Research Paper

Detection of gaseous nerve agent simulants with broadband photoacoustic spectroscopy

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HIGHLIGHTS

• Sub-ppm detection of nerve agent simulants.
• Low gas consumption of a few milliliters.
• High selectivity and possibility for multi-species detection.
• Fast response and recovery times.

GRAPHICAL ABSTRACT

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ABSTRACT

While recent high-profile assassination attempts have once again brought nerve agents (NAs) into the spotlight, the current portfolio of NA sensors lack a sufficient combination of high performance and field-deployability. Here, we report a novel optical sensor for the detection of gaseous NAs with a potential to fill this gap. The technique is based on Fourier transform spectroscopy with a supercontinuum (SC) light source and cantilever-enhanced photoacoustic detection providing fast multi-species gas sensing with high sensitivity and selectivity in a sample volume of 7 ml, which becomes advantageous when analysing limited NA samples in the field. We study the fundamental C–H stretch bands of four known NA simulants and achieve detection limits of 64–530 ppb in one minute and recovery times of a few minutes. In the near future, the technique has significant potential to improve through the development of more powerful SC sources further in the mid-infrared region.

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1. Introduction

The widespread use of chemical warfare agents (CWAs) was initiated in World War I, and despite international efforts to ban their production, stockpiling and exploitation under the Chemical Weapons Convention (1997), CWAs have remained a serious threat in both military and civilian scenarios (Chauhan et al., 2008; Sanderson et al., 2009). An especially lethal class of CWAs are nerve agents (NA’s) whose first extensive deployments were in the Iran–Iraq war (1980–88) (Haines and Fox, 2014) and the terrorist attacks in Japan (1994–95) (Sato et al., 2000; Okumura et al., 1996). Recently, NAs have once again ended up at the center of public attention due to incidents in the ongoing Syrian civil war (2011–) (Pita and Domingo, 2014; United Nations, 2013), the assassination of Kim Jong-Nam in Malaysia (2017) (U.S. Department of the Department of State, 2020) and the assassination attempts of Sergei Skripal in the United Kingdom (2018) (Vale et al., 2018; Organisation for the Prohibition of Chemical Weapons, 2018b) and Alexei Navalny in Russia (2020) (Organisation for the Prohibition of Chemical Weapons, 2018a) and the attempted assassination of Kim Jong-Nam in Malaysia (2017) (Organisation for the Prohibition of Chemical Weapons, 2018b).

The toxicity of NAs stem from their ability to irreversibly disturb the communication of the nervous system, which leads to a wide range of severe consequences depending on the type and dose of the agent and the route of exposure (Costanzi et al., 2018). The most effective passage of NAs into human body is through the respiratory system, where the typically liquid agents can end up as aerosols or vapours due to the volatility of the NAs (e.g., 2800 parts per million (ppm) and 49 ppm for sarin and tabun, respectively, at 20 °C (Wiener and Hoffman, 2004). Already extremely low NA doses are hazardous, lethal concentrations being 12 ppm and 22 ppm in one minute for gaseous sarin and tabun, respectively (Costanzi et al., 2018), and thus parts per billion (ppb) level detection of these substances in the gas phase is essential. Moreover, NAs are typically detected from urban air or heated liquid/solid field samples with varying concentrations of interfering species, calling for extremely high selectivity against numerous compounds.

The development of NA sensors is largely directed towards portable devices for on-site identification with a fast response time and as high sensitivity and selectivity as possible. The simplest detectors such as electrochemical (Liu and Lin, 2005), colorimetric (Davidson et al., 2020) and fluorimetric sensors (Khan et al., 2018; Meng et al., 2021), surface acoustic wave detectors (Kim et al., 2020) and ion-mobility spectrometers (Puton and Namie, 2016) provide a low-cost option for screening, but they suffer from poor sensitivity, insufficient selectivity and/or susceptibility to changes in temperature and humidity. Technologies with improved performance include gas chromatography mass spectrometry (Smith et al., 2004), Raman spectroscopy (Lafuente et al., 2020) and infrared absorption spectroscopy (Pushkarsky et al., 2006; Mukherjee et al., 2008; Gurton et al., 2012; Levy, 2009; Sharpe et al., 2003; Ruiz-Pesante et al., 2007; Ohru et al., 2020; Melkonian et al., 2020), which are preferred in different scenarios due to their specific characteristics. Infrared absorption spectroscopy is typically well suited for rapid identification of volatile NAs in ambient air, techniques ranging from extremely sensitive photoacoustic spectroscopy (PAS) (Pushkarsky et al., 2006; Mukherjee et al., 2008; Gurton et al., 2012) to Fourier transform infrared spectroscopy (FTIR) (Sharpe et al., 2003; Ruiz-Pesante et al., 2007; Ohru et al., 2020) capable of selective multi-species detection.

These two complementary methods have long been combined in Fourier transform photoacoustic spectroscopy (FT-PAS) (Farrow et al., 1990), which utilizes the parallel down-conversion of optical frequencies of a broadband light into acoustic frequencies, followed by the excitation of absorption-induced pressure waves through periodic thermal relaxations. However, only recent advances in light sources and pressure transducers have fully realized the potential of the technique (Karhu et al., 2019; Mikkonen et al., 2018, 2022b; Sadiuk et al., 2018; Wildt et al., 2020). For example, we have previously implemented a supercontinuum (SC) source and a cantilever microphone in a FT-PAS system, which provides fast and selective sensing of hydrocarbons with ppb-level detection limits in a few milliliter sample volume (Mikkonen et al., 2022b).

Here, we apply FT-PAS to the detection of gaseous NAs by analysing four known NA simulants. We utilize the volatility of the simulants in sampling, where the low gas consumption speeds up the gas exchange process, simplifies the cleaning of the gas cell and would enable the analysis of NA samples with limited availability, a realistic real-life scenario. We examine the unique C-H stretch bands of these species and report our sensor’s high performance in terms of detection limits (ppb-level), selectivity and recovery time (a few minutes), convincing the applicability of FT-PAS in reliable and rapid identification of NAs.

2. Materials and methods

2.1. Experimental setup

The experimental setup illustrated in Fig. 1 closely resembles our previously reported system (Mikkonen et al., 2022b) and has a footprint of about 40 kg and 50 cm × 35 cm × 35 cm when enclosed tightly. The sampling process, where the low gas consumption speeds up the gas exchange process, simplifies the cleaning of the gas cell and would enable the analysis of NA samples with limited availability, a realistic real-life scenario. We examine the unique C-H stretch bands of these species and report our sensor’s high performance in terms of detection limits (ppb-level), selectivity and recovery time (a few minutes), convincing the applicability of FT-PAS in reliable and rapid identification of NAs.

2.2. Materials and sampling

We analyse four NA simulants, namely trimethyl phosphate (TMP, Sigma-Aldrich, >99%), dimethyl methylphosphonate (DMMP, Fluka, 97%), diethyl methylphosphonate (DEMP, Sigma-Aldrich, 97.3%) and diisopropyl methylphosphonate (DIMP, Alfa Aesar, 95%), whose...
molecular structures and thus spectral properties are similar to G-series NAs such as sarin, tabun and soman (Ruiz-Pesante et al., 2007; Mott and Rez, 2012; Neupane et al., 2019; Kumar et al., 2019). Simulant samples in the gas phase are prepared by placing 20 $\mu$l of liquid simulant at the bottom of a one-liter container as illustrated at the bottom-right corner in Fig. 1. The liquid simulant in the sampling container is rested for at least one hour to evaporate, after which the equilibrium vapour pressure at room temperature is assumed to be reached. From the headspace of the container, the gas phase simulants mixed in laboratory air are pumped into the gas cell using a gas exchange system incorporated into the PA analyser. Considering the time to exchange the gas and the time to record a single spectrum, the response time of the sensor is less than ten seconds.

2. Results and discussion

2.1. Data processing

The measured raw absorption spectrum of TMP in air averaged over 12 scans (one minute) is shown in Fig. 2 b. Interfering absorption features in the high-frequency side of the spectrum are from water vapour which dominates the absorption spectrum of air in this spectral region. This interference is eliminated by recording a spectrum of laboratory air (Fig. 2 c), fitting that to the TMP-free region (3200–3400 cm$^{-1}$) of the raw spectrum to account for small changes in the water concentration, and subtracting the fitted water spectrum from the raw spectrum. The linear least squares spectral fitting algorithm was implemented using Matlab’s linsolve function which solves the matrix equation $Ax = B$ using QR factorization with column pivoting. The same algorithm was employed in all spectral fitting procedures appearing later in this work. The resulting spectrum of pure TMP is shown in Fig. 2 d, which is then corrected by the spectral envelope of the SC inside the gas cell shown in black in Fig. 2 a.

Fig. 1. A schematic of the experimental setup: SC - supercontinuum; BS - beamsplitter; $P$ - optical power; $\nu$ - wavenumber; $t$ - time; NA - nerve agent. Wavenumber-dependent intensity modulation of the SC source is illustrated in the bottom left corner, where the relative frequencies are exaggerated. The absolute wavenumber scale of the SC spectrum is shown in Fig. 2 a.

Fig. 2. a) Effective power spectral density (PSD) spectrum of the SC radiation inside the gas cell, measured FT-PAS spectrum of b) TMP in air and c) pure air (4 cm$^{-1}$ resolution, 60 s measurement time), and d) post-processed spectrum of TMP.

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Corrected FT-PAS spectra of TMP and other simulants are shown in Fig. 3 together with absorption cross section spectra recorded with a conventional FTIR system (Neupane et al., 2019). The measurements agree with each other, FT-PAS spectra exhibiting higher signal-to-noise ratios (SNRs). We note that a small TMP residual was subtracted from the DEMP spectrum. Different magnitudes in the measured spectra result from differences in the absorption cross sections and the concentrations of the simulants inside the cell. These concentrations, which depend on the equilibrium vapour pressures and adsorption properties of the simulant molecules, can be estimated after calibrating the system.
absorption cross sections. The standard deviation in grey for the FT-PAS spectra. Lower panels show the with the target gas concentration. The calibration process utilizes linear

2.2. Calibration

Calibration is required in PAS to relate the recorded PA amplitude with the target gas concentration. The calibration process utilizes linear dependence of the wavenumber \( \nu \) dependent PA amplitude \( S(\nu) \) on optical power \( P(\nu) \), absorption cross section \( \sigma(\nu) \) and concentration \( c \):

\[
S(\nu) = \Lambda(\nu) \cdot [AP(\nu)\sigma(\nu)c] = AP(\nu)\Lambda(\nu)\sigma(\nu)c,
\]

where \( \Lambda(\nu) \) is the instrument lineshape function (Fourier transform of the window function), \( A \) is the calibration constant, the symbol \(*\) denotes convolution and \( \sigma(\nu) = \Lambda(\nu) \cdot \sigma(\nu) \). The instrument lineshape function does not affect the smoothly varying SC spectral envelope.

As we currently have no reliable way to estimate nor vary the gas phase simulant concentrations in the gas cell, we characterized the calibration constant \( A \) by recording the absorption spectrum (fundamental asymmetric C-H stretch band) of methane (CH\(_4\)) with controlled volume mixing ratios between 0.2 and 50 ppm. These volume concentrations were prepared by mixing CH\(_4\) from a 400 ppm gas bottle with nitrogen using two mass flow controllers (Bronkhorst F-201CV). For simplicity, we only analyzed a single wavenumber (\( \nu_{\text{max}} \)) corresponding to the strongest PA amplitude of CH\(_4\) and measured the linear proportionality constant between \( S(\nu_{\text{max}}) \) and \( c \). We divided this constant by \( P(\nu_{\text{max}}) \) and \( \sigma(\nu_{\text{max}}) \), which was calculated by convolving the absorption cross section spectrum of CH\(_4\) (from the HITRAN database (Rothenberg et al., 2013)) with the instrument lineshape function. This division yields the calibration constant \( A \) for CH\(_4\).

Univocal calibration constant for different gas species necessitates constant non-radiative relaxation efficiency (here incorporated into \( A \)) between the considered species and possible gas mediums, which in general is not the case in PAS (Russo et al., 2021; Müller et al., 2022). However, the situation is considerably simplified here as our modulation frequencies around 300 Hz are unconventionally low for PAS and most importantly lower than the molecular relaxation rates in our gas matrices (Müller et al., 2022; Barreiro et al., 2012). Complete thermal relaxation enables the transfer of the calibration constant of CH\(_4\) to simulant substances and nerve agents. Simulant concentrations can then be calculated from Eq. 1, where the absorption cross sections of the simulants are collected from the reference FTIR data in Fig. 3. Again, only single wavenumbers corresponding to the maximum absorption cross sections of the simulants are utilized.

Using this calibration procedure, we estimated the simulant concentrations to be in the range of 110–300 ppm in the gas cell as summarized in the second column in Table 1. These concentrations are on average 35% from the initial concentrations in the sampling container (estimated from the vapour pressures of the simulants at 20 °C (Butrow et al., 2009; Cuisset et al., 2009)) due to the adsorption of simulant molecules on the sampling equipment and the surfaces of the gas cell. Sampling efficiencies \( (\eta_s) \), i.e., the relations between the concentrations in the gas cell and the sampling container, are listed in the third column in Table 1. The observed variations result from measurement errors and various parameters affecting the adsorption process such as polarity and molecular weight (Li et al., 2020). Lower sampling efficiencies of about 10% have been reported for a conventional FTIR system (Ohru et al., 2020), most likely caused by the significantly larger volume of the gas equipment. The uncertainties in the calibrated simulation concentrations shown in the rightmost column of Table 1 include errors in the calibration constant \( A \) (0.5% from the fitting, 3.1% from optical power (Mikkonen et al., 2022b), and 5% from the absorption cross section of CH\(_4\) (Daumont et al., 2013)), absorption cross sections of simulants (6.2–12% (Neupane et al., 2019)) and optical power again (3.1% (Mikkonen et al., 2022b)).

2.3. Detection limits

We estimated the limits of detection (LODs) for all simulants using LOD = 3NC/S, where \( S \) is the strongest PA amplitude of the simulant in the water-corrected spectrum and \( N \) is the noise level, calculated as the standard deviation of a non-absorbing part (2000–2800 cm\(^{-1}\)) of the water spectrum. The noise level is calculated from a measurement involving no simulant molecules in the gas cell, because significant simulant absorption raises the noise level (Mikkonen et al., 2022a). Calculated detection limits for one minute averaging and corresponding to the minimum concentrations that can be detected inside the gas cell are shown in the fourth column in Table 1. To illustrate the validity of

| Simulant | \( c \) (ppm) | \( \eta_s \) (%) | LOD (ppb) | \( \Delta c \) (%) |
|----------|--------------|-----------------|-----------|-----------------|
|          | In           | Out             |           |                 |
| TMP      | 310          | 36              | 130       | 360             | 14             |
| DMMP     | 160          | 20              | 110       | 530             | 10             |
| DEMP     | 160          | 43              | 79        | 190             | 10             |
| DIMP     | 120          | 42              | 26        | 64              | 10             |

Fig. 3. Measured, water-subtracted and PSD-corrected FT-PAS spectra (left axis) and FTIR reference (Neupane et al., 2019) (right axis, inverted) of a) TMP, b) DMMP, c) DEMP and d) DIMP. The average of 12 scans is shown in black and the standard deviation in grey for the FT-PAS spectra. Lower panels show the residuals between these two approaches, acquired by scaling the reference absorption cross sections.
this unconventional determination of the detection limit, we measured a small concentration (230 ppb) of DIMP in which case the noise induced by the simulant is negligible and the LOD can be obtained directly from the SNR of the spectrum. A single water-subtracted scan of this measurement is shown in Fig. 4 with a SNR of 7.7 ± 0.3 corresponding to a LOD of 26 ± 1 ppb in 60 s, in perfect agreement with the value in Table 1. The uncertainty includes only the fitting error (no calibration error).

In order to estimate the detection limits that can be reached from samples outside the sensor, the LOD values in the fourth column in Table 1 were divided by the corresponding sampling efficiencies resulting in values of 64–350 ppb (the fifth column in Table 1). By comparing the absorption cross sections of sarin and TMP (Sharpe et al., 2003; Neupane et al., 2019) and assuming 35% sampling efficiency, we estimated a detection limit of 180 ± 40 ppb for sarin which is approximately an order of magnitude higher compared to a LOD achieved with a commercial, high-performance and field-portable FTIR system when normalized by the acquisition time (Ohrui et al., 2020). However, it should be noted that the required sample volume of our system is 57 times smaller and the FTIR system capitalizes on stronger P–O–C stretch bands around 1000 cm⁻¹.

2.4. Selectivity

Similar features in the C–H stretch bands of some simulants (Fig. 3) and NAs (Sharpe et al., 2003) could indicate complications in the correct identification of these species. We investigated the selectivity of our sensor by compiling a spectral library of the simulants (and water) and performing new single-component and single-scan measurements with these four substances and concentrations ranging 20–40 ppm. Using the spectral library and the least squares spectral fitting algorithm, we estimated the concentration of each species in the gas cell. For each simulant, we repeated this process for five scans, averaged the retrieved concentrations simulant-wise and calculated the absolute values (for illustration purposes as negative values cannot be displayed in a logarithmic scale). The results are shown in Fig. 5 where each row represents the outcome for a specific simulant applied in the gas cell (applied simulant on the left panel, retrieved simulants on the bottom panel).

Noting the logarithmic color scale, Fig. 5 displays good selectivity of the system. All simulants were confidently identified and the average concentration for absent species is 300 ppb (values outside the diagonal). Most remarkably, small differentiating features in the absorption spectra of TMP and DMMP are successfully recognized with no particular cross-sensitivity between these simulants. The most prominent incorrect detection was 1 ppm of DMMP in the DIMP measurement (fourth row, second column), which however may be attributed to residual DMMP in the sampling container (DIMP sample was placed in a container that previously contained DMMP). Similar reasoning also holds for the second most prominent incorrect detection, 500 ppb of TMP in the DEMP measurement. This underlines the difficulty in handling volatile substances and the importance of thorough cleaning of all contaminated surfaces. Without these two doubtful incorrect identifications, the average concentration for absent species is 200 ppb, which is 0.8% from the average applied concentration and around the noise level of the high concentration (and therefore high noise level) measurements.

2.5. Recovery time

An important feature for a NA sensor is the ability to recover fast after encountering high concentrations. In our system, recovery time is limited by the gas adsorption onto the inner surface of the gas cell and the pump system whereof it evaporates back into gas phase after the cell is purged with clean air. It is therefore favourable to change the gas sample inside the cell after each scan which was the procedure in all our measurements. The duration of this cleaning depends on the substance, its initial concentration in the gas cell and the concentration in which the substance cannot be anymore detected, high initial concentrations of sticky molecules with low detection limits exhibiting the longest recovery times. Therefore, we characterized the cleaning of the gas equipment in the worst scenario by injecting a high concentration (100 ppm) of DIMP in the gas cell. We repeated 71 times a sequence of flushing the cell with clean air for two seconds and recording a single spectrum. The concentration of DIMP was retrieved from each raw spectrum by fitting DIMP and water references to the spectrum, and the result of this investigation is shown in Fig. 6.

The concentration of DIMP decreases three orders of magnitude during the flushing procedure. A three-term exponential function was fitted to the concentration trace as three separate evaporation processes during the flushing procedure. A three-term exponential function was fitted to the concentration trace as three separate evaporation processes resulting in a SNR of 7.7 ± 0.3 corresponding to a LOD of 26 ± 1 ppb in 60 s, in perfect agreement with the value in Table 1. The uncertainty includes only the fitting error (no calibration error).

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The mid-infrared region (Sharpe et al., 2003; Neupane et al., 2019), analysing the stronger and more selective $P$ in the range of a few minutes for an initially high sample concentration.

- 64

4. Conclusions

We have demonstrated Fourier transform photoacoustic spectroscopy (FT-PAS) with a supercontinuum (SC) light source for the detection of gaseous nerve agents (NAS). This approach combines the broadband nature of Fourier transform spectroscopy with the high sensitivity of cantilever-enhanced PAS for a field-deployable sensor with high performance. We analysed the C–H stretch bands of four NA simulants whose measured absorption spectra were in a good agreement with the literature (Neupane et al., 2019). We achieved detection limits of 64–530 ppb in 60 s for the simulants, which should be considered in the context of the system’s low gas consumption (7 ml), high selectivity and the possibility for simultaneous multi-species detection (Mikkonen et al., 2022b). While our attained detection sensitivity is an order of magnitude worse compared to a conventional FTIR system with similar footprint (Ohru et al., 2020), the required sample volume is nearly 60 times smaller providing a significant advantage when analysing field samples with limited availability. Furthermore, low gas consumption increases the sampling efficiency and is expected to decrease the recovery time of the sensor, which for our system was demonstrated to be shorter. Moreover, heated gas equipment would accelerate the recovery significantly.

Environmental implication

The materials studied in this work are four organophosphorus compounds, which themselves possess a moderate health hazard. However, here we use these compounds to simulate volatile nerve agents such as sarin, soman and tabun, which are one of the most lethal chemical weapons. Our work presents a novel technique for the detection of gaseous nerve agents with high performance and low sample consumption. The approach provides a complementary tool for the analysis of complex field samples with limited availability, thus contributing to faster and more reliable identification for forensic investigation, the diagnosis and treatment of poisoning and occupational health monitoring.

CRediT authorship contribution statement

Tommi Mikkonen: Conceptualization, Methodology, Formal analysis, Investigation, Writing – original draft, Visualization. Daniel Luoma: Investigation, Data curation. Hanna Hakulinen: Conceptualization, Resources. Goery Genty: Resources, Writing – review & editing. Paula Vanninen: Conceptualization, Resources. Juha Toivonen: Conceptualization, Resources, Writing – review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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