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Research Paper

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

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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 mg/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 °C to >45 °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.

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 (*Coptotermes 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

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-6-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.

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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.

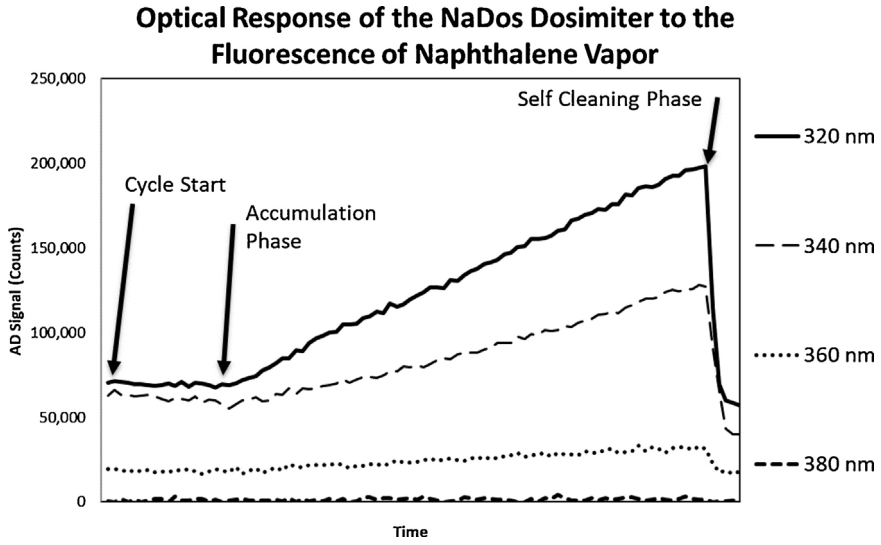

Fig. 2. Plot of one cycle of the NaDos sensor. The four curves above represent the signal level of four photodiodes, each using a different spectral bandpass filter. Total time of the cycle in this example is 25 s. The baseline signals for naphthalene are in the lower wavelength channels. The signal 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 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 mg/m^3, and the immediately dangerous to life or health (IDLH) is 1310 mg/m^3. 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-

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