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Multi-wavelength Laser Photoacoustics

by Kristan P. Gurton, Melvin Felton, and Richard Tober

ARL-TR-6147 **September 2012**

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14. ABSTRACT
An optical detection method designed to detect and identify the presence of macro-molecular gas species (e.g., organophosphate-based nerve agent simulants) at trace level concentrations is presented. The technique is based on a modified version of conventional laser photoacoustic spectroscopy (LPAS) in which optical absorption is typically measured using a single laser source. We demonstrate the ability to simultaneously measure multiple absorption related parameters that serve as a concentration independent identifier. Three continuous wave (CW) mid-infrared (MidIR) laser sources, operating at 8.68, 9.29, and 10.35μm, are combined and propagated axially through a specially designed flow-through photoacoustic cell. Each laser is modulated at a different frequency and the resultant acoustic signal(s) are detected and deconvolved using a PC-based 24-bit dynamic signal acquisition device. Species detection and identification is achieved by tabulating independent ratios of the acoustic response for each laser source. Quantitative absorption measured is verified using a Fourier transform infrared (FTIR) spectrometer. Results show good detection and species separation/identification at moderately low ppm concentrations.

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Photoacoustics, detection, nerve agents, DIMP, DMMP, DEMP, TEP

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Contents

List of Figures

1. Introduction

Currently, there is no reliable method for accurate real-time detection and identification of harmful vapors that is effective over a wide range of chemical species and concentrations. As a result, early warning systems that are capable of instantaneous detection of such materials are needed. Much research has been devoted to detecting and identifying gaseous chemical materials and can be generally categorized by two distinctly different approaches, i.e., a material science method in which species specific substrates are developed that change electrical characteristics when exposed to a particular gas, and the more conventional, laser-based spectroscopic approach (*1*–*6*). Although many of the material-based approaches claim good sensitivity, the degree of selective species identification over a wide range is poor. Similarly, such methods require time frames on the order of minutes to cycle through a single absorption/desorption process. Conventional laser-based spectroscopic techniques, such as multi-pass absorption spectroscopy, differential absorption spectroscopy (DOAS), and cavity ring-down spectroscopy (CRDS), offer exceptional sensitivity and specificity, but are complex and usually designed to detect a small number of very specific gases.

One of the more direct methods to implement in practice (without sacrificing sensitivity) is laser photoacoustic spectroscopy (LPAS). We have worked with both gas and aerosol photoacoustic (PA) systems for over 20 years but have been disappointed by the lack of convenient laser sources spanning the spectrally rich mid-infrared (MidIR) region. Similarly, traditional LPAS is usually limited to measuring a "single" absorption cross section at a time. In addition, traditional LPAS typically requires cumbersome and expensive signal processing instrumentation, e.g., data acquisition systems, preamplifier/lock-in amplifiers, etc. Taking these factors into consideration, conventional LPAS seems poorly suited as a viable gas "detection" technique.

Recent advancement in infrared (IR) laser technology and signal processing instrumentation has allowed us to reconsider using a modified version of LPAS for selective gas detection. First, the limitation imposed by a lack of convenient MidIR laser sources has been all but eliminated by the recent advancement of commercially available quantum-cascade (QC) lasers. These solid-state devices are custom-made to produce practically any MidIR wavelength the user desires. In addition, advancement in PC-based "virtual" instrumentation has eliminated the need for expensive and bulky analog signal processing devices. For example, we use a single National Instruments, Inc., PCI dynamic signal acquisition board (model PCI-4472), which when programmed appropriately, effectively functions identically as eight separate lock-in amplifiers.

With readily available MidIR sources and greatly simplified signal processing electronics, it now seems reasonable to consider a "multi-wavelength" LPAS approach. By propagating multiple laser sources through a single flow-through PA cell, in which each sources is modulated at a different acoustic frequency, one can deconvolve the resultant absorption-related signals by

using a multi-channel virtual lock-in. This effectively allows for a real-time measurement of multiple absorption-related coefficients that can be used to identify the presence of a particular gas species.

This report presents the final results of an ongoing study, first reported on in 2009 (*7*). Although the approach described here is relatively straightforward, we have found no similar studies in the literature in which multiple lasers sources are combined in a single PA cell, allowing for the simultaneous measure of multiple absorption cross-sections.

2. Method

For gaseous LPAS, a small-diameter laser beam is modulated at some convenient acoustic frequency, 1 kHz, for example, and is passed through a sealed cylindrical gas cell, often via two or more transmitting windows. The absorbed IR energy raises the absorbing molecules from a ground vibrational state to an excited vibrational-rotational state. Collisional processes then redistribute the energy into molecular translation and rotation, resulting in the localized propagation of compression waves. The resultant rapid change in pressure results in an acoustic signal that is detected by an electret microphone usually with the aid of a lock-in amplifier. The measured acoustic (or pressure) signal is found to be proportional to the absorption cross section of the species, the average power of the optical source, and the sensitivity of the electret. Since the last two parameters are usually known, a measure of the absorption cross section is fairly straightforward using various calibration techniques.

We have developed a modified flow-through PA cavity designed specifically for multi-wavelength operation albeit at the expense of some sensitivity, i.e., the cell was specifically designed to have a relatively low Q-value. We have found in practice that the benefit of using a highly tuned PA cells is often overshadowed by extreme variability that results from subtle environmental changes within the laboratory environment and other factors. In addition, an "un-tuned" type PA system is a natural choice if one is to consider multi-mode/multi-wavelength operation. A detailed description of the LPAS cell used for this study has been presented elsewhere so only a brief outline of the key components are presented here (*8, 9*). The PA cell is a windowless, flow-through design in which the laser beam(s) are propagated axially through the center (figure 1).

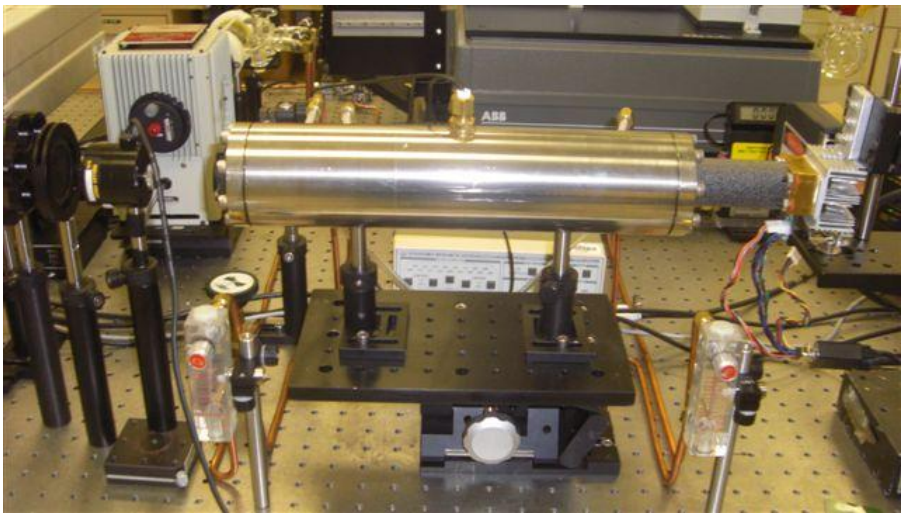

Figure 1. Photograph of the flow-through PA cell.

Not shown in the photograph is a series of acoustic dampeners mounted inside the cell at both ends of the tube that serve to suppress any ambient noise. Situated in the center of the cell is a small field-effect transistor (FET) based electret microphone. The faint acoustic signal resulting from the absorbing gas is amplified and fed into a 24-bit dynamic signal acquisition device that digitizes the analog signal. By accurately digitizing and processing the acoustic signal using a PC, we avoid having to use multiple lock-in amplifiers that are usually needed to deconvolve each signal. Instead we conduct a fast Fourier transform (FFT) on the signal and filter only frequency components that correspond to the modulation frequencies of the lasers. Using this approach, we are able to deconvolve up to eight separate laser-induced signals simultaneously with just a single PC.

In order to develop a reliable detection scheme, a metric that is insensitive to fluctuations in vapor concentration must be developed. Since the raw acoustic response from the PA cell is proportional to the absorption cross section (where the constant of proportionality is related to the cell path length and concentration), a simple concentration independent metrics can be formed by simple ratios of the deconvolved PA signal for each laser source.

For this proof-of-concept study, we used three MidIR wavelengths, operating at 8.68, 9.29, and 10.35 μm. However, in principle, there is no fundamental limitation on the number of laser lines one could consider. In fact, species specificity increases greatly as the number of wavelengths considered are increased (i.e., the number of independent ratios goes as n(n-1)/2, where n are the number of wavelengths available). For our case here, three laser sources produce the corresponding signals, $S_{\lambda 1}$, $S_{\lambda 2}$, $S_{\lambda 3}$, which, in turn, generate a set of three independent ratios, $S_{\lambda 1}/S_{\lambda 2}$, $S_{\lambda 1}/S_{\lambda 3}$, $S_{\lambda 2}/S_{\lambda 3}$. However for systems with 4 or 5 different wavelengths, the number of independent ratios becomes 6 and 10, respectively.

A schematic of the multi-wavelength LPAS experiment is shown in figure 2. Varying concentrations of simulant vapor and dry air are volumetrically controlled and combined inline via a series of calibrated pressure gauges, mass-flow meters, and needle valves. Vapor is fed into a 10-cm-long Fourier transform infrared (FTIR) transmission cell that is used as a quantitative reference for the multi-wavelength LPAS study. The spectral absorption is measured from 3 to 12 μm using a Bomem MR Series FTIR spectrometer operating with a spectral resolution of 4 cm^{-1}. A radiometrically stabilized IR Nernst glow-bar serves as the broadband source for the FTIR measurement. The simulant-air mixture exits the FTIR transmission cell and is passed through a flow-through PA spectroscopy (PAS) cell at predetermined flow rates.

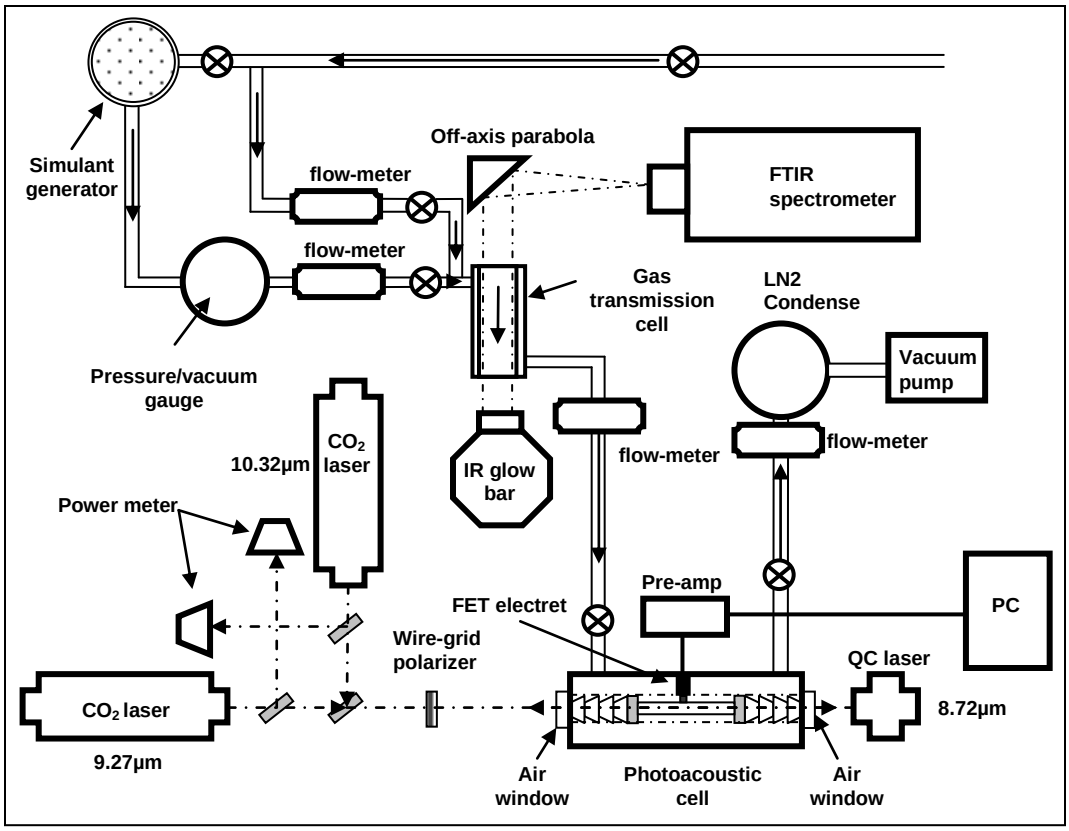

Figure 2. A schematic of the multi-wavelength LPAS experiment.

Three continuous-wave (CW) MidIR laser sources were used for the study, which consisted of two Universal, Inc., carbon dioxide (CO_2) lasers (operating at 9.27 and 10.54 μm) and one Maxion, Inc., QC laser (operating at 8.72 μm). For uniformity, all lasers were attenuated to the same value of 50 mW, which allowed simulant detection at the volumetric ppm levels. In order to separate the acoustic response for the different wavelengths, each laser was modulated at a different acoustic frequency, i.e., 10.35 μm at 1700 Hz, 9.27 μm at 1900 Hz, and 8.72 μm at 1300 Hz. Choice of specific laser modulation frequencies is usually dictated by the response of the electret and the acoustic spectrum of the ambient noise. However, for multi-wavelength

operation, care should be taken to avoid choosing frequencies with overlapping harmonics to avoid mixing of the signals.

For conventional LPAS, the amplitude of the acoustic signal is related to the absorption via a calibration process (*10, 11*). However, due to the qualitative nature of this particular study, no calibration was necessary, i.e., we are not interested in measuring absolute absorption cross sections, but are merely attempting to determine sufficient information in order to identify the presence of a particular nerve agent simulant species.

The acoustic signal(s) resulting from laser-line absorption is detected by the electret and amplified using a low-noise pre-amp. Analog-to-digital conversion of the amplified acoustic signal is accomplished using 8-chanel National Instrument 24-bit dynamic signal acquisition PCI card. Once digitized, the signal is deconvolved (much like a conventional analog lock-in amplifier) and individual AC components for each of the three modulation frequencies are recorded as a function of time. Residual air-simulant gas mixture is reconstituted and collected in a cooled condensing flask.

3. Results

The test materials include the following six nerve-agent simulants in vapor form: dimethyl methyl phosphonate (DMMP), diethyl methyl phosphonate (DEMP), diisopropyl methyl phosphonate (DIMP), dimethyl polysiloxane (DIME), triethyl phosphate (TEP), tributyl phosphate (TBP), and two volatile organic compounds (VOCs), acetone (ACE) and isopropanol (ISO). Figure 3 shows absorbance spectra measured using the FTIR spectrometer for the five nerve agent simulants.

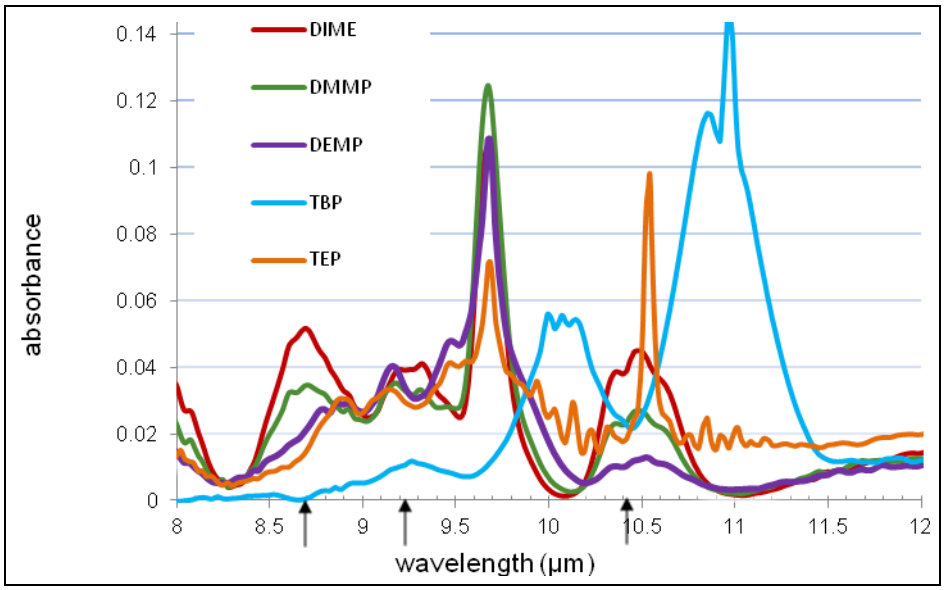

Figure 3. Representative measured absorbance spectra for the five nerve agent simulants, where the arrows identify the three laser wavelengths 8.68, 9.29, and 10.35 µm.

Test runs were conducted over multiple days for each simulant and VOC. Prior to switching out a particular simulant, all vapor/liquid handling glassware and transport tubes were thoroughly cleaned and baked to remove any residual material. PAS electret signals were continuously recorded and amplified as a function of changing simulant concentrations. Ratios of the three absorption-related signals showed little variance over the test period.

Response ratios of the three wavelengths for the five nerve agent simulants and two VOCs are plotted in figure 4. As seen in the figure, there is reasonable separation between different regions designating the various gaseous compounds. The only exception exists between the materials DMMP and DIME, in which the separation is more difficult to define. Unfortunately this problem will occur for spectroscopically similar compounds, but may be overcome with the introduction of an additional laser-line wavelength.

We are investigating several new PA cell designs to improve optical energy density in the cavity by inducing multiple reflections of the laser beams (figures 5a and b). Figure 5a shows the possible application of an integrating sphere to enhance signal and figure 5b shows two possible cylindrical cavity approaches in which the laser sources are propagated radially. It's our hope that these new designs will boost signal via multiple laser passes, and reduce unwanted laser attenuation by keeping the active volume in close proximity to the electret.

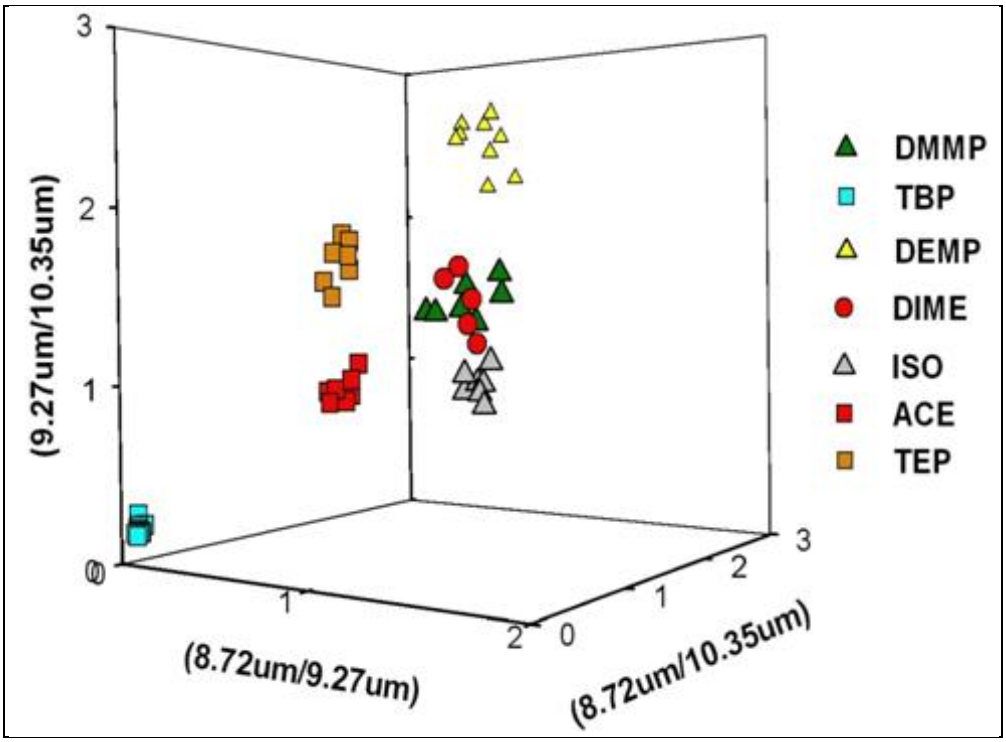

Figure 4. Ratios of the absorption response for the three wavelengths are shown for the five nerve agent simulants and two VOCs.

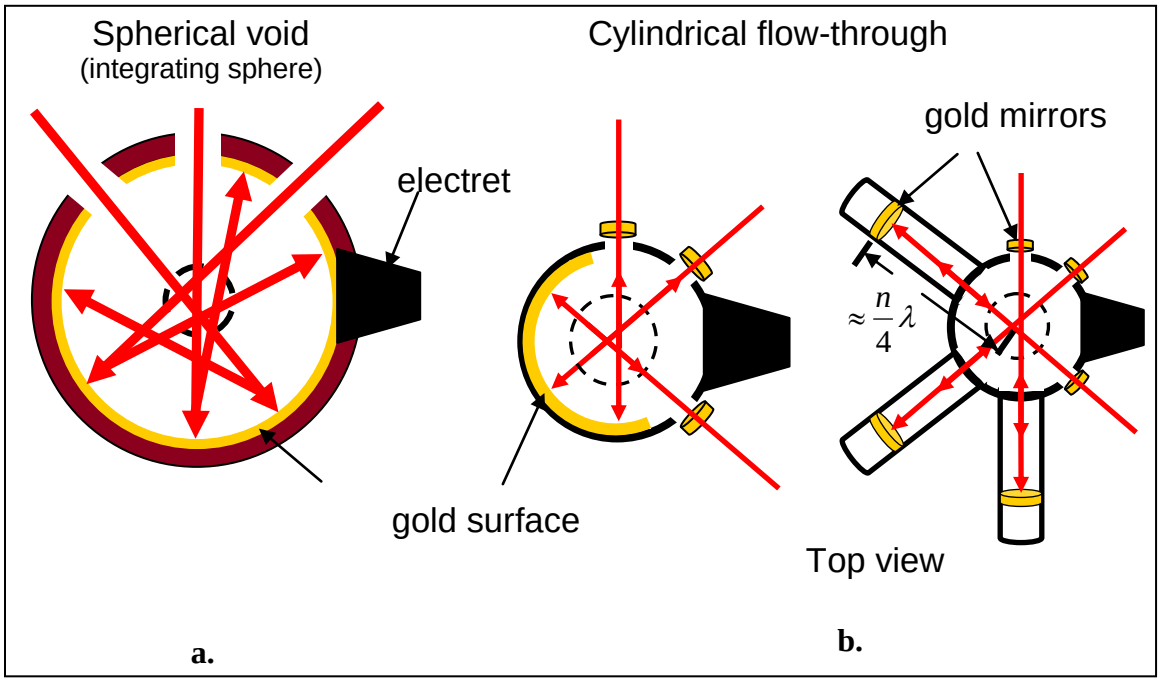

Figure 5. Enhanced spherical and cylindrical PA cell design(s). (a) A multi-pass system based on the internal reflections inherent in an integrating sphere. (b) A more conventional cylindrical column of vapor (into the page) but now the lasers are brought into the cell perpendicular to the flow. (b) Also shows possible enhancement of the signal by incorporating resonate effects by spacing opposing mirrors at distances on the order of quarter-multiples of the wavelength of sound associated with each modulation frequency.

4. Conclusion

We have shown that a novel application of a modified LPAS technique can be used to selectively detect and distinguish various nerve-agent simulant compounds in gaseous form. This was accomplished by simultaneous operation of multiple laser-line sources in the MidIR, each modulated at a distinctly different acoustic frequency and propagated through a conventional flow-through PAS cell. Separation and amplification of the various acoustic components is conducted and the resultant ratios of the absorption related acoustic response is shown to be a useful detection and identification metric. Only three wavelengths were used in this proof-of-concept study, which resulted in three independent metric ratios, but greater specificity is expected as the number of wavelengths is increased.

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List of Symbols, Abbreviations, and Acronyms

ACE	acetone
CRDS	cavity ring-down spectroscopy
DEMP	diethyl methyl phosphonate
DIME	dimethyl polysiloxane
DIMP	diisopropyl methyl phosphonate
DMMP	dimethyl methyl phosphonate
DOAS	differential absorption spectroscopy
FET	field-effect transistor
FFT	fast Fourier transform
FTIR	Fourier transform infrared
IR	infrared
ISO	isopropanol
LPAS	laser photoacoustic spectroscopy
MidIR	mid-infrared
PA	photoacoustic
PAS	PA spectroscopy
QC	quantum-cascade
TBP	tributyl phosphate
TEP	triethyl phosphate
VOCs	volatile organic compounds

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