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Non-contact detection of chemical warfare simulant triethyl phosphate using PM-IRRAS

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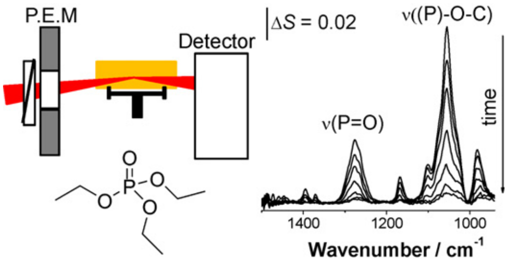
HIGHLIGHTS

- PM-IRRAS was employed to detect the chemical warfare agent (CWA) simulant triethyl phosphate.
- The targeted CWAs (G and V-series nerve agents) are characterized by phosphoric group vibrations.
- The P=O and (P)—O—C bands were used to determine the experimental limit of detection (LoD).
- The estimated LoD is 300 times lower than the typical lethal dose of G and V-series nerve agents.
- PM-IRRAS shows promise as a technology of an optically-based system for non-contact detection of persistent CWAs.

GRAPHICAL ABSTRACT



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ABSTRACT

Polarization modulation-infrared reflection absorption spectroscopy (PM-IRRAS) was employed to detect the chemical warfare agent (CWA) simulant triethyl phosphate (TEP) on gold, as well as on US military paint, i.e., chemical agent resistant coating (CARC). The targeted CWAs (G and V-series nerve agents) are characterized by phosphoric group vibrations present in the 1200 cm^{-1} region. TEP displays two prominent peaks at 1268 cm^{-1} and 1036 cm^{-1} corresponding to P=O and (P)—O—C vibrations, respectively. A droplet of TEP solution in cyclohexane was deposited on gold and CARC substrates and after solvent evaporation PM-IRRAS spectra were collected in the 1200 cm^{-1} region. The integrated peak area of the P=O and (P)—O—C vibrations was used to construct calibration curves and to determine the experimental limit of detection (LoD). In the case of gold as the substrate the estimated LoD of ~0.48 μg and 1.23 μg was obtained for the P=O and (P)—O—C vibrations, respectively. In the case of CARC, a LoD of 24 μg was determined. These detection limits are at least 3 orders of magnitude lower than the typical lethal dose of G and V-series nerve agents, demonstrating potential of PM-IRRAS for non-contact detection of these CWAs.

1. Introduction

With the end of the Cold War and ratification of the Chemical Weapons Convention by 188 States Parties (as of 27 May 2009) the threat of large-scale chemical warfare on the battlefield has decreased. However, the Sarin attack on the Tokyo subway in 1995 and the delivery of anthrax-contaminated letters following

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Abbreviations: PM-IRRAS, polarization modulation-infrared reflection absorption spectroscopy; TEP, triethyl phosphate; TMP, trimethyl phosphate; LoD, limit of detection; CWA, chemical warfare agent; CARC, chemical agent resistant coating; PEM, photoelastic modulator; SSD, synchronous sampling demodulator.

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the terrorist attacks on September 11th, 2001 have caused concern among both citizenry and governments, leading to significant research efforts and expenditures into both field- and laboratory-based detection and identification methods for chemical warfare agents (CWAs).

Research into CWA detection systems has resulted in robust, fielded systems for vapour detection such as ion mobility spectrometers (IMS) [1,2] and flame photometric detectors [2,3]. However, the robust, fielded detection of CWAs in condensed phases remains problematic. For example, the nerve agent VX (ethyl({2-[bis(propan-2-yl)amino]ethyl}sulfanyl)(methyl) phosphinate) has an extremely low vapour pressure (i.e., 7×10^{-4} Torr at 25 °C) making it challenging to detect with vapour detection systems. However its low volatility and relative stability make the liquid a persistent contact hazard and an inhalation hazard if it is re-aerosolized. Contact-based technologies exist which are suitable for detecting VX [4], but a contact-based approach typically requires resupply of consumables and possibly decontaminant solutions, neither of which are ideal for field applications. It is conceivable therefore that a military team wearing full personal protective equipment (PPE) and equipped with hand-held vapour-phase CWA detectors would rapidly secure a site and verify the absence of airborne contaminants, causing them to give an erroneous "all clear" to a follow-up investigation team. Such a follow-up team would in all likelihood also be wearing PPE however, unless team members had reason to suspect a low-volatility compound, the existence of such a contaminant could go undetected. The consequences of failing to detect such a contaminant could range from failure to investigate and prosecute a criminal to injury (including the possibility of death) to any civilians who subsequently enter the contaminated zone without the protection of PPE and decontamination procedures. It would be ideal to both of the two teams described above to have a rapid, optically-based system for non-contact detection of low volatility agents to rapidly assess contamination within an area.

A potential technique for non-contact detection of low volatility agents is polarization modulation-infrared reflection absorption spectroscopy (PM-IRRAS). PM-IRRAS is a very well-known technique for detecting monolayers or thin films adsorbed to smooth metal surfaces [5]. Its high sensitivity in the detection of surface species on metals relies upon the surface selection rule, which states that when the angle of incidence attains grazing values, the electric field strength of s-polarized light (oriented parallel to the surface) is close to zero, while the electric field strength of p-polarized light (oriented in plane of incidence, almost perpendicular to the surface) is enhanced at a metal surface [6]. As a result, the reflectivity of s-polarized light (I_s) is insensitive to the presence of the film of adsorbed molecules and can be used to obtain the background spectrum, while the reflectivity of p-polarized light (I_p) can be used to obtain the spectrum of the film. By determining the difference spectrum between p- and s-polarized light $|I_p - I_s|$, the spectrum is background corrected to remove significant contribution due to the atmospheric interferences that occur in the infrared beam with only the surface species being detected [7]. Due to these surface selective characteristics, PM-IRRAS has the potential to be an extremely valuable tool in non-contact detection of CWAs on surfaces.

Petryk [8] was the first to propose the use of PM-IRRAS for the non-contact detection of CWAs and their simulants in the condensed phase. Based on his preliminary experiments, he was successful in using PM-IRRAS to detect G-series nerve agent simulants, trimethyl phosphate (TMP) and triethyl phosphate (TEP), and to differentiate between TEP and TMP in neat and mixed (binary) samples on US military chemical agent resistant coating (CARC) paint [8]. Since it is possible to use PM-IRRAS to differentiate TMP from TEP [8], the structures of which are very similar to one-another, it should be facile to differentiate amongst the different CWAs whose structures are more disparate. In this paper, we further investigate the potential of employing PM-IRRAS in detecting CWAs on surfaces by determining the instrumental limit of detection (LoD) of the CWA simulant, TEP, on an ideal smooth reflective metal surface (gold). The use of an idealized surface such as gold is not without significance. Current CWA detection procedures rely upon a tiered approach, in which increasingly specific and sensitive technologies are brought to bear as the need arises. Smooth reflective metal surfaces such as gold can be considered to be a "cooperative" substrate for PM-IRRAS. In situations where signals from contaminants on common environmental surfaces (rough non-metallic substrates) which do not enhance the signal and lack sufficient intensity (termed as "non-cooperative" substrate) the contaminated surface can be swabbed with the residue deposited on a "cooperative" substrate where the signal is increased.

CWA simulants are compounds which cause responses in detection systems which are similar to those which occur when the detector is exposed to a CWA. Simulants are typically less toxic than are CWAs. Other considerations which can affect the choice of a simulant are stability, ease of preparation and dissemination, cost, and, in the case of outdoor release, environmental sensitivity, impact and fate. Since one of the primary means of poisoning by CWAs are through inhalation (the other being percutaneous exposure), the matching of the vapour pressure of the simulant with a given CWA may be a consideration. In this paper we investigate PM-IRRAS as a technique for the detection of liquid-phase contaminants on surfaces – as such, simulant vapour pressure is not a concern.

TEP has been used as an organophosphate (OP) nerve agent simulant for so many CWAs that it is a de facto standard, particularly for G-series agents. One of the earliest documented references to its use occurs in Ref. [9] where it is indicated to be useful in polymeric and paint penetration studies. Since all OP nerve agents possess O═P─O─C linkages, and since IR vibrational frequencies of functional groups such as O═P and P─O─C are conserved across molecules, TEP is a useful simulant for IR detection studies of OP nerve agents [2b].

In this work the expected LoD of TEP on gold was calculated assuming monolayer coverage of TEP at a gold surface. This expected value was determined via modelling of the experimental setup using Fresnel equations and optical constants of gold and TEP. The experimental LoD of TEP on gold was determined from a calibration curve obtained for a closed (or an "ideal") environment, in which PM-IRRAS spectra were collected for TEP/cyclohexane solutions of various concentrations on a gold substrate configured in a sealed micro-cell, minimizing the evaporation of TEP. Cyclohexane was chosen because the solvent bands overlapped with TEP bands and hence it was a good simulant of spectral interferences. In addition, the instrumental LoD of TEP was determined from a calibration curve of TEP on gold in an open (or "real") environment. A comparison of the LoD of TEP on gold between the expected, "ideal" and "real" systems was made. Finally, the instrumental LoD of TEP on a military relevant rough surface (CARC) was determined in an open environment to test the applicability of the method to field detection of CWAs. These detection limits are at least 3 orders of magnitude lower than the typical lethal doses of G and V-series nerve agents demonstrating potential of PM-IRRAS for non-contact detection of these CWAs.

2. Experimental

2.1. Chemicals and materials

Triethyl phosphate (99.8%, Sigma–Aldrich) was used directly without any further purification. The solvents were methanol