Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

**Research Paper** 

# NaDos: A real-time, wearable, personal exposure monitor for hazardous organic vapors

Michael Reid<sup>a</sup>, Ray D. Reid<sup>a,1</sup>, Prashant Oswal<sup>a,1</sup>, Kim Sullivan<sup>a,1</sup>, Rohit Bhartia<sup>b</sup>, William F. Hug<sup>a,\*</sup>

<sup>a</sup> Photon Systems, Industrial Park, Covina, CA, United States

<sup>b</sup> NASA, Jet Propulsion Laboratory, Oak Grove Drive, Pasadena, CA, United States

# ARTICLE INFO

Article history: Received 18 November 2016 Received in revised form 14 September 2017 Accepted 19 September 2017 Available online 23 September 2017

Keywords: Real-time detector Dosimeter Naphthalene BTEX UV LED sensor Integrated optics Gas sensor Optical device

# ABSTRACT

We have demonstrated an intrinsically safe, near-real-time, personal exposure monitor (PEM) for measuring naphthalene in the breathing zone of the wearer. The NaDos PEM is a fully integrated, battery powered, <1 kg PEM, small enough to be worn by personnel working in hazardous environments. The NaDos PEM was originally developed with high detection specificity for naphthalene vapor because of the wide range of health hazards association with naphthalene inhalation, but it can also measure a wide range of HOVs including benzene, toluene, xylene, naphthalene, anthracene, etc. with a real-time limit of detection less than  $10 \,\mu g/m^3$ . The performance of the instrument has been demonstrated across a range of naphthalene concentrations from  $10 \,\mu g/m^3$  to over  $100 \,m g/m^3$ . Performance was found to meet or exceed NIOSH recommended acceptance criteria of  $\pm 25\%$  of the true concentration, >95% of time. To deliver this accuracy in a real-world environment, the monitor accurately removes the effects of both humidity (0-95% RH) and temperature ( $0 \,^\circ$ C to >45  $\,^\circ$ C). A major feature is its real-time nature, giving highly specific, high sensitivity, real time data which is a superior predictor of human health outcomes. © 2017 Elsevier B.V. All rights reserved.

## 1. Introduction

Naphthalene is a naturally occurring white crystalline solid that is commonly found in petroleum, coal, and incomplete combustion sources [1]. Naphthalene is produced in living animals and has been documented in numerous organisms including: termites (*Coptoter*-

mes formosanus); numerous flowers of the Magnolia genus; and the forehead of male white-tailed deer (Odocoileus virginianus) [2,3,4]. In our homes, naphthalene was once ubiquitously used as a moth insecticide, and most people can still remember its pungent protective smell in closets. Home use of naphthalene fell out of public favor when research elucidated the chemical dangers it poses to humans. It was identified by the National Research Council (NRC) as a serious health hazard for personnel working with jet fuels and naphthalene containing and petroleum-based sealants. In 2003 the NRC published, "Toxicologic Assessment of Jet-Propulsion Fuel 8" which states that exposure to JP8 is the single largest chemical exposure experienced by war fighters and constitutes one of their largest health risks [5]. The NRC furthered this warning as it was found that naphthalene vapor exposure had been shown to cause physical damage to lung tissue to personnel working near JP8. In 2004, the U.S. EPA drafted a health risk assessment newly characterizing naphthalene as likely human carcinogen based on data derived from rodent exposure studies [6]. Furthermore, naphthalene is especially dangerous to individuals who harbor the genetic deficiency for glucose-6-phosphate dehydrogenase. When individuals with this genetic abnormality are exposed to relatively low





CrossMark

Abbreviations: BTEX, benzene, toluene, ethylbenzene, xylene; CDC, Center for Disease Control; DOD, Department of Defense; EPA, Environmental Protection Agency; FID, Flame Ionization Detector; G6PD, Glucose-G-Phosphate dehydrogenase; GC-MS, Gas Chromatography-Mass Spectrometry; NaDos, hazardous vapor monitor; HOV, hazardous organic vapor; IDLH, immediately dangerous to life or health; IRIS, integrated risk information system; JP8, jet propulsion fuel "8"; NIOSH, National Institute of Occupational Safety and Health; OSHA, Occupational Safety Health Administration; PPM PPB, parts per million, parts per billion; PEL, permissible exposure level; PEM, personal exposure monitor; PID, photoionization detector; STEL, short term exposure level; TEC, thermoelectric cooler; TWA, time weighted average; UVLED, ultra violet light emitting diode; VOC, volatile organic compound.

<sup>\*</sup> Corresponding author.

E-mail address: w.hug@photonsystems.com (W.F. Hug).

URL: http://mailto:W.Hug@photonsystems.com (W.F. Hug).



**Fig. 1.** (Left Panel) Picture of the NaDos, showing the ruggedized black ABS shell, Inlet and outlet ports and indicator LED lights, and recessed power/event maker button. (Right Panel) NaDos, being worn in the field by fuel handlers. In this photo, the fuel handlers are wearing the NaDos in both the horizontal and vertical orientations. The air inlet tubes (shown at the tips of the black arrows) terminate in the "breathing zone" to sample equivalent airspace as the workers respiration zone.



**Fig. 2.** Plot of one cycle of the NaDos sensor. The four curves above represent the signal level of four photodiodes, each using a different spectral bandpass filter. Total time of the cycle in this example is 25 s. The baseline signals for naphthalene are in the lower wavelength channels. The signal is flat at the beginning of each cycle (Cycle Start) as the detectors are observing a recently refreshed, clean, condensation chamber. Then the signal climbs as the sample accumulates in the chamber (Accumulation Phase). Lastly, after the data is taken the chamber cleans itself out (Self Cleaning Phase), returning itself to the clean condition.

levels of naphthalene, the result is life threatening hemolysis. The frequency of this genetic deficiency has been shown to be 11% in some ethnic populations [7,8]. In response to this, moth balls were banned in Europe in 2008 to prevent accidental mothball poisoning deaths in children deficient in G6PD [9]. While US government public safety regulations are not as drastic as the European union, they have continued to increase as the health risks of naphthalene exposure are better understood. The Occupational Safety and Health Administration (OSHA) permisible exposure limit (PEL), and the National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL) are both set to  $50 \text{ mg/m}^3$  (10 ppm) as an 8 and 10 h time weighted average (TWA), respectively. The NIOSH short term exposure limit (STEL), a 15-min TWA, is set at  $75 \text{ mg/m}^3$ , and the immediately dangerous to life or health (IDLH) is 1310 mg/m<sup>3</sup>. The REL, STEL and IDLH are advisory levels while the OSHA PEL is a regulatory level that is enforcable nationally.

To measure compliance with regulatory levels of hazardous vapors, one must first be able to reliably test for the chemicals of interest. There are several gold standard technologies for detecting levels of airborne naphthalene in both the laboratory and the field, but none of them provide *real time* detection with specificity and wear-ability. The most common types of measurements are: A)

active/passive collection on solid sorbent tubes, thermal desorption tubes or whole-air sampling followed by analysis with gas chromatography/mass spectroscopy (GC–MS) or GC-flame ionization detection; B) Photoionization detectors (PID); C) Flame ionization detectors (FID); and D) colorimetric tubes.

Traditional methods of sampling on portable media with laboratory analysis by GC offer high sensitivity and specificity, but they are not able to provide any real-time or spatially resolved exposure information. Due to their accumulative storage nature, the variables of time, concentration variation, or location of exposure are not preserved in adsorption tubes. This type of information is crucial when creating risk assessments for the workers exposed to hazardous vapor, as transient high-level spikes are completely unresolvable from low level long period exposure. It has been shown that accurate health prediction exposure outcomes vary drastically for low level long exposure vs. high level short exposure. [10]

The NaDos PEM provides a novel solution to these challenges, resulting in a laboratory and field capable instrument which is real time, portable/wearable, specific, and highly sensitive. The NaDos was originally developed under U.S. Army funding to be highly selective for naphthalene vapor within a wide range of interfer-



**Fig. 3.** Excitation (Dashed Line) and Emission (Solid Line) spectra for naphthalene. The excitation peak is at 275 nm. The horizontal axis is wavelength, on the left is the excitation curve denoted by a dashed line. On the right is the emission curve with a solid line. The grey line shows were we selected the UV LED peak spectrum to maximize naphthalene absorbance. Naphthalene spectra used from http://omlc. org/spectra/PhotochemCAD/html/001.html.

ents present in jet fuel and in the real world. The NaDos is currently undergoing qualifications to arguably be the first chemical near real time, high specificity, dosimeter. The NaDos version 4.0 can be seen in Fig. 1.

The most basic function of the NaDos detector is its data collection cycle. This 25 s cycle alternates between an accumulation phase and a refreshing phase. During the accumulation phase the sample is pumped into the system and is concentrated in a patented rapidly refreshable condenser [11,12]. During the refresh portion of the cycle the system purges the condensed analyte from the accumulator. A standard run of the NaDos can be seen in Fig. 2.

During the accumulation cycle, the condensed VOC vapors are excited with UV light and emit native fluorescence with a spectral distribution corresponding to the type of accumulating material, with lower ring PAHs emitting at shorter wavelengths and larger ring PAHs at longer wavelengths [13]. The naphthalene in this sample absorbs strongly in the UV, corresponding to its first excited singlet state, and its longer wavelength emission is associated with the two fused benzene ring structures with exceptionally high quantum efficiency. The UV LED excitation source we have chosen, specifically targets naphthalene's absorbance maximum at 275 nm. This provides maximal excitation of the molecule of interest while providing some chemical selectivity by increasing the relative amount of energy that naphthalene absorbs. (As shown by the vertical line in Fig. 3). This optical absorption measurement of Naphthalene were made by R.-C. A. Fuh on 06-09-1995 using a Cary 3 avalible on OMLC.

The emission spectrum for naphthalene extends from approximately 310 nm up to 390 nm. We collect this emitted spectrum from the sample using a high numerical aperture aspheric lens. The spectrum is then separated into 4 contiguous optical channels. Each channel's individual data is recorded using a photodiode. The optical data is computationally verified to be within a specified range. This ranging ensures that the channels are neither saturated nor outside of the calibration matrix in terms of humidity and temperature. Then, a chemical identity check is performed using a spectroscopic analysis algorithm, this ensures that the chemical being scanned has the band ratio signals corresponding to naphthalene. This computation results in a go/no-go analysis where a positive outcome results in an output of concentration, while a negative outcome disqualifies the data. If the spectrum is within range, the system then passes the photodiode intensities along with the temperature and humidity into an algorithm using a concentration predicting digital look-up-table (LUT). The LUT outputs the concentration for the sample which is then stored along with the photodiode intensities, temperature, humidity, spatial location stamp (GPS), time stamp, and user ID. This data is stored on a removable SD card for future analysis which can be retrieved via a hermetic USB micro port on the front of the instrument. The entire system is powered via a single cell lithium polymer battery which provides over 30 h of continuous use on a single charge. The electronics and optics are housed in a ruggedized aluminum and ABS shell providing a hermetic seal, making it intrinsically safe in explosive environments.

# 2. Materials and methods

Naphthalene vapor was generated using a calibration gas generator (Owlstone, Inc, OVG-4 and OHG-4). The analyte permeation tubes were gravimetrically determined at CDC-NIOSH using Naphthalene (Sigma-Aldrich (>99.7%, GC, analytical standard 84679), or alternatively NIST traceable permeation tubes were directly purchased from Owlstone Inc. The permeation tubes were both calibrated and used at 100°C. The permeation rates for the various naphthalene permeation tubes ranged from 3100 ng/min up to 3414 ng/min. The concentration was controlled by varying the flow rates of the nitrogen carrier gas (99.999%, Praxair) from 50 ml/min to 4000 ml/min. The gas transfer tubing was stainless steel and Poly-tetrafluoroethylene (PTFE) tubing. Highly flexible Tygon<sup>®</sup> F-4040-A Fuel tubing provides flexible connection and strain relief as well as being chemically inert. This tube was purged with dry nitrogen for 24 h (750 ml/min) before being used, to remove any contaminants that might affect the sample. The gas was plumbed directly from the nitrogen bottles using multi stage regulators to the Owlstone in Stainless steel tubes. Then the gas was carried into a flow meter, then into an aluminum manifold which provided both an overpressure exhaust and a space for mixing of the Owlstone vapor and makeup flow nitrogen gas. The manifold exhaust then proceeded into an environmental control chamber (ECC). The ECC was an insulated aluminum Box 18 inches  $\times$  10 inches  $\times$  10 inches with 500-W thermoelectric cooler/heater system attached with a water chiller. The system can control the air temperature up above 50 °C and down to 5 °C. It is also able to control the humidity from  $\sim 0 \text{ g/m}^3$  up to  $< 14 \text{ g/m}^3$ . The NaDos devices are placed into the chamber and the air flow into the NaDos device is governed by an internal Parker T2-05 micro diaphragm pump which ensures a constant 750 ml/min air flow through the detector.

#### 2.1. Pulsed flow of analytes into the NaDos and PID

The PID (PPB RAE 3000 from RAE Systems) and NaDos were run in parallel paths using the PTFE/Tygon Owlstone setup described above without the ECC. The mixing manifold exhaust was ported directly into the front of the NaDos unit as temperature and humidity were not controlled for in this set of experiments. In lieu of the ECC a preloading chamber was added which comprised a bidirectional port and small preloading chamber, which allowed the sample to be run in two sides in parallel. The air could either pass through the preload chamber or parallel though clean lines. Liquid aliquots of 2.5 µl of the fuels were directly injected into a preloading chamber upstream of the parallel split and then drawn into the NaDos sample line using the Owlstone mass controllers at 2000 ml/min nitrogen feed. This enabled the two devices to pull as much analyte as needed while providing the ability to divert the flow through the sample preload chamber and maintain uninterrupted flow into the two devices.

#### 2.2. Chemometric method using band ratio analysis

Each of the 6 analytes were generated by the Owlstone as described above. The analyte permeation tubes were gravimet-

rically determined at CDC-NIOSH using Fluorene (Sigma-Aldrich, Analytical Standard, 48568), Biphenyl (Sigma-Aldrich, PESTANAL, Analytical Standard, 35800), Benzene (Sigma-Aldrich, HPLC 99.9%, 270709), m-Xylene (Sigma-Aldrich, Analytical Grade 99.5%, 95670), Toluene (Sigma-Aldrich, Anhydrous 99.8%, 244511), 2methylnapthalene (Sigma-Aldrich, 97% m57006), ethyl-benzene (Sigma-Aldrich, Anhydrous 99.8%, 296848). Permeation tubes for each of the additional non-naphthalene samples were either created or purchased from Owlstone Inc (Permeation Tube manufacturing kit #00-0017). The gas samples were injected directly from the Owlstone OVG-4 (500 ml/min) into the mixing manifold. The sample gas was then passed from the mixing manifold directly into the NaDos and PID and not through the ECC. Dry nitrogen was introduced at a rate of 1500 ml/min for a total of 2000 ml/minute into the mixing manifold. This ensured that the PID and NaDos were both able to draw their minimum required volume of sample.

## 2.3. Naphthalene calculation of limit of detection (LOD)

Naphthalene vapor below 10 mg/ml was generated using the Owlstone OVG-4, above 10 mg/ml naphthalene vapor was generated using naphthalene solid in a 500 ml DURAN square bottle (Sigma Aldrich Z681121). This is achieved by feeding air into the bottle containing the solid naphthalene. The concentration was adjusted with makeup flow from 100 ml/min up to 9000 ml/min. The makeup flow was composed of dry nitrogen and the humidity was maintained at 0 mg/ml. Flow rates were controlled via the Owlstone nitrogen feed and verified using a ball flow meter. The sample concentration was verified using a PID 3000. The lines were allowed to equilibrate for 30 min between different samples, after this time they were verified to have settled at the recorded value with 3 data points, separated by 1 min between data points.

# 2.4. Discrimination: jet-A, syntroleum, Doped/Undoped

Air volumes were mass controlled using the Owlstone OVG-4. Naphthalene was also generated using the previously described permeation tube setup for Naphthalene. New unused connectors and tubes were used in for each experiment to ensure minimal carryover. Naphthalene doped samples were introduced by porting the naphthalene into the mixing manifold instead of equivalent volumes of dry nitrogen from the Owlstone OVG-4. Syntroleum (Synthetic Jet Fuel without naphthalene, Syntroleum Corp.) Samples were created in known volume Kynar Bags (KeikaVentures 10L bags, Roberts Valve, #TB-10LRoberts) with known gas volumes. Concentration volumes were generated by adding small liquid quantities of Syntroleum into the Kynar Bags. After waiting 30 min for the sample to evaporate the bags were at known Syntroleum concentrations. Data collection proceeded by connecting the Roberts Valves to EPDM tubing and into the NaDos and PID, bags using the onboard pump. This allows for the NaDos and PID to pull exactly the amount of volume that they require.

#### 2.5. Naphthalene calculation vs. temperature and humidity

Samples were generated using the Owlstone OVG-4 in our environmental chamber described above. Concentrations of naph-thalene were generated at 212 ug/m<sup>3</sup> and at 750 ug/m<sup>3</sup>. At each concentration, the humidity was set at the lowest value obtainable for the environmental chamber <1 g/m<sup>3</sup>. This was done by closing the OHG humidity port flow to zero. The resulting nitrogen feed was "Dry" as naphthalene was flowed at the correct humidity value. The temperature of this example data point was kept at 10 °C. The system was let to equilibrate for 10 min then data collection was taken using an automatic cycle on the instrument. The temperature was then automatically increased by 10 °C and the

data collection was repeated until the temperature reached 40 °C. The OHG humidity port was then increased until the value was at 2 g/m3. The wait and data collection cycle was repeated until every temperature and humidity was sampled, this entire procedure was reproduced at both concentrations. The humidity generated at each of these concentrations using the OHG and verified using the Owlstone humidity sensor as well as a NaDos onboard humidity sensor. The temperatures were measured by the thermistors in the ECC and verified by the onboard temperature sensor on the NaDos. Concentration is predicted by taking the variables of temperature and humidity and signal and plugging them into the embedded LUT to generate real time naphthalene concentrations, corrected for ambient temperature and humidity. The results were plotted using Microsoft Excel.

# 3. Results and discussions

# 3.1. Signal/concentrations accuracy against single chemical confusants

The spectral responsiveness of the device was evaluated to ensure the NaDos can discriminate naphthalene from other chemicals. The first step was to evaluate lower than STEL levels of benzene, toluene, ethylbenzene and xylenes (BTEX) confusants with the device. We chose sub STEL exposure levels of confusants due to the workers anticipated environment. In Fig. 4, five different chemical vapors were presented to the NaDos. Each chemical is introduced as a 10-min square wave pulse. The data is represented as either the solid line for the NaDos or the dotted line for the PID. The leading/lagging edges are rounded due to equilibration of the lines and the internal space of the instruments. The NaDos line is the solid line that shows near zero concentration for all 4 confusants, yet for the naphthalene pulse it produces an accurate concentration of 2750  $\mu$ g/m<sup>3</sup>. This demonstrates the NaDos's selectivity for naphthalene in the presence of BTEX compounds.

#### 3.2. Naphthalene discrimination from other chemicals

The ability of the sensor to spectrally separate chemicals was evaluated. We previously reported that chemical identity can be determined from fluorescence emission spectra using any of a variety of analysis tools, including simple spectral band ratios [11,12]. To generate 2D representations of chemical space we ratio the 320 nm (Ch 1) and 340 nm (Ch 2) photodiode signals, we plot this as the abscissa coordinate. We assign the ratio of the 360 nm (Ch 3) and 380 nm (Ch 4) photodiode channels to the ordinate axis. Multiple runs for each chemical were plotted to generate the data clusters shown in Fig. 5. The space in Fig. 5 is a chemical space where different chemicals are represented in different locations in this 2D space.

The NaDos chemometric comparison algorithm separates chemicals based upon spectral relatedness by using band ratios. Each chemical creates a cluster of points closer (Euclidian Distance) to itself than to its nearest relatives. The relatedness can clearly be seen when one takes the two naphthalene family members (naphthalene and 2-methyl-naphthalene). These two molecules' points cluster in a small region of the plot, while the two single-ring based molecules of benzene and toluene who cluster together in another region of the plot. The two groups of molecules cluster in different regions, yet the more closely related molecules clustering closer than the more distant molecules. Furthermore, it can be seen that each chemical occupies its own chemical space. This can be seen when considering the molecule grouping of naphthalene, and can be illustrated by circumscribing a bounding oval around the naphthalene cluster. This bounding oval centroid forms the basis of the

# BTEX and Naphthalene Concentration vs PID and NaDos



Fig. 4. Graphical representation of chemical sensing of the PPB RAE3000 and NaDos. Five chemicals were introduced into the sampling stream (benzene, ethylbenzene, xylene, and naphthalene). The dotted line is the PID data, and the solid line is the NaDos data. The PID is nonspecific and responds similarly to each of the five chemicals, while the NaDos generates signal only for naphthalene vapor.



# Chemometric Comparison using Channel Ratio Analysis (CRA)

Fig. 5. Chemometric comparison of all the chemicals tested. Y axis is the ratio of the first two spectral channels and the x axis is ratio of the second two channels. Notice the tight cluster of the ratios for an individual chemical compared to the large spread on the axis. All of these chemicals are easily differentiated.

chemical identification algorithm. When the NaDos takes data in the field, the system verifies that the spectral ratio occurs within the limiting oval bounded by the naphthalene values. The calculation then returns a positive identification for naphthalene and the system calculates naphthalene concentration from the signal level. If the signal is not enclosed by naphthalene's bounding circle, the data is not used to generate a naphthalene concentration, and an error is issued in the file.

#### 3.3. Naphthalene calculation accuracy and LOD

The range of linearity of detection for the sensor was evaluated. In Fig. 6 we see the graph of the NaDos signal vs. pure naphthalene vapor. The naphthalene concentration ranged from 43  $\mu$ g/m<sup>3</sup> up through 100,000  $\mu$ g/m<sup>3</sup> with an accuracy of correlation coefficient R<sup>2</sup> = 0.9929. For the duration of this experiment, humidity was maintained at <1.0 g/m<sup>3</sup> and temperature was kept at 25 °C. The signal vs. concentration for this device shows a linear response to naphthalene concentration.

A digital Look-Up-Table (LUT) for the calibration curve is generated using a large range of naphthalene vapor concentrations from the Owlstone OVG system. The resultant output of this look up table is represented as the vertical axis on the plot, showing the correct concentration.

# 3.4. Naphthalene concentration determination in multi-chemical environments with JET-A and syntroleum

The calculation of naphthalene concentration in the presence of jet fuel was evaluated. Jet fuel is composed of hundreds of chemicals that change their relative abundance depending upon the manufacturer and time of the year [14]. NaDos has the requirement to be able to report accurate naphthalene concentrations, despite the varying hydrocarbon background. To clearly show the invisibility of hydrocarbon background we use Syntroleum, a synthetic jet fuel

Calculated Concentration vs. Generated Concentration of Naphthalene

10,000

Fig. 6. Linear plot of concentration of naphthalene vs. signal showing the linearity of the NaDos with an increasing naphthalene concentration. The horizontal axis represents the calculated concentration of naphthalene molecule from the Owlstone. The vertical axis is the amount of naphthalene that the NaDos sensor predicts is present in the sample.

1,000

Calculated Concentration of Naphtalene (ug/m3)

100

#### Table 1

Representation of naphthalene sensing in fuel with and without naphthalene. The PID sees both fuels equally while the NaDos only sees signal in fuel containing naphthalene, even with the numerous amounts of the chemicals in the fuel.

	JET A (Contains		Syntroleum (Contains no		No Fuel (Contains no	
	Naphthalene) (Unspiked)		Naphthalene) (Unspiked)		Naphthalene)(Unspiked)	
	(Spiked)		(Spiked)		Spiked)	
Photoionization Detector (RAE PPB-3000)	21,011 μg/m <sup>3</sup>	24,024 μg/m <sup>3</sup>	19,891 μg/m <sup>3</sup>	23,117 μg/m³	400 μg/m³	3315 μg/m <sup>3</sup>
Naphthalene Monitor (NaDos 3.0)	12,418 μg/m <sup>3</sup>	15,310 μg/m <sup>3</sup>	4 μg/m <sup>3</sup>	2857 μg/m³	87 μg/m³	2718 μg/m <sup>3</sup>

manufactured free from naphthalene. We performed these experiments with Jet A with and without spiked naphthalene, and with Syntroleum with and without spiked naphthalene. A table of the specificity of the NaDos compared to a PID is illustrated in Table 1. In this table, the top row shows that the PID reports high concentrations of VOC from both jet fuel and Syntroleum. The bottom row shows the NaDos readings; Jet A shows large amounts of naphthalene and the Syntroleum gives a reading of almost no detectable amount of naphthalene. This demonstrates the specificity that the NaDos sensor achieves. Furthermore, we ran all the samples with and without a naphthalene addition via spiking. In all three samples, the PID saw accurate amounts of signal in the nitrogen-only samples and were unspecific in the others. The NaDos reports accurate values for all the spiked and un-spiked samples, even in the presence of JET A and Syntroleum.

100.000

10.000

1,000

100

10 + 10

Generated Concentration of Naphthalene (ug/m3)

## 3.5. Naphthalene calculation vs. temperature and humidity

The purpose of the NaDos is to generate a reliable concentration in the real-world conditions which has varied temperatures and humidities. To this end, we evaluated the NaDos over a large range of temperatures and humidities using our environmental chamber. Fig. 7 shows the ability of the NaDos to reproducibly predict the concentration of naphthalene with while varying the humidity and temperature, each concentration approximately 50 values are shown. The temperature and humidity matrix spanned 2 concentrations 212 and 750 ug/cm<sup>3</sup>. At each concentration, we varied the humidity 6 values (0, 2, 4, 6, 8 and  $10 \text{ g/m}^3$  unless saturation prohibited data collection.). Then, at each humidity value we varied the temperature 5 times. (10 °C, 20 °C, 30 °C, 40 °C). The plot shows that even though the temperature and humidity varied, the signal from the NaDos predicted the correct values for the entire operating range of varied humidities and temperatures. This figure shows that the NaDos can accommodate the various temperatures and humidities of the real world all the while being able to predict the concentration of naphthalene vapor.

100,000

# 4. Conclusions

We report that we have developed a novel personal exposure monitor technology that provides real-time quantification with high specificity for naphthalene vapor and other HOVs. We have shown that the system has a short (<30 s) response time, is repeatable and is stable. The concentration vs. signal is a linear function and the concentration prediction algorithm decouples the nonlinear environmental factors of temperature and humidity from the naphthalene signal to give an accurate concentration value. Interferents have been optically reduced via excitation and emission band selection. They have further been digitally eliminated via algorithms that remove their effects on concentration prediction based upon ratios of signal in adjacent bands. We have experienced little to no system contamination after weeks of field operations by fuel handlers and at fracking sites. On rare occasions where contamination occurred it was easily cleaned. The system has a high ease of use and offers stability and robustness, making this device a viable wearable detector for naphthalene and other HOVs. It also offers advantages over the current nonspecific/non-real-time devices in a wide range of domestic, commercial, and industrial settings. Future work will be focused upon further miniaturization of the device, improved signal to noise, faster cycle times and increasing its robustness and ease of use.

To date, NaDos PEM development has been an ongoing collaboration between Photon Systems Inc. as the tool developer and several organizations for independent laboratory and field validation, including: Army Research Laboratory, Army Corps of Engineers, NIOSH, and The Water & Environmental Technology (WET) Center at Temple University. Laboratory validation studies of the NaDos PEM have been ongoing since the beginnings of this program in 2008. Parallel validation studies have been ongoing



Concentration Predcted by NaDos 2.5 vs. Owlstone Setpoint Concentration

**Fig. 7.** This figure shows that at concentrations of 212 ug/m<sup>3</sup> and at 750 ug/m<sup>3</sup>, the NaDos is within the required  $\pm 25\%$  error margin >95% of the time. Across the bottom is the delivered naphthalene concentration values. On the vertical axis is the readout predicted concentration of naphthalene from the NaDos. Each point corresponds to a value of naphthalene in the 3d grid of temperature and humidity. The dark grey line represents the out of calibration zone at +.25% of the targeted signal.

at NIOSH/Cincinnati and the Water & Environmental Technology (WET) Center at Temple University under the direction of Prof. Rominder Suri.

# Acknowledgements

Photon Systems, Inc. would like to thank the U.S. Army Research Office for Phase I and II SBIRs and Enhancements for funding this work. Photon Systems, Inc. would also like to thank Dr. John Snawder, Dr. Janis Hulla, Dr. Susan Proctor, and Belinda Johnson for fruitful discussions and their hard work. This development effort has been supported by the U.S. Army Research Office starting Jan. 11, 2008 under Phase I and II SBIRs and Enhancements and review ed by the Naphthalene Advisory Committee since its inception.

#### References

- [1] J.Y. Batterman, Sources, concentrations, and risks of naphtlaene in indoor and outdoor air, Indoor Air 22 (Issue 4) (2012) 266–278.
- [2] J.W. Gassett, et al., Volatile compounds from interdigtal gland of male white tailed deer. (Odocoileus virginianus), J. Chem. Ecol. 9 (1996) 1689–1696.
- [3] H. Azuma, Naphthalene–a constituent of Magnolia flowers, Phytochemistry 42 (Issue 4) (1996) 999–1004.
- [4] J. Chen, et al., Termites fumigate their nests with naphthalene, Nature (1998) 558–559.
- [5] National Research Council, Toxicologic Assessment of Jet-Propulsion Fuel 8, The National Academies Press, Washington DC, 2003.
- [6] National Toxicology Program, Toxicology and Carcinogenesis Studies of Napthalene, NIH Publication No. 01-4434, Research Triangle Park, NC 27709, 2000.
- [7] K. Shannon, et al., Severe hemolytic anemia in black children with
- glucose-6-phosphate dehydrogenase deficiency, Pediatrics 70 (1982) 3649. [8] T. Valaes, et al., Acute hemolysis due to naphthalene inhalation, J. Pediatr. 63
- (1963) 904–915. [9] W.O. Tarnow-Mordi, et al., Risk of brain damage in babies from naphthalene
- in mothballs: call to consider a national ban, Med. J. Aust. 194 (3) (2011) 150. [10] J. Bailer, D.G. Hoel, Metabolite-Based internal doses used in aRisk assessment
- of benzene, Environ. Health Perspect. 82 (1989) 177–184. [11] W.T. Hug, R. Bhartia, & R.D. Reid (2014). Native fluorescence detection
- [11] W.I. Hug, R. Bhartia, & R.D. Reid (2014). Native fluorescence detection methods and detectors for naphalene and/or other volatile organic compound vapors. US Patent Office, U.S. Patent No. 8, 759, 791.

- [12] W. Hug, R. Bhartia, R. Reid, M. Reid, P. Oswal, A. Lane, S.P. Proctor, Wearable real-Time direct-Reading napthalene and VOC personal exposure monitor, SPIE Sec Def. (2014).
- [13] T. Vo-Dinh, J. Fetzer, A.D. Campiglia, Monitoring and characterization of polyaromatic compounds in the environment, Talanta (1998) 943–969.
- [14] J.E. Shepherd, et al., Flash Point and Chemical Composition of Aviation Kerosene (Jet A), California Institute of Technology, Pasadena, 2000.

# **Further Reading**

Naphthalene spectra available from http://omlc.org/spectra/ PhotochemCAD/html/001.html

# **Biographies**

Michael Reid is a Senior Scientist at Photon Systems with over 8 years of experience in chemical and biological research and development of electro-optical instruments and sensors, with long specific experience on vapor detectors. Mr. Reid, has worked at Monsanto, JPL, and Spector Virology Labs during his undergraduate career. Prior to joining Photon Systems in 2012, he had a research fellowship at California Institute of Technology in Molecular Biophysics from 2003 to 2011, working under Prof. Carl Parker. He has a B.S. from the University of California, San Diego, CA.

**Ray D. Reid** is President and COO of Photon Systems, Inc., founded to develop deep UV lasers and chemical, biological and explosives sensors enabled by these lasers. Previously he was General Manager of the Optical Radiation Division of Perkin Elmer, Corp. and Director of R&D. Prior to Perkin Elmer Mr. Reid was a founder and VP of Engineering at Omnichrome Corporation for 15 years and with Xerox Electro-Optical Systems. Mr. Reid has an M.S and B.S. in electrical engineering at Colorado State University. He has over 60 patents and publications.

**Prashant Oswal** is a Senior Software Engineer at Photon Systems and principal developer of the software used in the NaDos and VOCDos instruments. Mr. Oswal is a Certified LabView Architect with over 8 years of experience is the design of virtual instruments, with a focus on electro-optical instruments at Photon Systems. Certified LabVIEW Architect since October 2008. National Instruments Certified Architects have mastered not only the technical aspects of the product, but can implement the most efficient solution in a team environment. A Certified Architect is the highest level of certification available from National Instruments, and signifies the ability to lead complex projects from conception through completion. Mr. Oswal as an M.S. from Clemson University.

Kim Sullivan is an opto-mechanical engineer at Photon Systems with broad experience in optical components and opto-mechanical design. Mrs. Sullivan has over 15 years of experience designing optical systems and is the principal opto-mechanical designer for the NaDos and VOCDos sensors.

**Rohit Bhartia** is Deputy Principal Investigator for the 2020 Mars lander instrument, SHERLOC (Scanning habitable environments with Raman and Luminescence in search of Organic Chemicals). For the past 17 years, Dr. Bhartia has been leading research programs and developing lab and field hardware and software for Deep UV based native fluorescence and Raman instruments for NASA related organics and life detection as well as for DoD instruments for chemical, biological, and explosives detection. Dr Bhartia has a Ph.D. and M.S. from the University of Southern California, and a B.S. from the University of Wisconsin at Madison, WI. William F. Hug is Chairman and CEO of Photon Systems, Inc., founded to develop deep UV lasers and chemical, biological and explosives sensors enabled by these lasers. In 2004 he was awarded the DARPA/SUVOS Outstanding Performer Award. Previously, Dr. Hug was founder and president of Omnichrome Corporation for 15 years and with Xerox Electro-Optical Systems where he was Director of Light Source Technology. Dr. Hug was a postdoctoral fellow at the Institute for Space Propulsion at Univ. of Stuttgart, Germany, received a Ph.D. from Northwestern University, a B.S. from the Univ. of Notre Dame, and has over 100 patents and publications.