



Hyperspectral analysis for standoff detection of dimethyl methylphosphonate on building materials



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ABSTRACT

Detecting organophosphates in indoor settings can greatly benefit from more efficient and faster methods of surveying large surface areas than conventional approaches, which sample small surface areas followed by extraction and analysis. This study examined a standoff detection technique utilizing hyperspectral imaging for analysis of building materials in near-real time. In this proof-of-concept study, dimethyl methylphosphonate (DMMP) was applied to stainless steel and laminate coupons and spectra were collected during active illumination. Absorbance bands at approximately 1275 cm^{-1} and 1050 cm^{-1} were associated with phosphorus-oxygen double bond ($\text{P}=\text{O}$) and phosphorus-oxygen-carbon ($\text{P}-\text{O}-\text{C}$) bond stretches of DMMP, respectively. The magnitude of these bands increased linearly ($r^2 = 0.93$) with DMMP across the full absorbance spectrum, between $\nu_1 = 877\text{ cm}^{-1}$ to $\nu_2 = 1262\text{ cm}^{-1}$. Comparisons between bare and contaminated surfaces on stainless steel using the spectral contrast angle technique indicated that the bare samples showed no sign of contamination, with large uniformly distributed contrast angles of 45° – 55° , while the contaminated samples had smaller spectral contact angles of $<20^\circ$ in the contaminated region and $>40^\circ$ in the uncontaminated region. The laminate contaminated region exhibited contact angles of $<25^\circ$. To the best of our knowledge, this is the first report to demonstrate that hyperspectral imaging can be used to detect DMMP on building materials, with detection levels similar to concentrations expected for some organophosphate deposition scenarios.

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1. Introduction

Monitoring the indoor environment is an important priority because people spend large portions of time inside of buildings [24,26]. Indoor monitoring has been carried out for a wide range of conditions and air pollutants [7,9,13,21,29], and there is now a need to expand these efforts to address rising concerns related to the presence of organophosphate (OP) compounds on indoor surfaces. This may be caused by over-application of pesticides in homes, and in some cases by incidental transport from residential areas (e.g. gardens, playgrounds) or outdoor workplaces where pesticide

application is heavy [5]. Indoor OP exposure may also result from intentional or accidental release of compounds used as chemical warfare agents. There have been previous efforts to detect OPs on indoor surfaces [30]. OPs have been previously linked to leukemia [6,17], prostate cancer [2], Non-Hodgkin's lymphoma [6], and pediatric mental disorders such as pediatric attention-deficit/hyperactivity disorder (ADHD) [17]. Thus, severe public health consequences can result from OP exposure.

Decontamination of indoor surfaces would be greatly aided by fast and accurate screening and detection methods for OPs. Currently, OPs are often detected via chromatographic methods, which are expensive and require extensive sample preparation and laboratory analysis. Further, the current sampling collection methods rely on labor intensive surface wipe sampling. This limits the total number of samples that can be collected and increases the

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possibility that some contamination may go undetected. Shipping, handling, and processing of the number of samples generated from a contaminated area will also create a backlog during sample preparation and analysis, thus, delaying decontamination efforts and decision-making during the remediation phase of an incident. A standoff detection method, via use of field instrumentation, would be an effective tool to reduce the working time (i.e., time needed to survey, sample, analyze, and detect target analytes in an area) by fast screening large areas for potential OP contamination, identifying hot spots (as well as areas where contamination may not be present), allowing workers to decontaminate the surfaces immediately, enabling monitoring of the decontamination progress, and reducing sample load on the laboratory.

Optical imaging methods employing ultraviolet absorption or use of fluorophores have been reported for chemical detection (e.g. Refs. [18,27]). Optical spectroscopy, in particular, takes advantage of characteristic vibrational frequencies in the optical spectra for detecting various molecules [16]. used a high spatial resolution hyperspectral imaging system to reveal a chlorophyll absorption waveband (685 nm) and two bands in the near infra-red region to identify apples that were contaminated with soil or fungus. Similar work has been investigated for the detection of contaminated fruit [10,14] and the detection of fecal coliforms on poultry carcasses [12]. Hyperspectral imaging techniques have also been used to detect prostate cancer [1], damaged tooth enamel [23], and to detect water stress in plants [11]. Environmental monitoring can also benefit from using hyperspectral imaging techniques. A recent example from Ref. [4]; presents preliminary data which distinguished both VX (IUPAC name O-ethyl S-[2-(diisopropylamino) ethyl] methylphosphonothioate) and sulfur mustard from benign compounds using mid-wave infrared hyperspectral imaging. Thus, hyperspectral imaging, a technique well-established in other technical fields, may be a viable standoff approach for OP detection on indoor surfaces.

This study investigates the ability of hyperspectral imaging to detect OPs on common indoor building materials. Data processing approaches enabling qualitative and quantitative detection will be developed to demonstrate the proof-of-concept for this approach. This study utilized dimethyl methyl phosphonate (DMMP) as a surrogate for common organophosphate pesticides and structurally related chemical warfare agents.

2. Materials and methods

2.1. Equipment and materials

2.1.1. Hyperspectral imager

The instrument used for this investigation was a Telops Hyper-Cam (Telops Inc., Quebec City, Quebec, Canada) which is composed of a long-wave infrared (LWIR, 8–12 μm) imaging Fourier Transform Spectrometer, LW-IFTS, as shown in Fig. 1a. The LW-IFTS is described previously in Ref. [15]. A 320×256 pixel (30 μm pixel pitch) HgCdTe focal plan array (FPA) is integrated with a Michelson interferometer. A series of modulated intensity images corresponding to various optical path differences were collected on the FPA, forming a double-sided interferogram at each pixel. A Fourier transform of each pixel's interferogram produces an uncalibrated spectrum. Two internal blackbody sources at 25 and 50 $^{\circ}\text{C}$ were used to calibrate the instrument for absolute spectral radiance [20]. The interferometer has a native spectral resolution of 0.25 cm^{-1} , but this was degraded to 4 cm^{-1} in order to improve the signal-to-noise ratio. The spectral bandwidth is limited to 833–1250 cm^{-1} by the HgCdTe detector. The instantaneous field of view using an f/2 collection optic is 0.8 mm/pixel. Temporal averaging was used for 20–40 hyperspectral data cubes to improve the signal

to noise ratio. Typical signals at zero optical path difference were $10\text{ }\mu\text{W}/\text{cm}^2\text{ sr cm}^{-1}$, or 25% of the camera's 16 bit dynamic range. The 1σ variance in the spectral radiance was typically $\sim 0.002\text{ }\mu\text{W}/\text{cm}^2\text{ sr cm}^{-1}$.

2.1.2. Building material coupon preparation

Building materials included 4" x 4" coupons made of polished stainless steel (McMaster Carr, Elmhurst, IL) or laminate (Home Depot, Cincinnati, OH). DMMP (Alpha Aesar, Ward Hill, MA) was applied to a portion of the coupon yielding surface densities of $22\text{ }\mu\text{g}/\text{cm}^2 - 1.1\text{ mg}/\text{cm}^2$. The following materials were chosen because they will likely result in minimal target analyte loss into the material due to absorption, yet, still are common materials found within an urban setting. Several application methods were used. First, 10, 25 or 50 μL droplet of a 98% DMMP solution was applied to the surface and then smeared with the tip of a pipette. An additional method included applying 1, 5 and 10 μL volumes of 98% DMMP solution with methanol in a 1:1 ratio to the surface, covering half the coupon surface, then allowing the methanol to evaporate. Finally, a 10 μL of DMMP was applied in an "X" pattern in the center of the coupon.

2.2. Data collection

Contaminated surfaces were illuminated with an extended-area blackbody (Electro Optic Industries, Inc., Model CE600-06, Santa Barbara, CA, USA) and imaged by the LW-IFTS instrument as shown in Fig. 1b. Emissions from infrared sources may be attenuated by two passing through the contaminated film, reflecting off of the metal surface, and passing back through the film toward the imager. Alternatively, the source may preferentially heat the contaminant, leading to a positive temperature difference with the surface and an emission spectrum. The building material coupons were held vertically in a lab hood at a 45° angle relative to the face of the hood. The blackbody illumination source was placed inside the hood, facing the sample at a 45° angle. The Telops Hyper-cam was set up outside of the lab hood, also at a 45° angle to the surface. For each image collected, an equal number of acquisitions for each blackbody were also collected for calibration purposes. Once the sample was in place, the temperature of the illumination blackbody was adjusted so the signal in the contaminated area was between that of the two internal blackbodies.

3. Results

3.1. The effect of DMMP on spectral radiance

Typical spectra for DMMP on both stainless steel and laminate are provided in Fig. 2. These spectra were spatially averaged over the center of the image. The blackbody signal for the stainless steel surface was increasingly attenuated as the quantity of DMMP applied increased. The signal can be converted to absorbance,

$$A(\nu) = -\ln\left(\frac{I(\nu)}{I_0(\nu)}\right) \cong \frac{I_0(\nu) - I(\nu)}{I_0(\nu)} \quad (1)$$

where I_0 = spectral intensity of the bare sample, and I = spectral intensity of the contaminated surface, as shown in Fig. 3a. The absorbance values for the stainless steel samples were low and can be approximated by the fractional difference between the sample and bare sample. The observed spectra were well correlated with a standard reference absorption spectrum for liquid DMMP [19,22]. Absorbance bands at approximately 1275 cm^{-1} and 1050 cm^{-1} were associated with the phosphorus-oxygen double bond ($\text{P}=\text{O}$) and phosphorus-oxygen-carbon ($\text{P}-\text{O}-\text{C}$) bond stretches of DMMP,

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