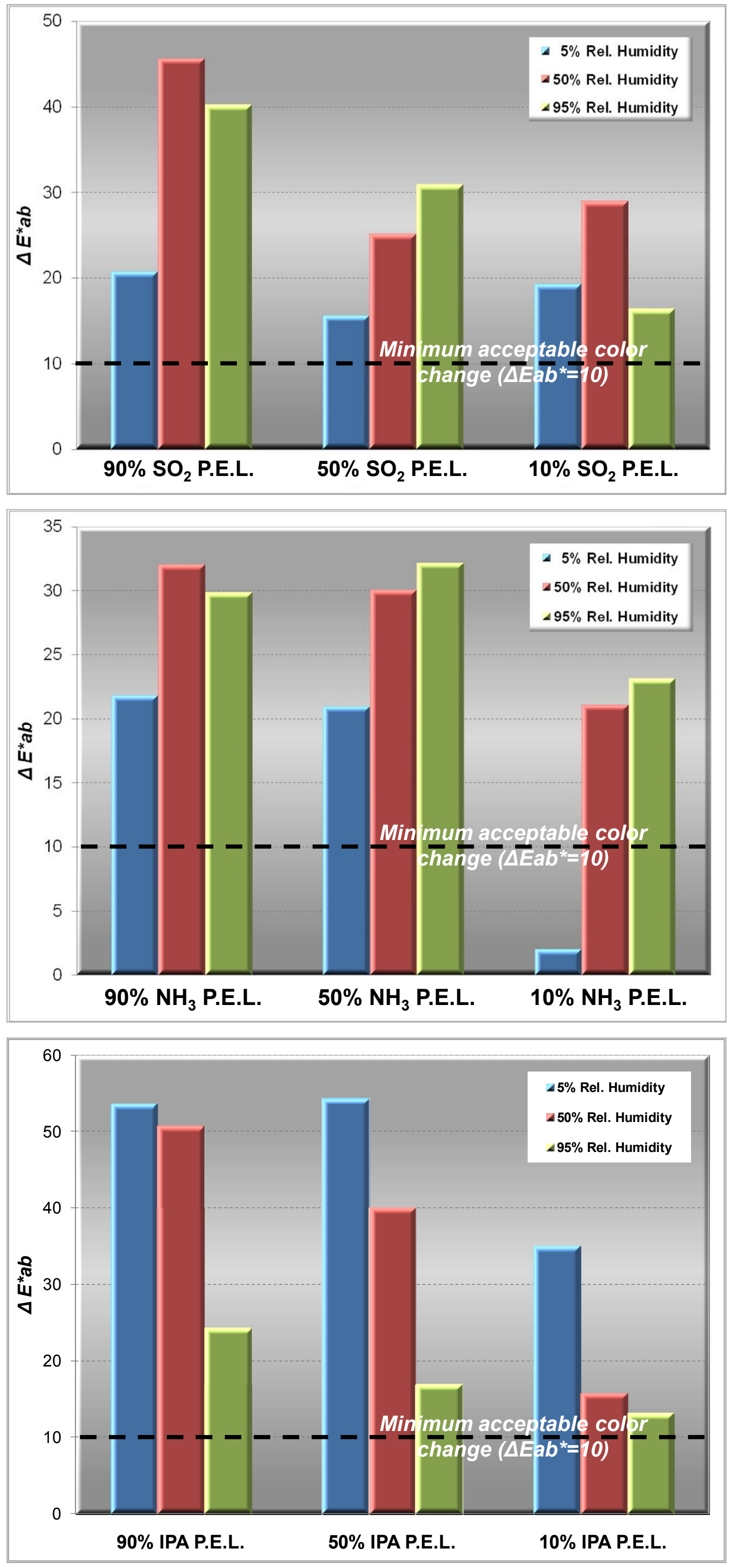


Figure 12. Indicator sensitivity test results at 20 °C and 5, 50, and 95% relative humidity. Top: acid indicator; middle: base indicator; bottom: VOC indicator.

was made based on the recommendation of Jay Snyder for the screening of similar devices; IPA is a common industrial solvent, and as such, respiratory protection is often required when working with IPA.

Figure 12 summarizes the color change magnitudes for the three indicators for gas concentrations of 10, 50, and 90% of the PEL under conditions of 20 °C and 5, 50, and 95% relative humidity, the most likely environmental conditions that the ESLIs will likely be exposed to. When using the criteria of $\Delta Eab^* \geq 10$ as a visible color change, the indicators were observed to react to the presence of the vapor in all cases, with the exception of ammonia at low humidity and low concentration. It is important to note that the criteria used for these tests included a test time limit of 15 minutes, thus in the case of the data in Figure 12, a $\Delta Eab^* \geq 10$ does not indicate that an indicator cannot necessarily be used under the conditions tested, but rather that the time required to change color that is visible to the human eye may require a period longer than 15 minutes. Since PEL's, the target gas concentrations used for these tests, are measured for 8-hour periods, as long as the color change does not exceed the 8-hours, the indicator could potentially be used under those conditions.

Statistical Analysis of Indicator Sensitivity Test Results. In addition to the results summarized in Figure 12 for 20 °C, similar tests were also performed for each indicator at -10 and 40 °C (*i.e.*, 27 total tests for each indicator as mentioned above).

Due the large number of conditions and tests performed for each indicator, the data set was analyzed using a 3^3 factorial design in order to evaluate the effect of each variable on the indicator. The following paragraphs explain the ideas behind the statistically designed factorial experiment. A brief example is given because at first, the idea of changing more than one variable in an experiment seems counterintuitive. The one variable at a time approach is completely valid in many cases, but it is a less efficient method to use for screening a large number of variables or generating a model for the performance of a system that has several controlling variables. In addition, the effects of multiple variables that may interact with one another and optimum operating conditions are easy to miss when using a one variable at a time approach.

One of the best examples to illustrate the full factorial experimental design approach is the so-called 2^3 full factorial, statistical experimental design that examines the effects of three variables evaluated at two levels each (high and low). The notation used when discussing factorial designs is 2^p for *p* variables examined at 2 levels, 3^p for *p* variables examined at 3 levels etc. Three level designs are about as large as practical since the number of required experiments increases to the *p* power. Returning to the 2^3 full factorial design as an illustrative example, this design is the most productive and efficient method for screening the effects of 3 variables in most systems. In the *full* factorial case, all possible combinations of the variables are run as experiments resulting in 2^3 = 8 individual experiments. Table 2 shows the combinations listed in so called "standard order" where the pattern of experimentation is clearer. In actually executing the experimental design, the runs *must* be done in random order to the eliminate statistical bias that occurs if for example all of the low values of X_1 were run first (Box et al. 1978).

Table 2. Layout of a 2^3 full factorial experimental design (Box et al. 1978)

Run	X_1	X_2	X_3	R_1	R_2
1	-	-	-	A	I
2	+	-	-	B	J
3	-	+	-	C	K
4	+	+	-	D	L
5	-	-	+	E	M
6	+	-	+	F	N
7	-	+	+	G	O
8	+	+	+	H	P

In the 2^3 full factorial statistical experimental design, each variable (X_i) is investigated at a low level and a high level. In Table 2, the notation **+** is used to designate that a particular variable is at its high level during that individual experiment. Similarly a **-** indicates that the lower value should be used. All possible combinations of the three variables are run in the *full* factorial design. For cases where there are many variables making the total number of experiments very large, so-called fractional factorial designs can be used to reduce the number of runs required albeit with some loss in information. Fractional factorials were not used and are therefore not discussed – details can be found is several excellent references (Box et al 1978; Box and Draper, 1987; Montgomery 1976).

By running the correct combinations of variables (Table 2), an empirical model can be developed for the response being measured (the result of the experiment) (Box et al 1978). From the results of this matrix of experiments, one equation is generated for each response (R_i) measured. The responses are the variables of interest and in the example in Table 2 are designated R_1 and R_2. The responses can be anything such as product yields, color changes (our case for the ESLI), temperatures, number of defects in a part, etc. depending on the application. In Table 2, the "values" of the two responses are given by the letters A through P. For example the value of R_2 measured during run 5 (X_1 low, X_2 low, X_3 high) is R_2 = M.

Knowing the values of R_1 and R_2 for each run, an empirical model of each response is calculated in terms of the three variables: X_1, X_2 and X_3. This is shown for R_1 in Equation 2,

$$R_1^{predicted} = \mu + \frac{1}{2}\left[\beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 + \beta_{123} X_1 X_2 X_3\right]$$

Equation 2. Model for response R_1 in terms of variables X_1, X_2 and X_3

where μ is the global mean of all the responses; for R_1, μ = (A+B+C+D+E+F+G+H)/8. The β terms give the magnitude of the effect of each variable on the response for which they were calculated; for example the magnitude of β_1 indicates the effect of X_1 on R_1, β_2 the effect of X_2 and β_3 the effect of X_3 on R_1 (the β values for each variable are different for each response). *The β values will be different in each of the equations generated for each response being modeled.* The values of the β terms are obtained by subtracting the average response when each variable is low from the average response when the variable is high. Referring to Table 2, the value of β_1 (for response R_1) is calculated from β_1 = [(B+D+F+H)/4 – (A+C+E+G)/4]. The β_{ij} values with two subscripts are a *quantitative* indication of the magnitude of the effect of the interaction between variables on a given response. For example the quantity β_{23} is a measure of the effect of the interaction between variables X_2 and X_3 on R_1. Interpretation of exactly what the response equation means physically has to be provided by the person analyzing the data since Equation 2 is simply an *empirical* model. For brevity, the rules for calculating the two-variable interaction (β_{ij}) and three variable interaction term (β_{123}) are not discussed here but are similar to those used to calculate the individual terms. All of the β terms are calculated using Yates Algorithm (Box et al 1978). Three variable interactions are usually not important (Box et al. 1978), and they are frequently used as an approximate value of the statistical error (noise) in the response.

The response equation (Equation 2) is a so-called first order model because even though it gives information about the interactions between variables, it is linear in each variable. In many cases this is sufficient to obtain a model good enough to determine the effects of each variable and to make predictions about optimum conditions. A more refined model is a so-called second order model that contains quadratic terms (e.g. X_1^2 etc.), which is better for modeling systems where one expects nonlinear relationships between the responses and one or more variables (if the relationship turns out to be linear, then the β terms for the quadratic terms become very small or zero). The disadvantage of statistical experimental designs that are used to generate nonlinear models is that they require more runs. For example, in our case we performed a 3^3 full factorial experimental design to determine the effects of humidity, gas temperature and gas concentration on our ESLI indicator strips for SO_2, NH_3 and isopropanol. Therefore for each vapor required a minimum of 3^3 = 27 individual experiments. In contrast, a two-level design (2^3 full factorial) requires only 8 runs. In addition, five "center point runs" are done with the 3^3 full factorial to estimate the error giving a total of 32 runs. The layout for the 3^3 full factorial for the acid indicator (SO_2 test gas) is shown in Table 3. In this case there were 27 runs and we assumed that the five center runs were identical. Similar experimental designs were used for the base indicator (ammonia) and VOC indicator (isopropanol).

Table 3. 3^3 full factorial layout for testing the acid indicator.

	Factor A	Factor B	Factor C	R1	R2	R3	R4	R5	R6	R7
	T	RH	SO2	Pre	Pre	Pre	Post	Post	Post	CIE L*ab
	Temp	Test	Conc.	Cie Color	Cie Color	Cie Color	Cie Color	Cie Color	Cie Color	Color
Std #	C	R.H.%	ppm	L	a	b	L	a	b	Delta
1	-10	5	0.5	62.86	12.08	-34.65	64.29	9.53	-32	3.945871
2	20	5	0.5	62.86	12.08	-34.65	67.64	3.09	-18.33	19.23567
3	40	5	0.5	62.86	12.08	-34.65	70.54	1.09	-12.37	26.00309
4	-10	50	0.5	62.86	12.08	-34.65	67.26	5.21	-23.74	13.62296
5	20	50	0.5	62.86	12.08	-34.65	70.76	0.02	-9.5	28.98924
6	40	50	0.5	62.86	12.08	-34.65	73	0.82	-2.52	35.52385
7	-10	95	0.5	62.86	12.08	-34.65	67.66	4.36	-20.08	17.17333
8	20	95	0.5	62.86	12.08	-34.65	68.58	5.04	-20.96	16.42243
9	40	95	0.5	67.14	6.56	-26.21	69.27	6.8	-23.26	3.646505
10	-10	5	2.5	62.86	12.08	-34.65	64.16	9.68	-31.97	3.825232
11	20	5	2.5	62.86	12.08	-34.65	68.02	4.99	-21.77	15.58166
12	40	5	2.5	66.3	6.97	-26.65	67.64	4.45	-20.33	6.93458
13	-10	50	2.5	62.86	12.08	-34.65	67.35	5.39	-23.36	13.87012
15	20	50	2.5	62.86	12.08	-34.65	67.31	1.31	-12.4	25.11688
15	40	50	2.5	63.08	12.01	-35.62	75.94	-4.78	11.27	51.43885
16	-10	95	2.5	62.86	12.08	-34.65	66.77	5.43	-20.61	16.01974
17	20	95	2.5	62.86	12.08	-34.65	70.15	-0.36	-7.27	30.9445
18	40	95	2.5	66.04	7.16	-26.88	78.73	-4.29	13.05	43.43436
19	-10	5	4.5	69.45	4.39	-27.23	69.78	4.25	-25.32	1.943348
20	20	5	4.5	62.86	12.08	-34.65	69.64	2.73	-17.49	20.68469
21	40	5	4.5	76.06	0.99	-15.96	79.57	-2.33	-4.46	12.47367
22	-10	50	4.5	68.75	4.96	-28.57	69.12	4.86	-26.27	2.331716
23	20	50	4.5	62.86	12.08	-34.65	73.87	-3.39	6.83	45.61942
24	40	50	4.5	62.86	12.08	-34.65	78.64	-3.82	12.58	52.27324
25	-10	95	4.5	62.86	12.08	-34.65	68.3	4.4	-21.32	16.31763
26	20	95	4.5	62.86	12.08	-34.65	72.38	-2.67	1.54	40.22324
27	40	95	4.5	66.52	7.1	-26.94	80.58	-4.62	17.27	47.84941
28	20	50	2.5	62.86	12.08	-34.65	67.31	1.31	-12.4	25.11688
29	20	50	2.5	62.86	12.08	-34.65	67.31	1.31	-12.4	25.11688
30	20	50	2.5	62.86	12.08	-34.65	67.31	1.31	-12.4	25.11688
31	20	50	2.5	62.86	12.08	-34.65	67.31	1.31	-12.4	25.11688
32	20	50	2.5	62.86	12.08	-34.65	67.31	1.31	-12.4	25.11688

In the 3^3 full factorial experimental design, each variable is tested at a low, intermediate and high value, and the responses are measured in each of the individual experiments. For example, the values of the variables for run 9 for the acid indicator in Table 3 were T = 40°C, relative humidity, RH = 95% and SO_2 concentration = 0.5 ppm.

The responses we measured were the CIE Lab colors (L, a, and b in Table 3) before and after

$$R_i = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2$$

Equation 3. 3^3 full factorial response model that includes quadratic terms (NIST 2010).

exposure of the appropriate indicator strip (in the case of SO_2 it was the acid indicator that contained bromocresol purple). We modeled response R_7, the delta value, which is the color *change* (*ΔEab**).

The response model is very similar to the model from the 2^3 full factorial but now contains quadratic terms for each of the three variables (compare Equation 2 with Equation 3). Since there are three independent variables (temperature, relative humidity and challenge vapor

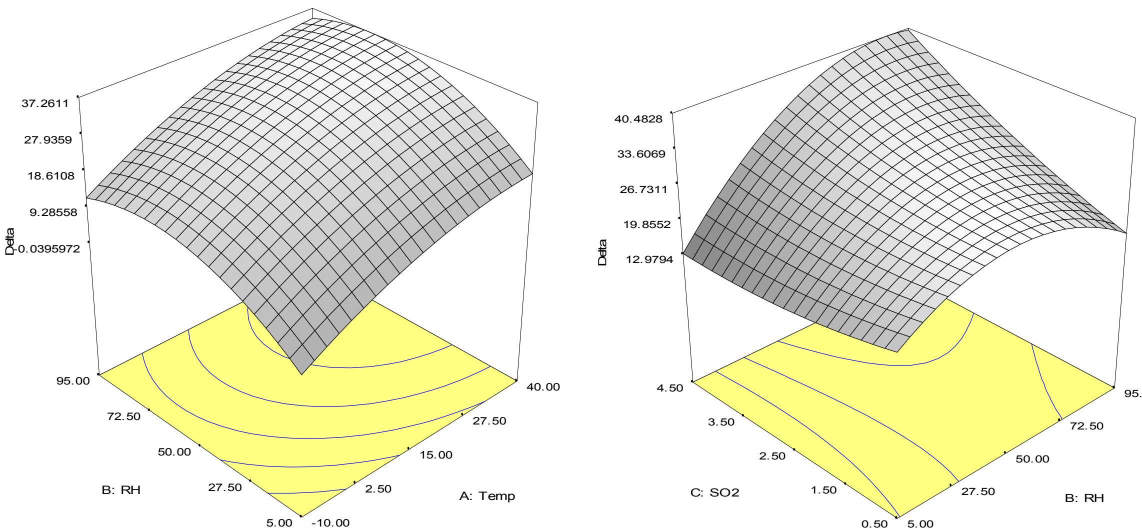


Figure 13. Response surfaces for SO_2 from analysis of 3^3 full factorial experimental design (RH and Temp (left), SO_2 concentration and RH (right)).

concentration) and one response (color change), the entire response cannot be plotted because it is 4 dimensional. By plotting the response vs. two variables at a time however, we can generate a series of 3-dimensional response surfaces that show how the color change is affected by changes in temperature, humidity or challenge concentration.

Figure 13 shows the response surfaces for how temperature, relative humidity and SO_2 concentration affected the color change (the *ΔEab** response) of the acid gas indicator strip (bromocresol purple). On the left is the plot for the effects of temperature and relative humidity (RH), and on the right is the response surface for the effects of RH and SO_2 concentration. Sulfur dioxide is an acid gas because it reacts with water according to Reaction 1, which in turn causes the color change in bromocresol purple. Therefore, not surprisingly, the acid gas strip in the ESLI exhibited greater color change (for the fixed test time) with increasing relative humidity (which increases the H_2O concentration) and higher temperatures (which increases the reaction rate) as shown by the upward slope of the response surfaces in Figure 13 as these variables are increased. Importantly, the greatest response occurs when RH and temperature are *simultaneously* increased indicating that there is an interaction between these variables. This is an example of an interaction effect that can be easily missed when using a "only change one variable at a time" approach. Finally, as expected, the color change response also improves as the SO_2 concentration is increased.

Figure 14 shows response surfaces for the color change for the base indicator strip for ammonia (NH_3). Ammonia reacts with water according to Reaction 2 producing hydroxide ions that

$$NH_3 + H_2O = NH_4^+ + OH^-$$

Reaction 2. Reaction between ammonia and water.

change the color of the brilliant yellow indicator. As was the case for SO_2, increasing the relative humidity, temperature and NH_3 concentration increased the response of the ESLI base indicator strip and the greatest color change is effected when all three increase simultaneously. The response of the potassium permanganate ($KMnO_4$) indicator to isopropanol was different

$$SO_2 + H_2O = H^+ + HSO_3^-$$

Reaction 1. Reaction between SO_2 and water.

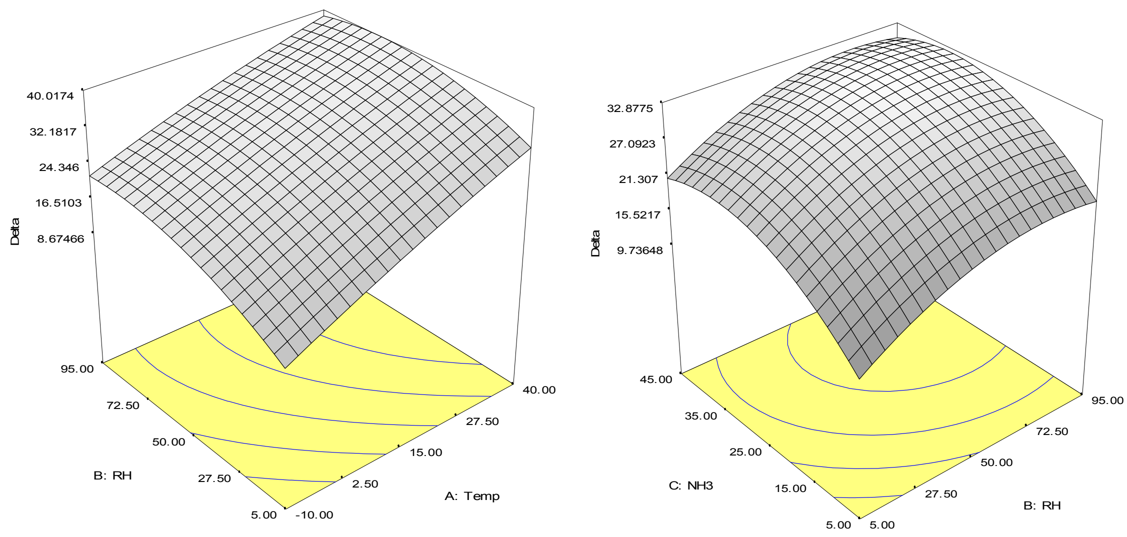
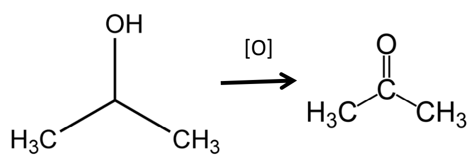


Figure 14. Response surfaces for NH_3 from analysis of 3^3 full factorial experimental design (RH and Temp (left), NH_3 concentration and RH (right)).

than the behavior observed for SO_2 or NH_3 with their acid and base indicators. As an indicator, purple $KMnO_4$ changes color when it oxidizes organic compounds producing Mn in a lower



Reaction 3. Oxidation of isopropanol to acetone.

oxidation state that is brown (MnO_2 with possibly lower Mn oxidation states). In the case of isopropanol, the major product most likely to be formed is acetone (the corresponding ketone; Reaction 3). The identity of the manganese products produced when MnO_4^- is reduced (at least

in aqueous solutions) depends on the pH. For the purposes of the ESLI and presumably the effects of humidity, the pH is close to neutral. Under these conditions, hydrous MnO_2 is a common product (Reaction 4) (Pisarczyk 2005). The three electrons for the reduction are

$$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$$

Reaction 4. Reduction of permanganate ion.

supplied by oxidation of the (usually carbon) of the organic compound (Reaction 3).

Figure 15 shows that the response of the permanganate indicator strip in the ESLI decreased slightly with relative humidity and increases with increasing isopropanol concentration. Surprisingly (and unlike SO_2 or NH_3) increasing the temperature actually *decreased* the response of the permanganate indicator. The reasons for this are not clear, however, it may be that the permanganate indicator responds more strongly at lower temperatures because the absolute humidity naturally decreases with temperature (for a given relative humidity) and possibility higher concentrations of adsorbed isopropanol are possible at lower temperatures (however the reaction kinetics might be slower).

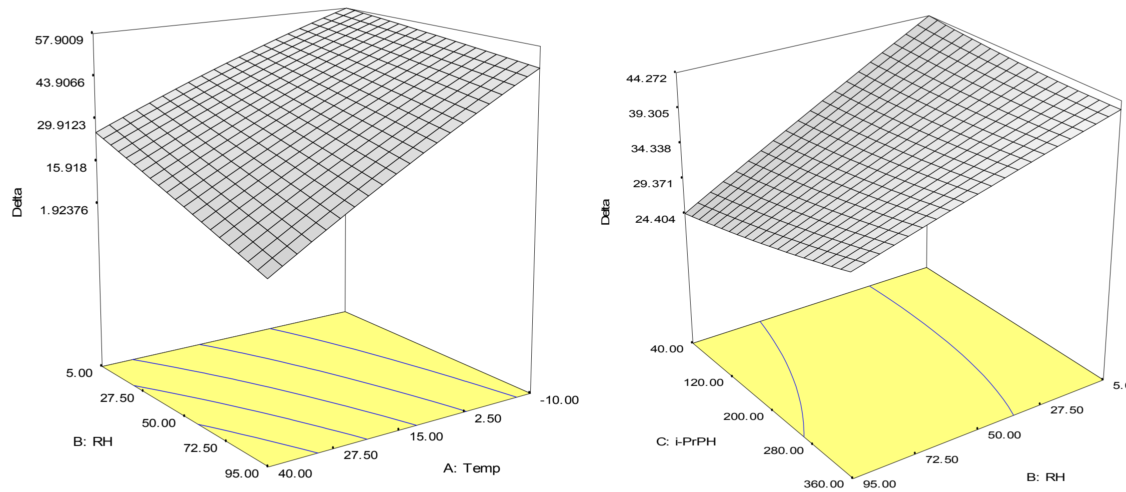


Figure 15. Response surfaces for isopropanol (i-PrOH) from analysis of 3^3 full factorial experimental design (RH and Temp (left), *i*-PrOH concentration and RH (right)).

Based on the sensitivity results for all of the indicator formulations prepared in Task 2 (Section D.4.2.2), the sensitivity of the indicators strips prepared in TDA's labs appeared to be excellent for the purposes of fabricating the ESLI prototypes.

Additional VOC Testing. For the factorial design test, we chose to use *iso*-propyl alcohol (IPA) as a VOC test contaminant as recommended by Jay Snyder of NPPTL (National Personal Protective Technology Laboratory, NIOSH) since it gave a vivid color change within the timeframe (15 minutes) chosen for the factorial design analysis. However, due to the sheer number of VOCs that a potential VOC indicator must protect against, TDA tested several VOCs of industrial concern that were not included in the original Phase I work plan. Additional VOCs were tested at their PEL and the time for a complete color change to occur was determined. For these tests, the same 4 L/minute flow rate that was used for indicator sensitivity tests was chosen. Though not tested as extensively as IPA, it is assumed that the general conclusions obtained from the factorial analysis for the VOC indicator apply to these VOCs as well. Table 4 shows the additional VOC gases tested at their respective PELs and the time it took for the color change to occur; in all cases, the color changes observed were between ΔEab^* 20-30. As can be seen, though many gases, especially the more hydrophobic gases, cause a longer indicator response time, each indicator changes color well before the 8-hour PEL time has passed, thus demonstrating the usefulness of our VOC indicator for a large variety of VOCs.

Table 4. Time needed to achieve a color change of additional VOCs ($\Delta Eab^* \geq 20$) at the PEL.

VOC	P.E.L. (ppm)	time for color change at P.E.L.
IPA	400	< 10 minutes
Toluene	200	< 60 minutes
Ethanol	1000	< 25 minutes
Acetone	1000	< 75 minutes
DCM	25	< 45 minutes
Cyclohexane	80	< 45 minutes
Pentane	1000	< 15 minutes
Xylene	100	< 30 minutes

D.4.2.4 Task 4. Phase I Prototype Fabrication and Testing

Based on a prototype cartridge designed by TDA in conjunction with our industrial collaborator MSA, TDA fabricated a respirator cartridge containing our prototype ESLI. The prototype was constructed using one each of the three indicator strips developed and tested in Tasks 2 and 3. Following construction of the prototype ESLI, it was integrated into a transparent polycarbonate respirator cartridge, which was subsequently filled with activated carbon. Figure 17 shows the assembled respirator cartridge containing our 3-indicator-ESLI prototype. Each indictor consists of a pair of indicator bands - the indicator and a reference band. The reference band does not change color and thus provides a comparison so the user will quickly recognize if a color change has occurred.

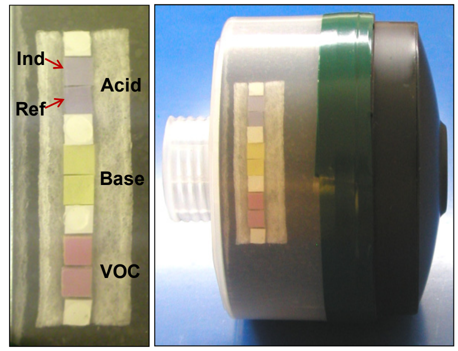


Figure 17. TDA's ESLI prototype in a transparent respirator cartridge. (Ind=indicator; Ref=reference strip)

The ESLI prototype assembly process is generally depicted in Figure 16. The indicator strips were first prepared as described above in Task 2. Following indicator strip preparation, the indicator strips were cut into ~0.2 in^2 bands. Reference bands were prepared in the same manner, followed by lamination to prevent color change upon exposure of the ESLI to the test vapors; in this manner, we produced an accurate reference band that retained the original indicator color upon vapor exposure. The indicator bands were then paired with a corresponding reference band and assembled linearly with a non-colored spacer between each of the three indicator types (*i.e.*, acid, base, VOC), as shown in Figure 17 (left). The linear indicators were assembled on a highly gas permeable polypropylene random fiber mat that was subsequently used to attach the assembled ESLI to the interior wall of the transparent gas mask carbon cartridge. Following the integration of the ESLI prototype into the transparent cartridge, the cartridge/ESLI assembly was then filled with activated carbon and sealed. The assembled ESLI prototype incorporated into a filled cartridge is shown in Figure 17 (right).

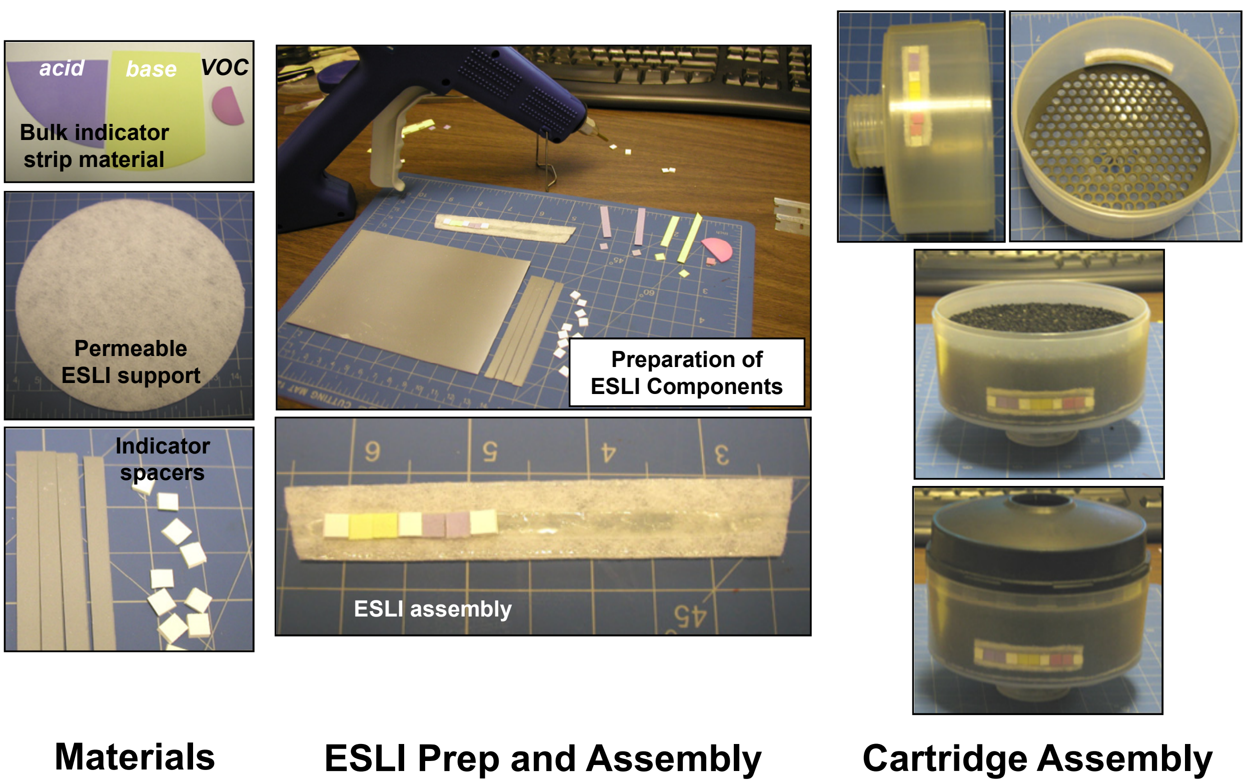


Figure 16. Pictures of the prototype ESLI assembly and integration into the gas mask activated carbon cartridge.

Following assembly of the ESLI prototype in the respirator cartridge, the prototype ESLI performance in the carbon cartridge was evaluated using the vapor test apparatus constructed in Task 1. For these tests, mixtures of vapors were flowed into the ESLI prototype while a video camera monitored the ESLI for any color change. In this manner, we could monitor the ESLI's activity in an actual gas mask cartridge in which carbon was actively adsorbing test contaminants. Figure 5 shows the testing of one of the ESLI prototypes using the apparatus and Figure 18 shows a close-up of the ESLI prototype being monitored for color change using a video camera.

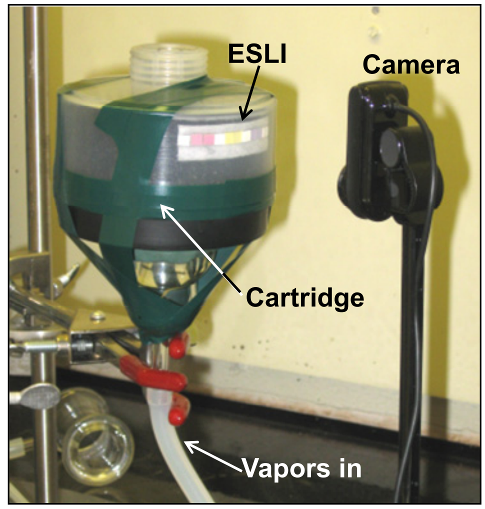


Figure 18. Picture of the ESLI prototype being monitored for color changes. For a picture of the entire test apparatus, see Figure 5.

For these tests, we used the same challenge vapors that were used during the indicator sensitivity testing in Task 3, SO_2 gas, ammonia gas, and *iso*-propyl alcohol (IPA). For the prototype tests, since one of the goal of the Phase I testing was to demonstrate the effectiveness of our ESLI prototype to respond to multiple gaseous contaminants, we performed two tests in which we flowed gas mixtures through the prototypes carbon cartridges. The two mixtures chosen were IPA/SO_2 and IPA/NH_3; a mixture of SO_2 and NH_3 was not tested since the combination of these two vapors in a gas mixture would result in an acid-base neutralization causing both gases to react prior to being exposed to the prototype.

Unlike the indicator sensitivity tests performed in Task 3, since the prototype ESLI's were in a bed of activated carbon, in order to observe the ESLI response in reasonable amounts of time, for these tests we evaluated the prototypes using gas concentrations several times the PEL of the gas. Gas concentrations for the two mixtures were 9,000 ppm IPA (23 times the PEL) with 75 ppm SO_2 (15 times the PEL), and 9,000 ppm IPA with 10,000 ppm NH_3 (200 times the PEL). The low concentration of SO_2 was chosen because the activated carbon used in our prototype cartridges was optimized for protection against basic gases, thus the adsorption capacity for acid gases was extremely low, resulting in an almost immediate color change of the acid indicator during tests in which SO_2 was a part of the gas mixture. By using a very low concentration of SO_2 in these experiments, we were able to delay the response of the acid indicator to help offset the effect of the low acid adsorption capacity of the activated carbon. In contrast, the relatively high ammonia concentration was chosen to help offset the high adsorption capacity of the carbon for ammonia.

Using the elevated gas concentrations, a flow rate of 4 liters/minute was chosen for testing the the prototype cartridge to closely simulate actual working flows caused by human breathing. The flow rate was calculated (scaled down) based on an actual 64 l/min flow rate for a cartridge. All ESLI prototype testing with the gas mixtures was performed at 20 °C and 30% relative humidity. Under these conditions, the IPA/NH_3 mixture resulted in an ESLI response to both gases in 97 minutes, while the IPA/SO_2 mixture resulted in an ESLI response to both gases in 120 minutes. Figure 19 shows the visual results of these two mixed vapor prototype tests. As can be seen, the appropriate indicators have changed color according to the gas mixtures they were exposed to, while the indicator for the gas not included in the mixture remains unchanged. For example, in Figure 19 (top) when IPA/ammonia was the test vapor, the VOC indicator and base indicator change colors while the acid indicator remains unchanged.

Though the ESLI prototype has the ability to detect multiple gases, it is very important to note that the ESLI indicates the expiration of the gas mask cartridge once a single indicator has changed. Thus, though in the examples above, the acid and base indicators changed well before the VOC indicator changed, in a real-life scenario, the cartridge would have been replace once the first indicator changed color. Allowing the ESLI to continue to be exposed to the contaminant vapors following the initial indicator color change was done only for testing purposes and is not indicative of how the ESLI will actually be operated.

The ESLI prototype exceeded expectations during all phases of testing and no mechanical failures were observed at any time. It worked quite well in all aspects of test vapor evaluation indicating a response to the breakthrough of all tested gases and gas mixtures.

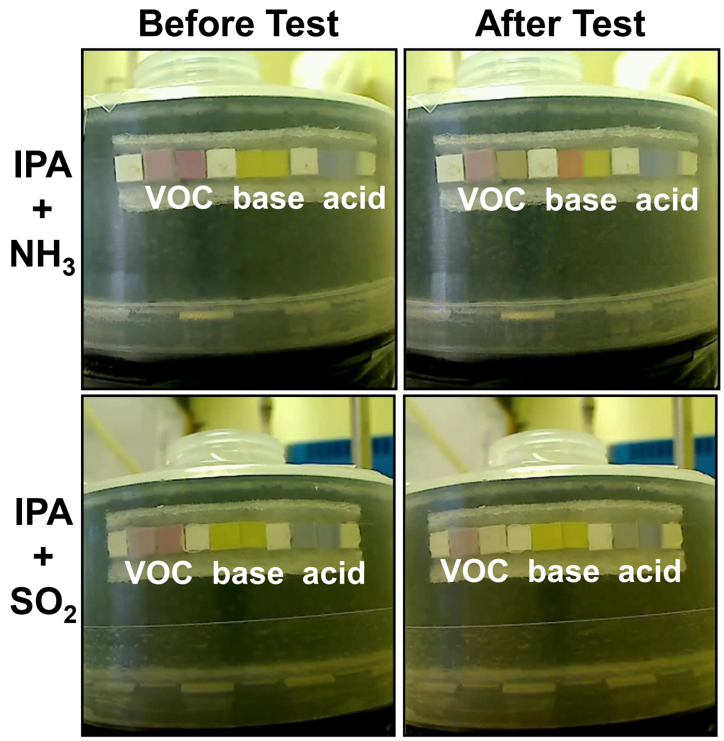


Figure 19. Pictures showing the ESLI color change for two, multiple-gas testing experiments.

D.4.2.5 Task 5. Engineering and Cost Analysis

TDA's collaborator on this Phase I project was Mines Safety Appliances (MSA). MSA is (a $1 billion/year) the world's largest company that provides a complete range of equipment and systems for workers and plant protection. TDA will work with MSA closely during the Phase I project. They have followed our progress, guiding us during the project and providing us with cartridge components for use during fabrication of our working ESLI prototype. MSA is ultimately interested in licensing our technology for use with their carbon canisters. As part of our collaboration with MSA, MSA provided valuable feedback and analysis for our Phase I prototype design, as well as valuable information for performing an initial cost analysis for our prototype.

As part of the Phase I project, TDA and MSA performed a brief engineering and cost analysis of TDA's tested ESLI prototype design. For an ESLI that is incorporated into gas mask carbon cartridges during manufacturing, MSA believes the incremental increase in sales price must be less than $5/per mask. Based on the materials costs for TDA's Phase I ESLI prototype, the cost of the incorporation of an ESLI based on TDA's design should be able to meet this goal. TDA has demonstrated to operation of its ESLI using common, cheap materials and the small amount of colorimetric indicator chemical required for each indicator is small and therefore inexpensive. Furthermore, due to the simple design and operation of TDA's ESLI prototype, incorporation into existing gas mas cartridge configurations is easy to perform, requiring little modification to cartridge manufacturing processes already in place.

Table 5. Preliminary cost estimate for TDA's ESLI.

Materials and Labor	Cost ($)	Number of Units	Cost per Unit ($)*
	Materials		
Polypropylene Filter Mat (per 100 ft2)	$50	10000	$0.0050
Whatman Filter Paper (per 4 in. pack of 50)	$9	15000	$0.0006
Gamma Alumina (per 100 lb)	$1,600	473175	$0.0034
Alumina Tape (per 10 ft2)	$500	40000	$0.0125
Laminating (per 10 sheets)	$5	125	$0.0400
Hot Glue (oper 165 sticks)	$181	8250	$0.0219
Brilliant Yellow (per 25 g)	$81	100000	$0.0008
Bromocresol Purple (per 25 g)	$87	100000	$0.0009
Potassium Permanganate (per 500 g)	$50	10000	$0.0050
Prism	0.50	1	$0.5000
	Labor		
Labor (per hr)	$40	40	1
Total			$1.59

* Cost of tooling not estimated

A detailed ESLI prototype cost and engineering analysis is being performed and is included in the Commercialization Section of the Phase II proposal. A preliminary cost estimate for TDA's ESLI is provided in Table 5. The table lists each material cost, and the total cost of assembling the ESLI. Our total estimated cost of $1.26/cartridge is well below MSA's threshold costs of $2/cartridge. The material cost estimates are dominated by the cost of the prism, which is used to provide a line of sight for the cartridge user. We will work on reducing the cost of the prism in the proposed Phase II project.

E. Conclusions

In the Phase I project, with the help of its collaborator MSA, TDA has successfully designed, fabricated, and demonstrated an ESLI prototype for indicating the expiration of activated carbon respirator cartridges. The ESLI prototype was then successfully integrated into a transparent activated carbon filter cartridge supplied to TDA by its collaborator, MSA. Using a newly constructed vapor test apparatus, TDA was able to demonstrate the prototype carbon cartridge containing a colorimetric ESLI that changed color just prior to exhausting the capacity of the activated carbon bed for any of the three main classes of toxic industrial chemical (TIC) vapors – VOCs, acid gases, and/or basic gases. By integrating these indicator chemicals into an array, a visual ESLI was constructed that allows the user of the gas mask to unambiguously determine if the capacity of an activated carbon respirator cartridge is approaching saturation. As the carbon bed reaches its adsorptive capacity and vapors begin to break through (this is well before the bed is totally saturated) the vapors react with the ESLI indicators, producing color changes that indicate that the cartridge must be replaced.

TDA's ESLI prototype consists of three, non-specific colorimetric indicators that were individually developed and tested for vapor indicating sensitivity prior to their integration into the ESLI prototype. The three indicators – bromocresol purple (acid gas indicator), brilliant yellow (basic gas indicator), and sodium permanganate (VOC indicator) – once impregnated onto compatible supports were subsequently incorporated into a colorimetric pass/fail sensor array that served as the basis of the ESLI prototype; the incorporation of three, non-specific indicators allows a single ESLI to indicate the breakthrough of any contaminant vapor from the three major TIC vapor classes. Following prototype fabrication, the prototype was demonstrated to respond to carbon bed saturation for all three vapor classes, as well as mixtures of vapor containing either VOC and acids, or VOCs and bases. During the testing and demonstration of the ESLI prototype, no mechanical failures of the device were observed and bed saturation was consistently indicated.

The successful fabrication and testing of TDA's ESLI prototype demonstrates the effectiveness of an inexpensive, colorimetric ESLI for indicating the expiration of activated carbon respirator cartridges. TDA's concept for developing a simple, inexpensive, colorimetric ESLI for use in carbon cartridge gas mask filters can be used as a basis for optimizing the design and constructing a manufacturing prototype in Phase II.

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Appendix I. Description of the CIE L*a*b* color space.

The CIE L*a*b*-system, the most complete color space specified by the International Commission on Illumination (Commission Internationale d'Eclairage, hence "CIE"), is meant to quantitatively describe all the colors visible to the human eye and was created to serve as a device independent model to be used as a reference (CIE, 1986). Using a handheld colorimeter during the Phase I project allowed TDA to evaluate the color of an indicator on the support material both before and after exposure to TICs according the CIE L*a*b* color system. Using the colorimeter and the CIE L*a*b* color system, the indicator colors observed were evaluated quantitatively and we were thus able to perform statistical analyses on the resulting calculated color changes to evaluate variables such as color-change reproducibility, lightness and darkness of the colors produced, and the total color difference before and after test vapor exposure.

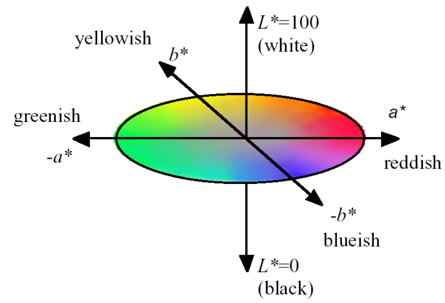

Figure 20. CIE L*a*b* color space (Ohno, 2000).

The CIE L*a*b*-system, the most complete color space specified by the International Commission on Illumination (Commission Internationale d'Eclairage, hence "CIE"), is meant to quantitatively describe all the colors visible to the human eye and was created to serve as a device independent model to be used as a reference (CIE, 1986). It measures color in 3 dimensions (Figure 20), L*, a*, and b*, where L* = 0 yields black and L* = 100 indicates diffuse white, a* = negative values indicate green while positive values indicate magenta, and b* = negative values indicate blue and positive values indicate yellow. In addition, by obtaining values for L*, a*, and b* for two different colors, the <u>color difference</u>, ΔE_{ab}*, can be calculated according to Equation 4. Using this system, ΔE_{ab}* values ≥ 10 represent a noticeable difference between two colors for the human eye (Fraser, 2004).

Equation 4.
$$\Delta E^*_{ab} = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

Using TDA's handheld colorimeter, the color of each indicator test strip was measured before and after vapor exposure during the experiments performed in Task 3. The values of L*, a*, and b* were recorded, and with this data, ΔE_{ab}* was calculated from Equation 4 and used to evaluate the magnitude of the color difference for indicators before and after exposure to the vapor at different concentrations, temperatures, and relative humidities. Using the metric of ΔE_{ab}* ≥ 10, it was then be determined if the measured indicator color change that results from vapor exposure is intense enough to be detected by the human eye (Fraser, 2004).