Wearable Real-Time Direct-Reading Naphthalene and VOC Personal Exposure Monitor

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Abstract

Naphthalene has been identified by the National Research Council as a serious health hazard for personnel working with jet fuels and oil-based sealants containing naphthalene. We are developing a family of miniature, self-contained, direct reading personal exposure monitors (PEMs) to detect, differentiate, quantify, and log naphthalene and other volatile organic compounds (VOCs) in the breathing zone of the wearer or in the hands of an industrial hygienist with limits of detection in the low parts per billion (ppb) range. The VOC Dosimeter (VOCDos) described here is a PEM that provides real-time detection and data logging of exposure as well as accumulated dose, with alarms addressing long term and immediate exposure limits. We will describe the sensor, which employs optical methods with a unique excitation source and rapidly refreshable vapor concentrator.

This paper addresses the rapidly increasing awareness of the health risks of inhaling jet fuel vapors by Department of Defense (DOD) personnel engaged in or around jet fueling operations. Naphthalene is a one to three percent component of the 5 billion gallons of jet fuels used annually by DOD. Naphthalene is also a component of many other petroleum products such as asphalt and other oil-based sealants. The DOD is the single largest user of petroleum fuels in the United States (20% of all petroleum fuel used). The VOCDos wearable sensor provides real-time detection and data logging of exposure as well as accumulated dose. We will describe the sensor, which employs endogenous fluorescence from VOCs accumulated on a unique, rapidly refreshable, patent-pending concentrator, excited by a unique deep ultraviolet excitation source.

Keywords: naphthalene personal exposure monitor, direct reading personal exposure monitor, volatile organic compound personal monitor

1. INTRODUCTION

Development of a miniature, inherently safe, wearable, direct reading personal exposure monitor to detect, differentiate, quantify, and log naphthalene and other volatile organic compounds (VOCs) with high sensitivity and chemical specificity addresses the rapidly increasing awareness of the health risks of inhaling jet fuel vapors by DOD personnel engaged in or around jet fueling operations.

Naphthalene is a one to three percent component of the 5 billion gallons of jet fuels used annually by DOD and 58 billion gallons worldwide. Naphthalene is also a component of many other petroleum products. It is a large component of asphalts and other oil-based sealants. The DOD is the single largest user of petroleum fuels in the United States. In 2002 the National Research Council (NRC) published, “Toxicologic Assessment of Jet-Propulsion Fuel 8”. **This report states that exposure to JP8 is the single largest chemical exposure experience by war fighters and constitutes one of the largest health risks.**

In the near term, the VOCDos naphthalene dosimeter will bring real-time exposure protections where there are none currently. In the longer term, new efficiencies are captured with the shift to real-time sensors/dosimeters such as the VOCDos sensor. Compliance data are downloadable and can be logged directly into worksite databases rather than sent to off-site analytical lab to be retuned weeks later and transcribed into the records. In this regard, VOCDos real-time sensor technology brings increased sustainability as it, a) reduces use of the solvents otherwise used in the analytical laboratory and, b) reduces the record keeping burden.

The benefit of this naphthalene sensor is to improve worker protection, both in the DOD and commercial arenas. Chemical–specific direct reading instruments, especially those with data logging capabilities, can provide a detailed record of chemical exposures throughout the work shift. The data can be immediately evaluated and used to alert workers and adjust work place controls when episodic exposures above established exposure limits occur. Traditional integrated industrial hygiene air sampling does not provide these benefits.

2. RISKS & REGULATION

In 2004, the U.S. EPA drafted a health risk assessment newly characterized naphthalene as likely human carcinogen based on data derived from rodent exposure studies[1]. This Integrated Risk Information System (IRIS) risk-assessment applied a model that arrived at a *de minimus* cancer risk level of 2 parts per trillion. The current OSHA PEL is based on a non-cancer endpoint and is 10 parts per million (ppm) or 50 mg/m^3. In 2007, the DOD's Chemical and Materials Risk Management (CMRM) Directorate elevated naphthalene to its "Action List" through a process of evaluating the impacts of evolving regulations on five defense functional areas. Impacts to the health and safety programs and the environmental cleanup programs were assessed as among the highest. Although the US EPA's naphthalene health risk assessment won't be finalized before 2012, the California EPA's Office of Health Hazard Assessment determined naphthalene to be a human carcinogen in 2002. The American Congress of Government Industrial Hygienists is in the process of changing the carcinogenicity class of naphthalene from A4 (not classified as a human carcinogen) to A3 (confirmed animal carcinogen). In 2009, the Feasibility Advisory Committee of the California Division of Occupational Safety and Health recommended the State's PEL be revised from 10 ppm to 0.1 ppm (0.5 mg/m^3). Because naphthalene has both a high probability and high severity of adverse health impact, regulations are rapidly evolving.

Current regulation is based on Immediate Danger to Life & Health (IDLH), where the OSHA limit is 1.31 g/m^3 as well as regulations on longer term exposure. PELs are based on an 8-hour time weighted average (TWA). Some regulations are based on a Short Term Exposure Level (STEL) using a 15 minute TWA. The current NIOSH STEL is 75 mg/m^3 or 15 ppm. The STEL may decrease as understanding of the hazards increases. These regulations have been driven by the state of the art of real-time, *in situ*, sensors. Figure 1 below illustrates the variability of vapor concentration versus both time (on the left) and space (on the right). At present, variability of exposure cannot be monitored. In addition, there are spatial and orientation mismatches in current data health risk data when air samples are directionally mis-oriented between the source and the individual whose exposure is being monitored.

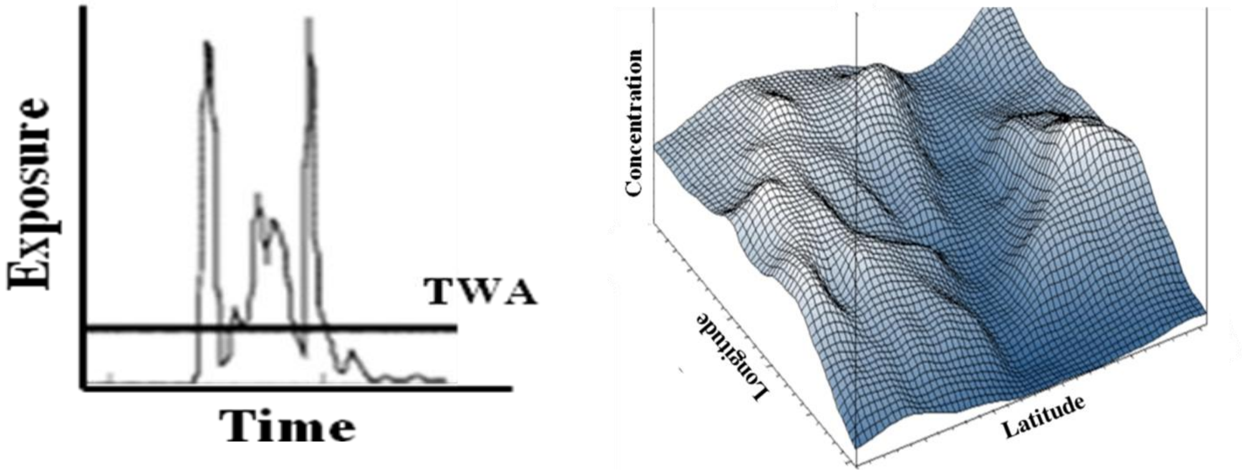

Figure 1. Variation of naphthalene and VOC concentration versus time (left) and space (right)[2]

The near term design path for the VOCDos sensor is near real-time detection of naphthalene over 4 orders of magnitude in concentration from about 100 μg/m^3 (20 ppb) to nearly 1 g/m^3 (200 ppm) with a measurement cycle time less than 3 minutes, and to accomplish this in a miniature, wearable, inherently safe, sensor with battery life over 8 hours. This is illustrated in Fig. 2 below.

Figure 2. Illustration of the application of the VOCDos (in red above) real-time wearable naphthalene and VOC sensor

3. OVERVIEW OF THE METHOD

The VOC detection and discrimination method used in the VOCDos sensor is based on native or endogeneous fluorescence. When excitation occurs in the deep UV below 250 nm, and more ideally below 240 nm, chemical compounds and composite materials with "similar" characteristics fall within or "cluster" in the same region in a "chemometric" space. As a result, if a target material is "unknown" it can be more easily "inferred" if it is within or near a known chemical component or cluster[3,4].

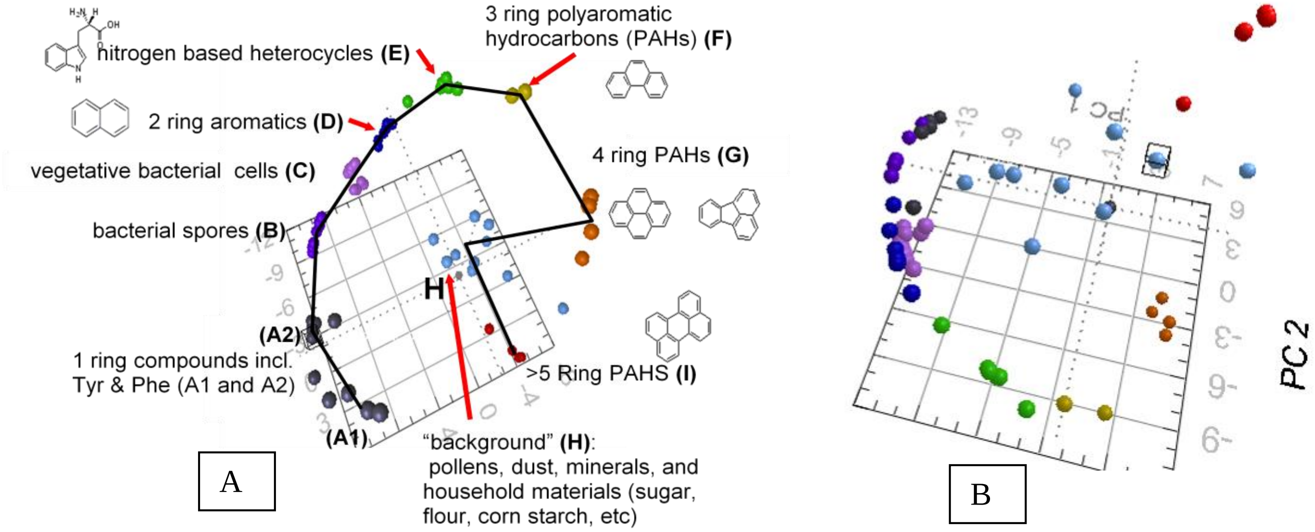

Figure 3. Native fluorescence chemical clustering with excitation at 235 nm (A) on left and 280 nm (B) on right. Colors of similar chemical groups are the same between the two figures.

Detection of materials with any analytical method requires a database of samples against which an unknown sample can be compared. To understand the effect of a changing parameter, e.g.,spectral resolution or spectral range, one needs to "visualize" changes in the relationship between samples as a parameter is varied. Multivariate analyses offer a solution by reducing the dimensionality of the input data; isolating components that provide the greatest separation. Using an approach like principal component analysis (PCA), samples that are spectrally alike, will cluster together. This alone is not sufficient and an expert must determine whether the materials in the groups are, in fact, related. For example, if one were to observe fluorescence from 270 nm to 400 nm, groups will have a first order separation based on their aromaticity (number and arrangement) and a second order effect that separates small aromatic compounds based on how they may be functionalized (-OH, -CH3, Cl, NH3, COOH, etc). However, when one decreases the observed spectral range to 270 - 350 nm, larger ring organics begin to "cluster" with small ring organics. Small fluorescence features in the lower wavelength region that do not account for the majority of the fluorescence begin to predominate when the longer wavelengths are ignored. This effectively "breaks" the chemometric analysis and relates chemicals that have little in common.

When chemical clustering occurs correctly, samples in one cluster should have some commonality where nearby clusters should consist of samples with minor variations associated to small changes in the chemistry (i.e., the second order separation). If these changes are small, e.g., benzene versus a spore (containing dityroine), these clusters should be closer than chemicals like benzene and anthracene (one ring versus 3 ring aromatics). In the case above, where aromaticity drives separation and a reduction in spectral range causes anthracene to closely cluster with benzene, these should never be nearby in chemometric space. In this case, the cluster containing anthracene can technically be a separate cluster. However, the gap between them limits the variations that may exist in nature and it is likely that a secondary effect that slightly alters the benzene fluorescence may appear in the anthracene cluster.

Figure 3 illustrates chemical clustering, where groups of similar compounds such as naphthalene and higher order polycyclic aromatic hydrocarbons (PAHs) cluster together in the same region of a chemometric space. Similar compounds are similarly colored in Figure 3 starting with the (A) group of single ring organics (black) including BTEX (benzene, toluene, ethylbenzene and xylene), bacterial spores (B), cell clusters (C), napthalenes including pure naphthalene and with various functional groups(D), nitrogen based heterocycles (E), 3-ring PAHs such as anthracene and phenanthrene (F), 4-ring PAHs such as pyrene or chrysene (G), PAHs with 5 or more rings (I), and a variety of interferents including pollens, minerals, etc. (H). Illustrated in the two figures in Figure 3 is the influence of excitation wavelength in the ability of similar chemical groups to cluster.

In Figure 3 the 3D chemometric space the first three components of PCA, although any number of other analytical methods would show a similar grouping relationship. In Figure 3 the fluorescence spectra of hundreds of compound and composite materials are illustrated with excitation at 235 nm. The data were obtained using a Hitachi F4500 spectrofluorometer with a wide array of excitation wavelengths from 200 nm to 400 nm. The best clustering was shown to occur with excitation at 235 nm. However, excellent clustering of similar groups of materials occurred with excitation at 224 nm and to a lesser extent with excitation at 248 nm. Above 250 nm, clustering of material is poor and also the fluorescence interferes with detection of Raman emissions. This is illustrated in Figure 3B, where the same color scheme is used to describe similar chemical groups as in Figure 3A. As seen in Figure 3B, when excitation occurs at 280 nm, many of the chemical groups merge together and spread out and clear chemical clustering does not occur. This makes is more difficult to identify chemical unknown compounds and complicates any chemometric method for identification.

Within any group in Figure 3A, it is possible to "zoom" in and tease apart any particular group. Within the 2-ring PAH group are 8 different forms of naphthalene including pure naphthalene, three forms of dimethylnaphthalene, ethylnaphthalene, and naphthalene with different functional groups. Each of these forms modifies the native fluorescence signature enough to enable differentiation.

4. VOCDos Sensor Design & Operation

The VOCDos sensor is illustrated below in Figure 4. The sensor is a battery operated device in a hermetic envelope. It has been tested to be inherently safe and can be operated in environments with explosive gases or vapors. The batteries provide continuous operating lifetime over 9 hours. Within the sensor we currently employ a 250 nm light emitting diode (Deep Ultraviolet LED). In future versions we will incorporate a shorter wavelength light emitting triode (LET) emitting at 235 nm to enable better chemical differentiability, especially for single ring organics. The LED/LET is used to excite VOC which are concentrated on a rapidly refreshable surface within the sensor to improve signal strength and enable detection at concentrations in the low ppb range (low $\mu g/m^3$). Native fluorescence from the concentrated vapor is collected into a high NA spectrograph and captured using a photodiode array.

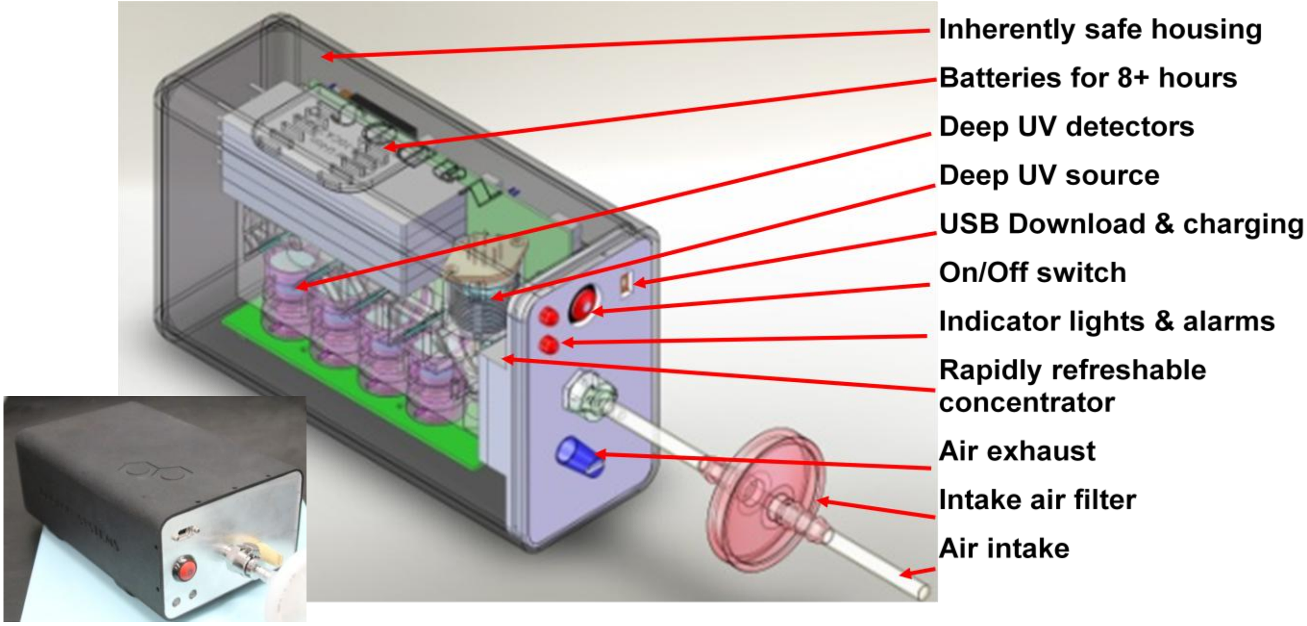

Figure 4. Illustration of VOCDos sensor with key features along with a photo of Gen 3 version (inset)

The sensor is operated cyclically with outside air being continuously drawn into the sensor from the breathing zone of the wearer. This cyclic operation is shown in Figure 5 for four cycles beginning with refreshing of the VOC concentrator to eliminate any residue from a prior cycle.

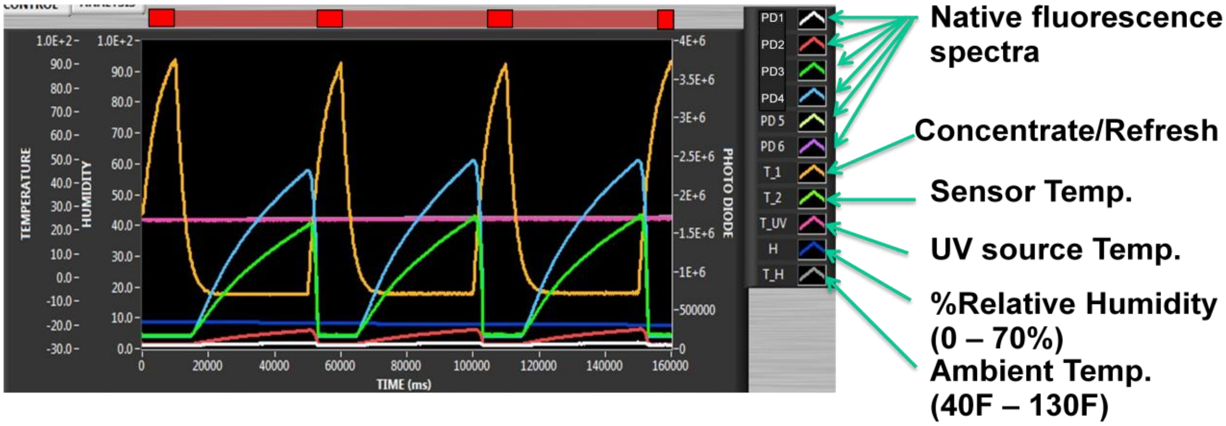

Figure 5. Illustration of cyclic operation of VOCDos sensor. Shown for 4 measurement cycles, time shown in miliseconds.

A typical sensor cycle is 6 seconds to refresh the concentrator, 30 seconds to stability, and 20 seconds to concentrate VOCs on the concentrator surface. Total time of a single cycle is presently less than 60 seconds although the sensor cycle rate can be varied to accommodate lower concentrations (longer cycle time) or higher concentrations (shorter cycle time). The present limit of detection with 60 second cycle time, measured at a signal to noise of 3:1, is about 40 $\mu g/m^3$ or 8 ppb. The upper limit is about over 800 mg/m^3, although current testing has only been done to about 300 mg/m^3.

Also measured and logged by the VOCDos sensor, together with the chemometric data, are the relative humidity and ambient temperature and GPS coordinates of the measurement. On-board processing determines the type of VOC and the concentration. On-board processing compensates the radiometric measurements for variations in source power and effects of both humidity and temperature. Audio and visual alarms can be pre-set at, or in anticipation of, values for permissible STEL and PEL values.

5. VOCDos Sensor Calibration

Several methods were employed to calibrate the VOCDos sensor over a large range of naphthalene concentration from 40 ug/m3 to 500 mg/m3 as well as relative humidity from 0% to 70%, and ambient temperature from 40^0F to 110^0F. The most convenient, flexible, and accurate method to produce a range of naphthalene and water vapor concentrations is using a Owlstone OVG-4 vapor generator, which can generate NIST traceable, precise, repeatable and accurate concentrations of chemicals such as naphthalene. It can also co-mix with accurate generation of water vapor. A photo of our Owlstone generator next to a vent hood with a VOCDos 3.0 sensor and a Rae ppb PID (photoionization detector) is shown in Fig. 6. The range of capability of the Owlstone ranges from 1 μg/m^3 to about 6 mg/m^3.

Figure 6. Photo of Owlstone OVG-4 vapor generator and chemical hood with PID and VOCDos 3.0 sensor

At naphthalene concentrations above 6 mg/m^3 other methods for vapor generation must be employed. Figure 7 shows the other methods employed for the ranges from 2 mg/m^3 to 20 mg/m^3 (bag method), from 30 mg/m^3 to 100 mg/m^3 (recirculation bottle method), and from 200 mg/m^3 to 500 mg/m^3 (large recirculation bottle method). For reference, the equilibrium vapor pressure of naphthalene at 25^0C is about 800 mg/m^3, below the IDLH regulated value.

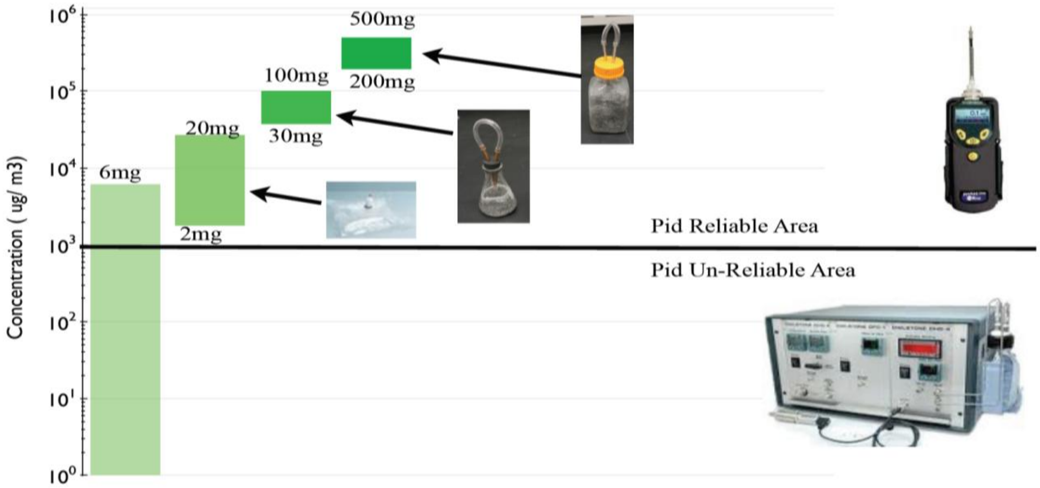

Figure 7. VOCDos sensor calibration methods for naphthalene concentrations from 1 μg/m^3 to 500 mg/m^3.

Photoionization detectors (PIDs) detect a broad range of organic gasses and vapors but cannot differentiate the types of vapors being detected. However, in a pure environment, such as naphthalene, they are reliable for measuring concentrations between about 1 mg/m3 and 500 mg/m^3. As a result, we used the Owlstone for accurate calibration of naphthalene concentration below 1 mg/m^3. Above 1 mg/m^3, we used the PID to calibrate concentrations for our VOCDos. For concentrations in the 1 mg/m^3 to about 20 mg/m^3, it is essential to purge all manifold lines prior to any measurement to ensure there is no residual naphthalene in the measurement system. A major benefit of the VOCDos over the PID is not only the wider range of concentrations but also the ability to identify the VOC being measured. PIDs do not provide any chemical specificity. Figure 8 below show the VOCDos signal level as a function of naphthalene concentration over more than three orders of magnitude from 200 μg/m^3 to 400 mg/m^3.

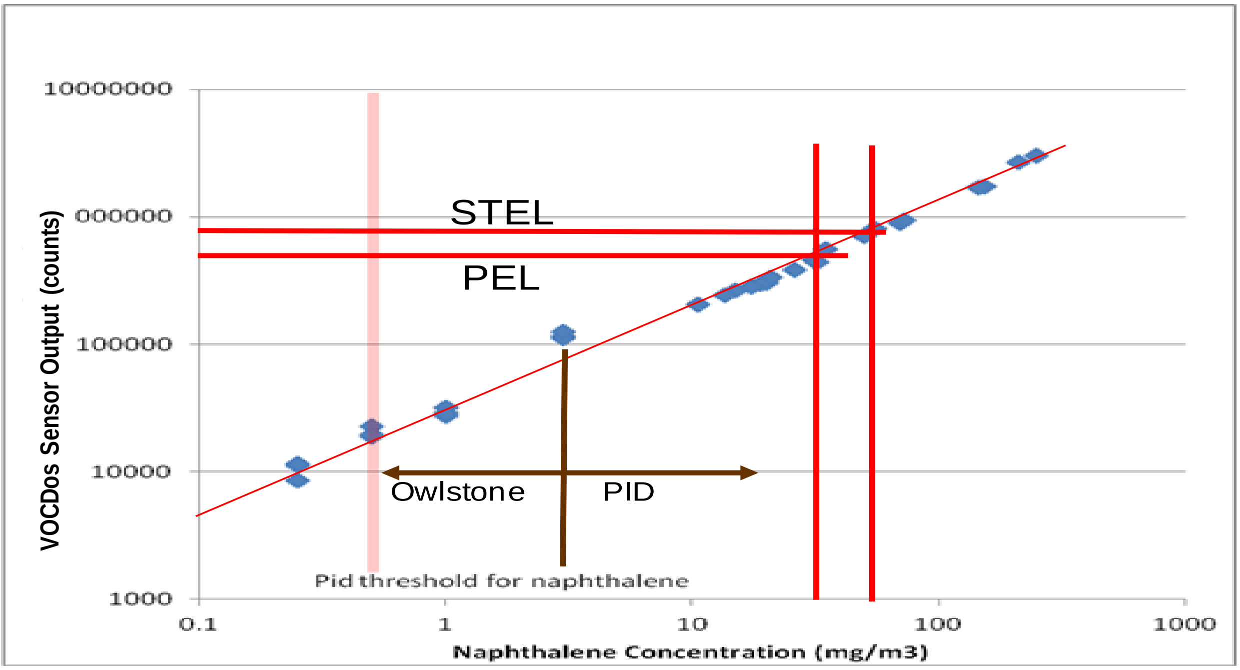

Figure 8. VOCDos signal strength versus naphthalene concentration

In the concentration range from 2 mg/m3 to 20 mg/m3, we injected known amounts of naphthalene (known volume and density) into a Kynar bag which was then recirculated through the VOCDos sensor. For the higher concentration we evolved to using a large flask filled with stainless steel wool saturated with naphthalene to provide a high surface area for evaporation. By flowing air or nitrogen through the flask and VOCDos sensor with varying amounts of make-up air/gas, we could regulate the naphthalene concentration over a range from about 30 mg/m3 to a bit over 500 mg/m3. The PID was uses as the reference point for vapor concentrations in these regions.

6. Field Trials

Initial field validation trials are currently underway under the direction of the government team including Dr. Janis E. Hulla (USACE), Dr. John Snawder (NIOSH), and Dr. Susan Proctor (USARIEM protocol #H10-10; A-15468)

Figure 9. Photos of VOCDos personal exposure monitor during JetA fueling operations

Results from one data collection run are shown below in Fig. 10, where the concentration of the naphthalene component of the jet fuel (JetA) vapor was measured using a VOCDos 3.0 sensor as a function of time. Absolute concentrations have not yet been validated. For these trials the cycle period was 3 minutes per file number (measurement point). The minimum possible cycle period is currently 1 minute although we are working to reduce this time in the future.

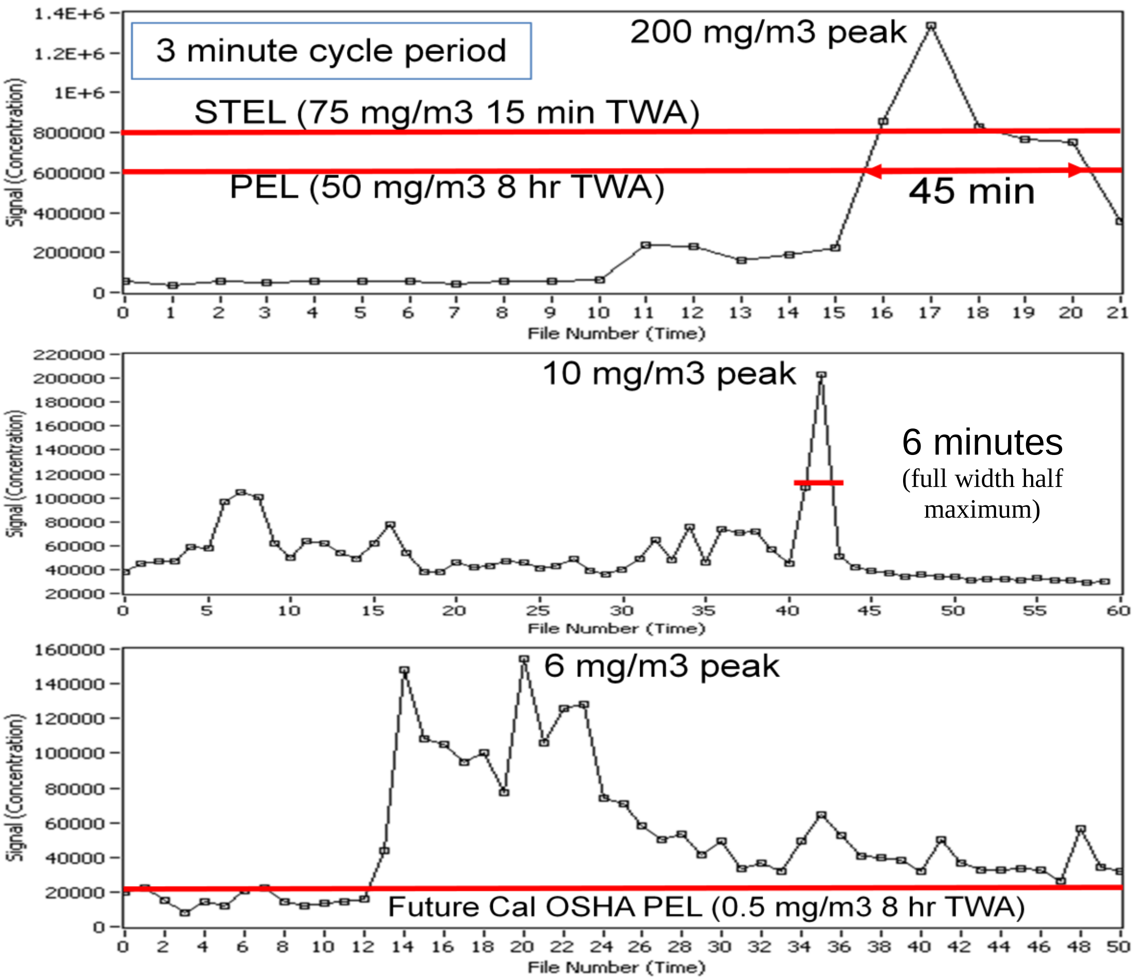

Figure 10. Preliminary field test results for VOCDos sensor showing naphthalene concentration versus time

7. Acknowledgements

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