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**Towards Greater Sensitivity: A Brief FTIR
and Infrared-Based Cavity Ring Down
Spectroscopy Comparative Study**

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RESEARCH AND OPERATIONS DIRECTORATE

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Disclaimer

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorizing documents.

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14. ABSTRACT The Office of the Deputy Assistant Secretary of the Army for Defense Exports and Cooperation funded the U.S. Army Combat Capabilities Development Command (DEVCOM) Chemical Biological Center through the International Cooperative Research and Development program to perform work on comparing efficacy of a traditional IR method used as a standard within DEVCOM and by international collaborators with that of an emerging technology, cavity ring down spectroscopy (CRDS). CRDS provides a stronger response per volume than traditional IR for vapor analysis at the same concentration via use of a reflective cavity. Although this technique is normally employed in a very select bandwidth in the IR, commercial products that can interrogate a greater bandwidth have only recently become available. Herein, we directly compare a commercial CRDS unit with a commercial IR instrument and evaluate system response and estimated limits of detection for both instruments for the Gas Distribution Integrity Management program, methyl salicylate, and ethanol. CRDS offers up to two orders of magnitude greater sensitivity than the traditional IR instrumentation. The CRDS and the traditional IR instruments have greater spectral noise in different areas of the spectra. Care should be taken when identifying the peaks to evaluate.					
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PREFACE

The work described in this report was started in Apr 2022 and completed in Sep 2022.

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TOWARDS GREATER SENSITIVITY: A BRIEF FTIR AND INFRARED-BASED CAVITY RING DOWN SPECTROSCOPY COMPARATIVE STUDY

1. OVERVIEW

This work was completed by U.S. Army DEVCOM CBC personnel in the CBRNE Assessment Science & Technology Laboratory within the Advanced Chemistry Laboratory on Aberdeen Proving Ground during the 2022 fiscal year.

2. SCOPE

The scope of this work is to identify advantages and disadvantages of a traditional Fourier-Transform Infrared Spectrometer (FTIR) instrument to that of a commercially available cavity ring down spectrometer (CRDS) for applications towards gas-phase perimeter monitoring. The work completed in FY22, which is detailed here, evaluated and assessed a commercially available FTIR system from Gasmet Oy (Vantaa, Finland) alongside a CRDS prototype system from RingIR (Albuquerque, NM) that was on loan from the manufacturer. As a result, the analytes were very limited to non-corrosive, low-toxicity, high vapor pressure gas-phase compounds for a one-to-one comparison.

3. INTRODUCTION

A threat in the form of chemical vapor may not be visible, but rapid detection is critical for preservation of life and property. In addition, understanding the surrounding environment informs the posture that the Warfighter will need to take. The field of chemical vapor detection spans far beyond the Warfighter and is rich in research. A search in SciFinder for “chemical vapor detection” provides over 400,000 results with over 3,000 books, 26,000 reviews, and nearly 300,000 journal articles. The focus of this document will be with an eye towards perimeter monitoring for a wide range of gas-phase chemicals. To accomplish such sensing, compound-specific sensors should not be employed as they lack capability to detect or inform about the presence of many potential threats outside of their selected targets. A viable technique for sensing a wide range of compounds is infrared absorption as most potential threats provide an infrared absorbance spectrum which arises from each compound’s unique molecular structure.

The purpose of this document is to provide a comparison between a commercially-available instrument long utilized as a standard within several defense laboratories around the globe which employs FTIR methods for detection of environmental gasses in industrial environments to a newer class of IR absorption-based detectors that use cavity ring-down to determine the absorption profile.

3.1 FTIR

While there are many ways to sense gases¹⁻², optical, infrared absorption-based techniques offer the capability to perform real-time, *in situ* analysis and direct measurement of the vibrations of a molecule (in near- and mid-IR techniques).³ A keen advantage is gained when

using infrared absorption techniques by applying a Fourier transform to the IR signal which allows for increased throughput (known as Jacquinot's advantage) and multiplexing (known as Fellgett's advantage) and can increase the signal-to-noise.⁴

Detailed information on the mechanism of IR absorption is extensively documented in scientific literature.⁴ In short, gas-phase IR analysis of a chemical provides vibration-rotation spectra. For a compound to be IR-active, there must be a change in the molecule's dipole moment with respect to the molecular vibration; this is the basis of the absorption of the IR radiation and thereby a change in the spectral absorption profile. In addition to individual bonds within a molecule, there are also larger moieties within the molecule which vibrate at characteristic frequencies which provide structural or functional information and are nearly independent from the rest of the molecule's structure.

The absorption (A) of IR radiation is defined by the Beer-Lambert law:⁴

$$A = -\log \frac{I}{I_0} = \sigma Cl \quad \text{Eq. 1}$$

Where I is the intensity of light entering the sample, I_0 is the intensity of the light leaving the sample, σ is the absorption cross section of the molecule at a particular wavelength, C is the concentration of the analyte, and l is the optical path length. From Eq. 1, it is evident that increasing signal strength ($\frac{I}{I_0}$) requires an increase in either the concentration of or the path length through a particular analyte. When sampling for environmental or perimeter monitoring, the concentration is unknown and the path length restricted by the form factor of the instrumentation. The sensitivity is defined by the optical cross section of the analyte and the path length.

3.2 Cavity Ring-Down IR

Cavity Ring-Down spectroscopy (CRDS) is a newer IR absorption-based technique made possible by the use of tunable pulsed lasers.⁵ Rather than using a broadband (blackbody) emitter as is done with traditional IR techniques, a pulsed laser is tuned across wavelengths into an optical cavity. Instead of measuring the absorption directly, the amount of light leaking through a highly reflective mirror within the cavity is measured with respect to time at each wavelength and a time constant for the decay can be measured.⁵⁻⁸ The ring down time (RDT) of an empty cavity can be determined by measuring the time-dependent decay of light exiting the cavity using the following equation:

$$I(t) = I_0 e^{\left(-\frac{t}{\tau_0}\right)} \quad \text{Eq. 2}$$

Where t is time, ring down time is $\tau_0 = l/c|\ln(R)|$, R is the reflectance of the mirrors within the cavity of length l , and c is the speed of light. When the cavity contains an absorbing medium such as a gas or aerosol, ring down time is affected by the absorption of the light by the absorber. Rearranging Eq.1 to $I = I_0 \exp(-\sigma Cl)$ and combining with Eq. 2 provides:⁹

$$I(t) = I_0 \exp \left[-\tau \left(\frac{1}{\tau_0} + (\sigma Cl) \left(\frac{c}{l} \right) \right) \right]. \quad \text{Eq. 3}$$

Therefore, absorbance can be written as:⁹

$$A = \frac{l}{c} \left(\frac{1}{\tau} - \frac{1}{\tau_0} \right). \quad \text{Eq. 4}$$

Using Eq. 4, an absorption profile obtained with CRDS and an absorption profile obtained with an FTIR (Eq. 1) are directly comparable as they are both measuring a wavelength-dependent absorption of a molecular vibration.

The sensitivity of the CRDS system is defined primarily by the reflectance of the mirrors in the optical cavity.⁶ Increased reflectivity increases the time to measure the light decay profile (i.e. ring down time with or without analyte) which also improves the accuracy with which the ring down time can be measured. Furthermore, the higher the reflectivity, the more passes the light will make prior to leaking out, therefore increasing the effective path length of the cavity, providing a relative parameter for comparing CRDS systems to non-CRDS system.

4. SYSTEM DESCRIPTION

4.1 Gasmeter DX4000

The Gasmeter DX4000 is a portable Fourier-transform infrared (FTIR) spectroscopy system, weighing in at 30.6 lbs. and a size of 17.5 x 15.5 x 6.5" (approximately 1 cubic foot, roughly the size of a large briefcase). It contains a gas cavity 500 mL in volume and heated to 180°C when performing measurements. Sampling is automated using the external Portable Sampling System (PSS), which automatically switches the line feeding the gas cavity between a zero gas line of dry air or N₂ and the sample inlet, as well as heats the sample gas to 180°C before introduction to the DX4000 to avoid thermal shock damage to the system's gas cavity. The PSS weighs 27.1 lbs. and is 15.7 x 11.8 x 8.3" in size and connects to the DX4000 by a transfer line also heated to 180°C to avoid condensation or cooling in the transfer process. It also contains a particulate filter to avoid introduction of solid particulates into the DX4000.

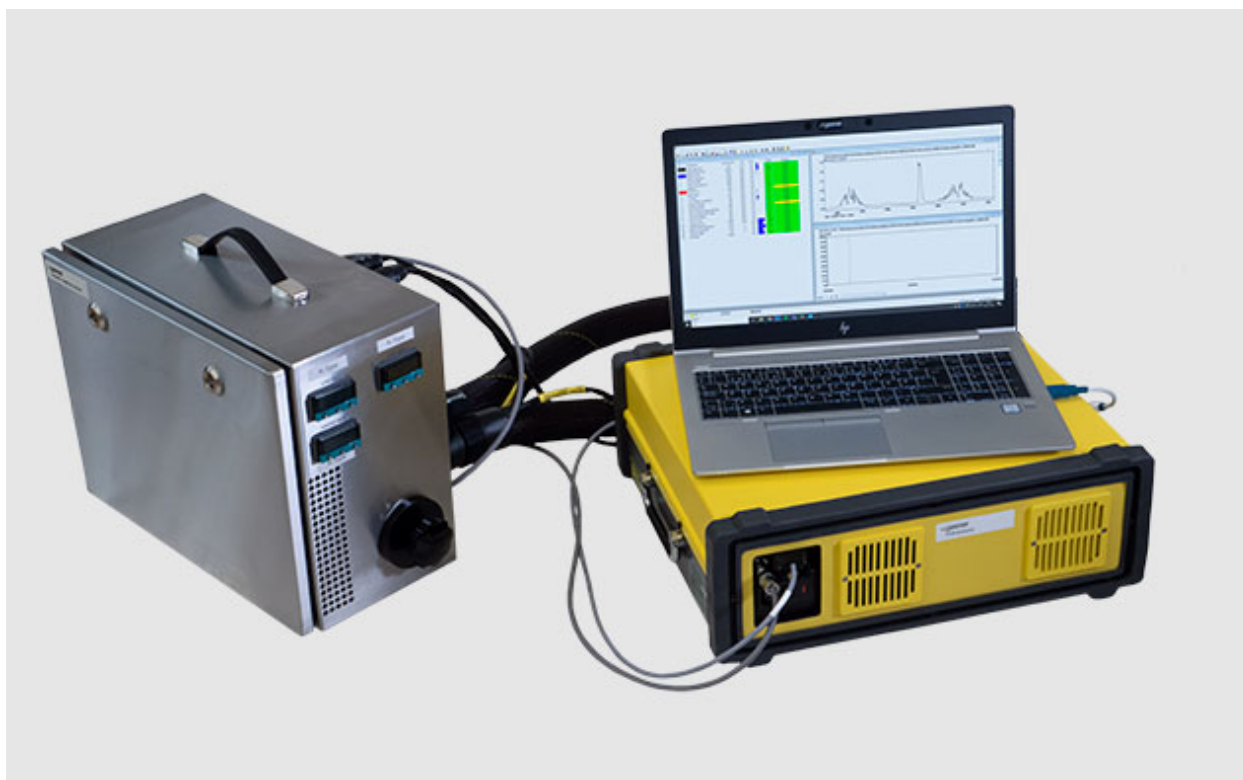


Figure 1 Gasmet DX4000 gas analyzer (bottom right) with PSS (left) and external laptop (top right)

The system feeds the zero gas line as a default state and only switches to the sample inlet while actively sampling. The zero gas line must be manually fed at a rate of 2-3 L/min, while the sample inlet is automatically fed by a 4 L/min pump which powers on when the system enters the sampling state.

The system is controlled using Gasmet's Calcmeter software on a laptop connected via an RS-232 cable connection, which can be used to adjust measurement parameters such as sampling time and integration time from a few seconds to several minutes each. The Calcmeter software also has spectral analysis and library matching features which were not utilized in this study.

4.2 RingIR AG-4000

The RingIR AG-4000 (Figure 2) is a portable cavity ring-down spectroscopy (CRDS) system, weighing in at 26.4 lbs and a size of 21.6 x 17.3 x 4.9" (approximately 1 cubic foot, roughly the size of a large briefcase). It contains dual gas cavities of 75 mL each in volume connected in series from an inlet valve. Sampling is done manually by flipping a toggle switch to power on a pump which is completely independent of the system's software controls and has no automatic timer. The pump itself only pulls at a single rate, however the rate can be manually controlled by an analog needle valve; this requires opening the instrument case to access the valve and measuring the flow rate with an external flow meter to actually know the flow rate for the sampling pump. The needle valve allows modulation of the flow rates from 5 L/min down to approximately 1.5 L/min.



Figure 2: RingIR AG-4000 unit

The AG-4000 can be controlled entirely via a touch screen located on the top of the instrument case. Instrument operation is basic and customizability options are limited: integration times are not adjustable; measurements take approximately 2 minutes to acquire, process, and save the data. The only options are to set a background (of ambient air without analyte), and measure samples with or without the ability to name the individual files. The instrument also has the capability to be operated with an external keyboard, mouse, and monitor, connected by USB and HDMI ports, respectively, as an external keyboard is needed to name individual files (data is otherwise saved as a timestamp of the collection time in UST).

5. EXPERIMENTAL

5.1 Vapor Generation Setup

A schematic detailing the vapor generation system utilized in this work is shown below in Figure 3. The system is largely comprised of 1/4" OD PTFE tubing connected with 1/4" Swagelok unions, bulkheads, and valves.

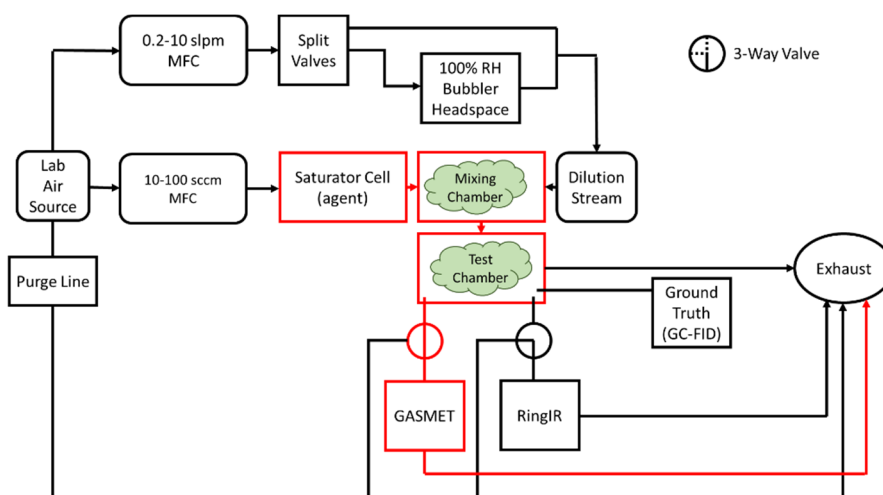


Figure 3 Test schematic: the red lines indicate flow with analyte present—in this example the Gasmet system is sampling

The analyte vapor at each concentration was generated by mixing a low flow of saturated analyte vapor with a high flow of humidified dilution air at controllable volumetric ratios to achieve the desired concentration. All supplied compressed air was sourced from CBC's in-house compressed air system which treats and dries the air supply to trace relative humidity levels. All flow rates are set using calibrated mass flow controllers (MFC) from either Matheson Gas (Irving, TX) or Aalborg Instruments (Orangeburg, NY).

Saturated chemical vapor was generated using a saturator cell (Glassblowers.com, Turnersville, NJ), which consists of a thimble-shaped ceramic wick fit inside of a U-shaped glass tube. The liquid analyte is loaded into the cell and absorbed into the high-surface area porous wick. The controlled evaporation from the wick surface allowed for continuous steady generation of saturated analyte vapor. Additionally, different vapor pressures allow any impurities to evaporate off before the target analyte, allowing for purer vapor generation than a headspace oven. At room temperature, the vapor pressures of the analytes tested in this work allowed for a continuous generation of 5-300 mL/min of saturated analyte vapor as necessary.

Dilution air was humidified to 50 +/- 5% relative humidity at RT by splitting the dilution line into two separate lines and diverting one of the lines through a bubbler system to create separate dry and humid lines. The volumetric ratios of the dry and humid lines were manually adjusted using a needle valve on each line. The bubbler system consisted of a 4 L Nalgene carboy half filled with water, an air inlet which fed to a bubbler stone submerged in water, and an outlet which was then recombined with the dry air line. The total flow into both lines was regulated with an MFC and the total flow of the recombined lines was checked to ensure that there was no loss of flow through the bubbler system. A temperature and humidity probe (E+E Elektronik, Engerwitzdorf, Austria) placed after the recombination of the two lines gave a real-time reading of the relative humidity, allowing lab personnel to adjust the needle valves as necessary to maintain the target humidification.

Both the analyte and dilution streams are then combined into a mixing chamber (1 L glass jar) before flowing into the sample chamber (5 L glass jar). The sample chamber then has lines to the inlet ports on both the RingIR and Gasmet systems which can be opened and closed, as well as a port for taking samples for concentration monitoring and an outlet to an activated charcoal filter which is always left open to maintain atmospheric pressure throughout the system and prevent backpressure from building up at any point thereby mitigating a potential safety hazard.

The inlet port on the RingIR system is directed by a manual three-way valve which can be directed either toward the sample chamber or directly to the dilution stream, for sample introduction and purging, respectively. The inlet for the Gasmet system is controlled internally by the Gasmet PSS which automatically handles sampling and purging.

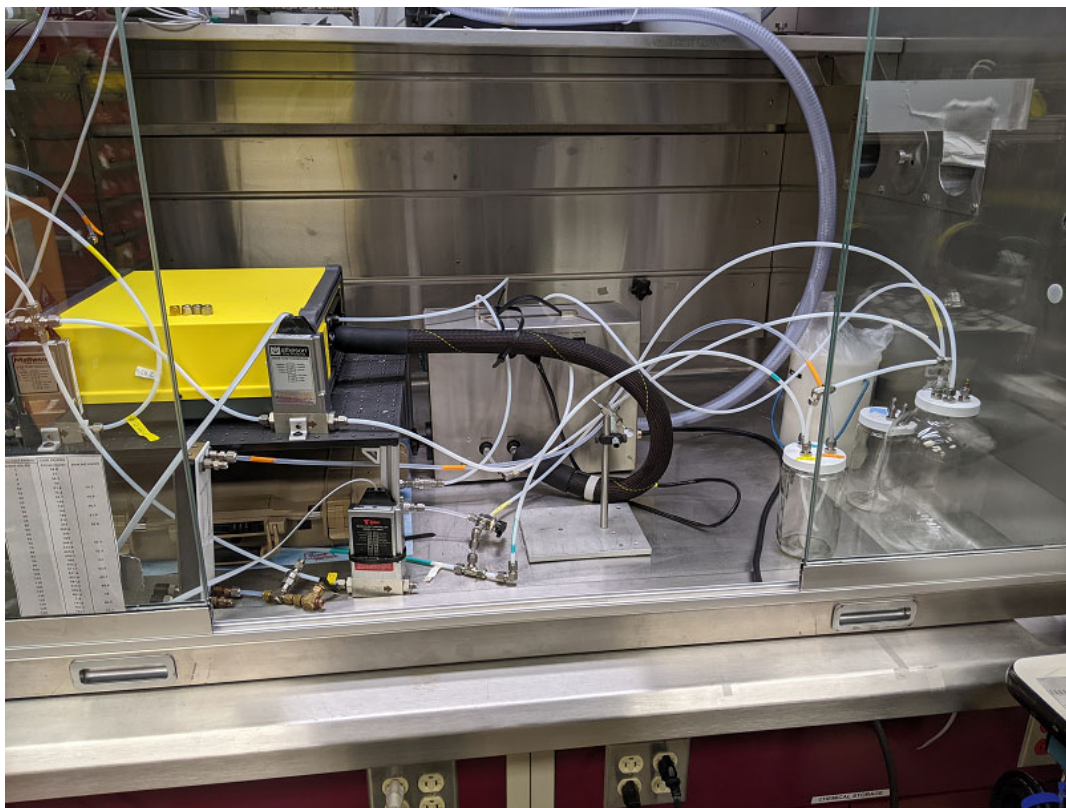


Figure 4 Test setup and instruments in fume hood

5.2 Cavity Fill Procedure

5.2.1 t_{99}

All work described in this paper was carried out modeling the concentration in each relevant chamber (mixing chamber, sampling chamber, as well as both the RingIR and Gasmet systems' cavities) using the t_{99} metric laid out by MacFarland.¹⁰ According to the model, the concentration inside of a chamber, C , will reach 99% of the concentration of the vapor stream flowing into the chamber, C_0 , after a period of time t_{99} defined as $t_{99} = 4.605 \cdot (V/F)$, where V is the volume of the chamber and F is the flow of the vapor stream at concentration C_0 in volume/time. After time t_{99} because the concentration inside the chamber can never exceed the introduced flow the analyte concentration can be considered stable within 1% as it will only asymptotically approach C_0 from then onward. Such a model gives a more accurate profile of the concentration inside the chamber as a function of time than a simple measure of air exchanges per unit time. Additionally, the same model can predict the purge of a chamber if the initial concentration is C_0 and the introduced flow is blank air with an analyte concentration of zero. Figure 5 below illustrates a time profile of the filling and purging of a chamber under this model.

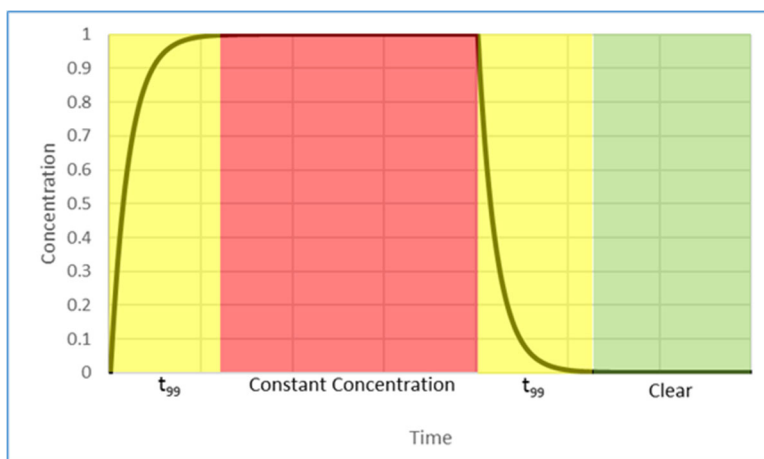


Figure 5 Time profile of chamber fill and purge according to t_{99} model

5.2.2 Gasmeter

The gas cavity on the Gasmeter is filled using the Portable Sampling System (PSS), which is a separate unit which connects to the gas analyzer via heated transfer lines. When operational, the default state of the PSS is to open the transfer line connecting to the gas cavity to the zero gas line so the system is continuously purged when not actively sampling. When the system is set to actively sample, a pump inside the PSS turns on and a multi-way valve inside the PSS redirects the line to the gas cavity from the zero gas line to the sample inlet line. Because the default state of the PSS is open to zero gas, it is assumed that each sample starts with a fully purged cavity. When the PSS samples, the pump pulls 4 L/min of air through the sample inlet. Assuming a 500 mL cavity plus 100 mL volume in tubing, the t_{99} for the Gasmeter cavity comes out to 0.69 minutes (41.5 seconds). Sampling is performed for 60 seconds to ensure the t_{99} is reached.

5.2.3 RingIR

The RingIR system does not contain any automated sampling unit, so filling the gas cavity is performed manually. A three-way valve was affixed to the inlet of the unit, allowing the line to the inlet to be manually switched between the dilution line (clean air) and the sampling chamber. The unit has a pump which pulls 1.6 L/min into the gas cavity when turned on via a separate toggle switch located on the front of the unit. To fill the cavity with sample gas, the three-way valve is manually switched to the sample chamber position and the pump turned on. As the RingIR system contains two 75 mL chambers, plus 10% volume for tubing, at a flow of 1.6 L/min the t_{99} becomes 0.48 minutes (28.5 seconds). Sampling is performed for 60 second to ensure the t_{99} is reached.

5.2.4 Library Data

Library data were obtained from the NIST Chemistry WebBook Standard Reference Database Number 69.¹¹ The IR spectrum for each analyte was downloaded in JCAMP-DX format and imported into MATLAB R2021b for analysis and comparison to the data obtained by the Gasmeter and RingIR systems. The library data shown in Figure 6 shows that

each analyte chosen has distinct peaks that can be identified spectrally and are significantly different from one another.

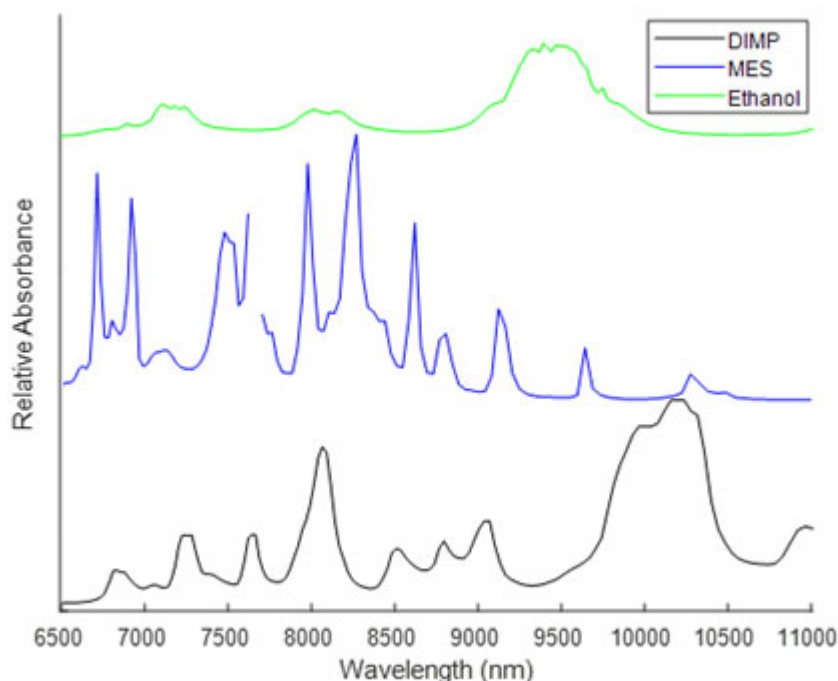


Figure 6: Library data obtained from the NIST Chemistry WebBook with each spectrum offset for visual acuity.

6. TEST PROCEDURES

6.1 Test Matrix

Due to safety and security protocols, the Phase I test could not involve introducing any chemical warfare agent (CWA) nor any corrosive chemical to the RingIR system. As such, three non-corrosive chemicals were chosen for testing:

1. Diisopropyl methylphosphonate (DIMP) – a breakdown product of sarin (GB) and common simulant for G-type nerve agents,
2. Methyl salicylate (MES) – a legacy simulant, better known as oil of wintergreen, its spectral properties are well-characterized due to its long history of use as a test agent,
3. Ethanol (EtOH) – a non-toxic organic solvent which allowed CBC to compare data 1-to-1 with data collected by RingIR during their development of the system.

Each chemical would be tested at three different concentrations (low, medium, and high) with the goal of crudely testing the upper and lower limits of sensitivity for each system; full limit of detection (LOD) testing for various chemicals will be carried out in later phases of testing. Measurements of each chemical at each concentration were performed in triplicate. Chemicals were used as received without further purification.

6.2 Daily Background Measurement

At the start of each testing day, after each system was allowed to warm up sufficiently, both systems collected a background of ambient air without analyte to function as a baseline response for each system to use for processing collected data throughout the whole testing day. The dilution air stream, lab air conditioned to 50% relative humidity at ambient lab temperature, was used for the background. Because the background measurement is subtracted from each measurement, the signal from the analyte is isolated in each collected spectrum.

6.3 Ethanol Confidence Check

At the beginning of each day, before any data was collected, a confidence check was performed by squirting a droplet (~0.5 mL) of ethanol onto a kimwipe in a 1 L glass jar, allowing the ethanol to saturate the jar headspace, and allowing both systems to sample the headspace. Because the spectra for ethanol was well-characterized on both systems, it provided a daily check that each system was functioning properly.

6.4 Humidity

The dilution stream was conditioned to 50 +/- 5% relative humidity at room temperature. The flow from a Matheson mass flow controller (MFC) was split into two separate flows controlled volumetrically using two analog needle valves. One flow was sent into an air bubbler stone in a 5 L sealed Nalgene container approximately half-full of water; the bubbling generates a fully saturated (100% RH) headspace within the container. The other line is kept completely dry. By then recombining the two lines and using the needle valves to volumetrically control the proportion of the wet and dry lines, control can be kept over the humidity level of the dilution line.

6.5 Concentration Verification

The concentration of analyte in the sample chamber was measured before and after each set of collected data. The average of the measured samples was taken to be representative of the concentration across the collected data set.

6.5.1 GC-FID

For DIMP and MES testing, a sample was collected from the test chamber on a sampling sorbent tube (10 mm O.D., 4 5/8 in. long, packed with 20:35 Tenax-TA sorbent) at a rate of 5–500 mL/min for 1–5 min using a vacuum source (SKC; Eighty Four, PA); rates and times were adjusted as appropriate. The sorbent tube was placed in an ACEM model 900 Dynatherm system (CDS Analytical; Oxford, PA), which is a thermal desorption unit (TDU). A vacuum source continuously drew N₂ into the TDU, where the sorbent tube was dried by a clean N₂ purge gas, and the sample was conveyed toward the focusing trap (4.5 in. long, 1/8 in. stainless steel, 6.3 cm of Tenax TA). The sample was then heated and transferred to the focusing trap (which was also heated). The data acquisition analysis cycle was started by the transfer of

the collected sample onto the networked Agilent (Santa Clara, CA) 6890N GC column for GC–FID. This allowed for verification of the concentration at the time of sampling as well as during the sample (analyte) test and the clearance checks. The calibration standards (all prepared in isopropanol) were spiked onto the sorbent tube to calibrate the TDU–GC–FID system. A linear regression fit ($r^2 = 0.999$) of the standard data was used to calculate the concentration of each chamber sample test and to perform clearance checks.

6.5.2 MultiRAE

For ethanol, concentrations in the sampling jar were measured in real-time using a MultiRAE (Honeywell, Charlotte, NC) photoionization detector (PID). The MultiRAE contains its own internal sampling pump and PID which reads out a generic ppm measurement for volatile organic chemicals (VOCs). The generic VOC concentration was then multiplied by a calibrated correction factor of 7.9, supplied by Honeywell. Because the concentration of ethanol in the sampling chamber tended to change rapidly, the real-time concentration was taken immediately before and after filling the gas cavity for each system for each individual trial, and the average of the two readings taken to be representative of the concentration measured in that specific trial.

7. RESULTS AND OBSERVATIONS

Using the library data and data obtained at high concentrations with each instrument, peaks were identified that could be used to assess the sensitivity of each instrument. In Figure 7, each chemical is shown with representative spectra from the NIST Chemistry WebBook, RingIR system, and Gasmet system stacked on one other to show overlapping vibrational bands. The red-shaded regions are the areas that are compared here; the blue shaded regions are areas that were also analyzed but are not presented in detail here. There is general agreement between the three spectra for each compound. Of note, at 8600 nm in the RingIR data, because two lasers are employed within the system there is a discontinuity in the data as the system does not stitch the data from both lasers. This can be seen well in the DIMP and the MES spectra in Figure 7. Furthermore, it appears as if the RingIR system is not particularly sensitive between 7000–7500 nm as there is no peak evident from the ethanol, which is expected within that region.

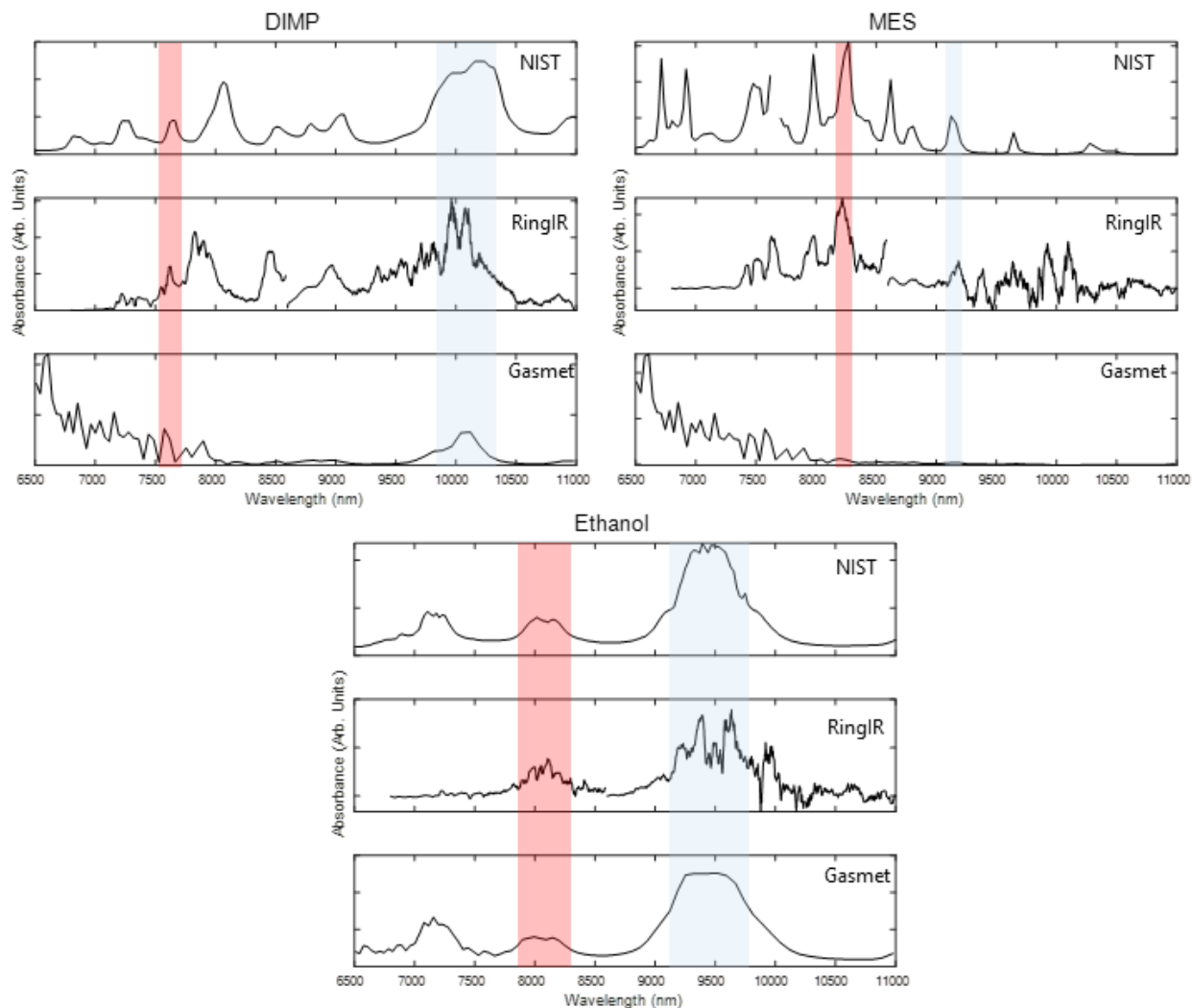


Figure 7: NIST, RingIR, and Gasmet data shown for each chemical analyzed. The red shaded region indicates data from which sensitivity is determined and the blue shaded region is data that is briefly discussed here qualitatively but not quantitatively

The two systems have reproducible noise within different regions of the spectrum. Areas with increased noise can potentially negatively affect a quantitative analysis of the spectral content within that region. In Figure 8, it can be shown that the Gasmet system is generally noisier from 6500 nm to 8000 nm whereas the RingIR system is generally noisier with the second laser in the system, from 8600 nm to 11000 nm; this particularly affects the data when the signal-to-noise is low. Figure 7 illustrates this issue for the Gasmet system in the spectra for DIMP and MES, with the peak of interest falling in the noisier decreasing absorbance region from 6500 nm to approximately 8000 nm; however, with ethanol there is sufficient absorption to overcome the noise. The noise issue is also observable in the RingIR data for the peaks shaded in blue for DIMP and ethanol, as the noise degrades the ability to reliably quantify those large peaks.

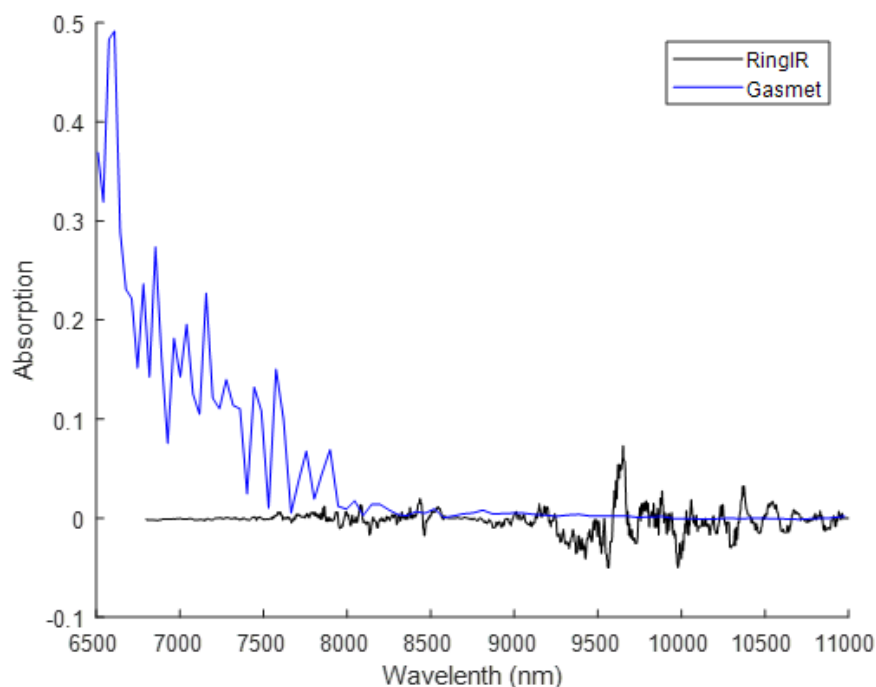


Figure 8: Blank data from the RingIR (black) and Gasmet (blue) showing areas within the spectra that are noisier than others.

The RingIR system is generally more sensitive than the Gasmet system. Figure 9 shows absorbance vs. concentration lines of best fit for all three chemicals. For DMMP and MES (top left and top right), the RingIR data (black solid line) has a greater slope than the Gasmet (blue solid line). The slope of the line, the change in absorbance with respect to concentration, defines the sensitivity of the instrumentation.¹² The RingIR system is 5.6 times and 3.6 times more sensitive than the Gasmet system for DMMP and MES, respectively, covering a range from approximately 1 mg/m³ to 300 mg/m³.

When evaluating ethanol, the calculated sensitivities were close to the same, with the Gasmet system actually showing slightly greater sensitivity over the whole range. However, upon closer inspection (Figure 9, red-dashed insert) it can be seen that the Gasmet data are poorly fit near the estimated limit of detection (LOD, horizontal blue dashed line). Additionally, data obtained below the estimated LOD (not shown) all provided an absorbance equal to the background (blank) data with no change in absorbance with respect to a change in the concentration. The poorly fit lower concentration data for the Gasmet likely artificially increases the sensitivity of the Gasmet. To better understand this, additional data must be collected between 700 mg/m³ and 2700 mg/m³ with the Gasmet system. The RingIR system, however, shows the data fitting well down to ~50 mg/m³ ethanol with good linearity between the lower and higher concentration. Therefore, we believe that the sensitivity of the RingIR system is truly represented here, and that it is of similar sensitivity to MES.

The similarity in sensitivities is to be expected as the region of the spectrum evaluated is similar between these two analytes (approximately 8200 nm and 8150 nm for MES and ethanol, respectively) whereas DIMP was evaluated in a different spectral region (approximately 7800nm). The spectral band evaluated with MES at ca. 8200 nm (1219 cm⁻¹) is

associated with the in-plane deformation of the C-H bond.¹³ Similarly, the spectral band evaluated in ethanol at ca. 8150nm (1227 cm^{-1}) is associated with the symmetric bending of hydrogen in about the C-C axis.¹⁴ These two vibrations are closely related and are expected to have similar sensitivities. In contrast, the spectral band evaluated in DIMP at ca. 7830 nm (1277 cm^{-1}) is associated with the P=O stretch and is not associated with the C-H stretching thereby having expectedly different sensitivities.¹⁵

A more sensitive instrument with a lower limit of detection may provide a greater capability of sensing potential threats at lower concentrations. The instruments tested herein provide signal for DIMP, MES, and ethanol below prevailing military exposure guidelines (MEG) for 1 hour critical (i.e. potentially lethal) exposure and to the Department of Energy's protective action criteria (PAC). For these compounds, a mixture of the Acute Exposure Guideline Levels (AEGLs) and the Temporary Emergency Exposure Limits (TEELs) are the criteria in which the MEGs and the PACs are defined by. If a system is less sensitive, it becomes more difficult to detect the differences between a small exposure and a large exposure and be informed of the best protective posture, a limitation which should be considered when identifying the correct instrument for the desired outcome.

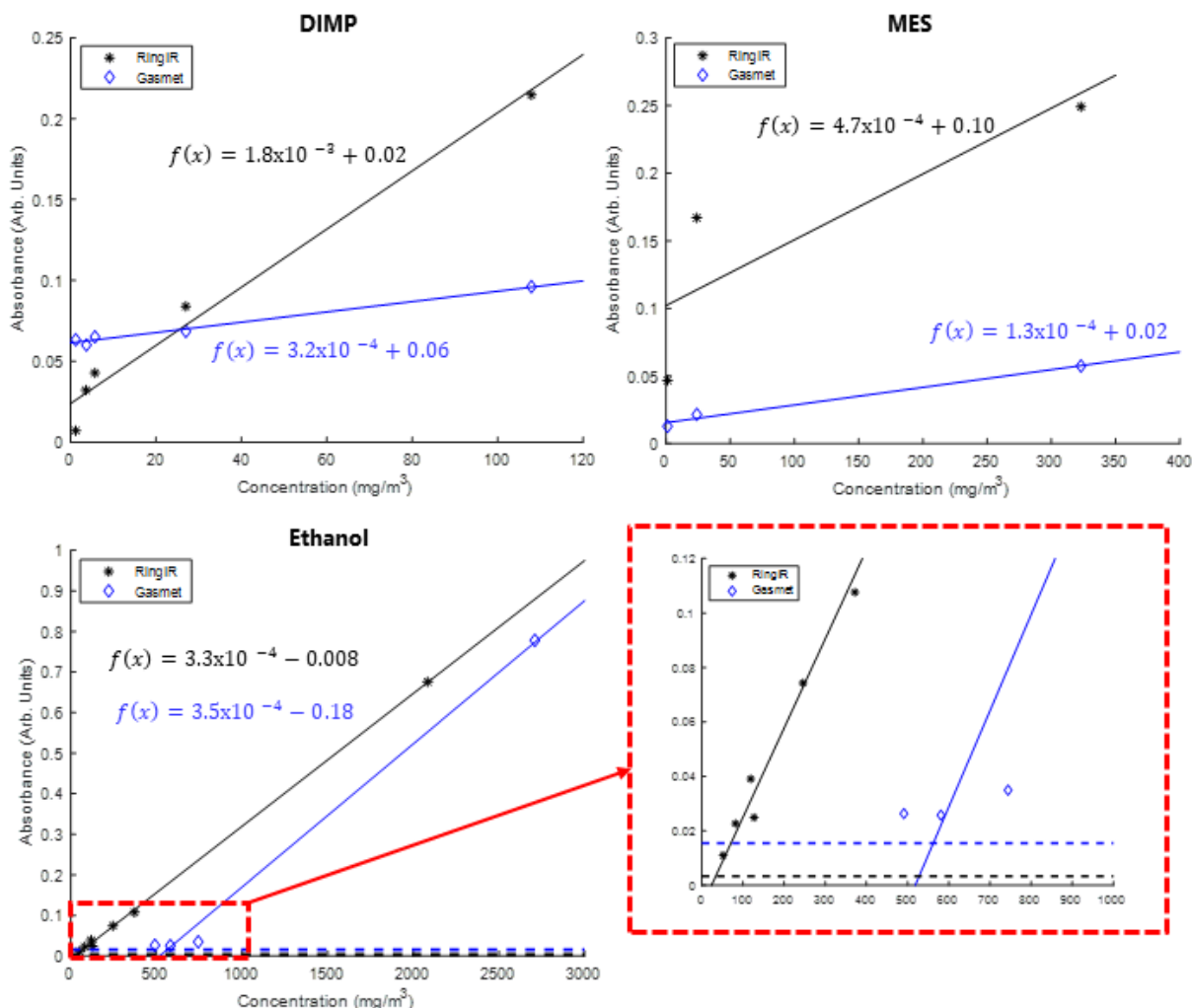


Figure 9: DIMP, MES, and ethanol concentration dependence and calculated sensitivities. The insert (red-dashed box) shows ethanol at the lower concentrations for each system with the black and blue dashed lines showing an estimated LOD for the RingIR and Gasmet systems, respectively.

8. FUTURE WORK

The work presented herein was accomplished in the first year (FY22) of a two-year program. The chemicals evaluated were restricted to non-caustic materials due to the RingIR system being on loan from the manufacturer. FY23 will focus on caustic toxic industrial compounds and CWAs thanks to procurement of a purchased RingIR system. The three compounds herein will be reevaluated with the new instrumentation to confirm functionality at least as good if not exceeding the prototype system and additional compounds will also be evaluated. Estimates of the limit of detection of several CWAs and toxic industrial compounds will also be evaluated.

9. CONCLUSIONS

The RingIR and Gasmet instruments both exploit the absorption of vibrational bands of a gas-phase chemical to provide chemical-specific information. The Gasmet system is a

standard FTIR instrument that is used in industry and as a standard in some laboratory settings whereas the RingIR system is a newly commercially available instrument. The use of each instrument is similar whereby a sample is obtained via pulling of a volume of air into a cell, a spectroscopic measurement is completed, and a spectrum is saved. The RingIR and Gasmet output agree well with library data. The RingIR system appears to have a greater sensitivity and a lower limit of detection than the Gasmet system.

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ACRONYMS AND ABBREVIATIONS

AEGLs	acute exposure guidelines levels
CRDS	cavity ring down spectroscopy
DIMP	diisopropyl methylphosphonate
EtOH	ethanol
FTIR	Fourier transform infrared
GC-FID	gas chromatography – flame ionization detector
IR	infrared
LOD	limit of detection
MEG	military exposure guidelines
MES	methyl salicylate
MFC	mass flow controller
NIST	National institute of science and technology
OD	outer diameter
PAC	protective action criteria
PID	photoionization detection
PSS	portable sampling system
PTFE	polytetrafluoroethylene
RDT	ring down time
RH	relative humidity
RT	room temperature
TDU	thermal deposition unit
TEELs	temporary emergency exposure limits
VOC	volatile organic chemicals

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