Real-Time Measurement of Ammonia (NH₃) in Artillery Smoke Using a Passive FT-IR Remote Sensor

Jong-Seon Kim,* Hyunwoo Nam, Hyeon Jeong Kim, Jae Hwan Lee, and Byeong Hwang Park

CBR Technology Directorate, Agency for Defense Development, Daejeon 34186, Korea

ABSTRACT: Early alerts for avoiding exposure to toxic chemical threats are critical applications of sensors to protect both military troops and civilian populations. Among the various sensing techniques developed, the passive Fourier transform-infrared (FT-IR) spectroscopy method has been demonstrated to work well as a remote (kilometer-scale) sensor for such early-alert systems. The passive type FT-IR detector is capable of mobile detection of toxic gas clouds because of its small-scale interferometer and optical instruments. In this article, real-time FT-IR measurements of ammonia (NH₃) in 76 mm artillery smoke are reported using a commercial remote sensor and scored by a real-time analysis conducted using a custom algorithm based on the generalized likelihood ratio test (GLRT). Using these methods, we measured the real-time change in the ammonia spectrum and GLRT scores against concrete and forest backgrounds following artillery propellant detonation. We confirmed that the GLRT score characteristics depend on the background and found that the effect of rapid heat transfer from the propellant detonation to the ammonia was detected in the accumulated ammonia FT-IR spectra.

■ INTRODUCTION

Early detection of chemical warfare agents, toxic industrial chemicals, and leaked chemical threats is important for providing effective protection and improving the survival rates of military personnel and civilians in the chemical industry,1,2 environmental monitoring,3 and military field operations.4 When chemicals are released outdoors, they are typically in the gaseous phase, and as such are colorless and odorless. Therefore, a remote and early detection of chemical exposure is essential to prevent causalities. Several early detection techniques have been suggested and developed for the early detection of chemical exposure, including gas chromatography/mass spectrometry (GC/MS),5,6 ion mobility spectrometry (IMS),7 chemi-electronic chip,8 active/passive Fourier transform-infrared (FT-IR) spectroscopy,9,10 and colorimetric11 approaches. Among the various techniques, the passive FT-IR sensor system is particularly promising because it provides rapid and highly sensitive remote detection. Furthermore, with the development of a rugged and minimized interferometer, FT-IR has become more portable, and thus more useful in field applications. Indeed, the U.S. Army has utilized passive FT-IR systems to protect troops from chemical warfare agent attacks since the 1990s.12

Theoretically, the passive FT-IR technique directly measures mixed IR radiance from three layers: target chemical plumes, the atmosphere, and the background. Indeed, the application of the IR radiance principle in this technique can be explained using this three-layer model under ideal conditions,13 in which the detection limit of a passive FT-IR detector for a gas is defined as

\[
\text{intensity of IR radiance} = \epsilon (cd\Delta T)_{\text{limit}}
\]

where \(\epsilon\) is the gas absorption coefficient, \(c\) is the concentration of gas in the target chemical plume, \(d\) is the optical path length through the atmosphere, and \(\Delta T\) is the temperature difference between the gas and the background.

In passive FT-IR remote-sensing research, the detection limit, or minimum temperature difference that can be resolved by the spectrometer, of an FT-IR detector is described by the NEΔT (noise-equivalent delta temperature).13 As described in eq 1, the detection limit of a passive FT-IR detector is predominantly determined by three variables \((c, d, \text{and } \Delta T)\). In real applications, because chemical toxicity is related only to the concentration of a leaked gas \((c)\), the effect of the optical path length \((d)\) and temperature difference \((\Delta T)\) should be separately evaluated to reduce the likelihood of false alerts during the development of passive FT-IR systems. However, though much research has succeeded in improving the FT-IR, it remains difficult to distinguish between the effects of the three variables measured in the IR spectrum. For example, even when the concentration of the toxic gas is higher than EC₅₀ or LD₅₀, if the temperature difference is imperceptible, \(cd\Delta T\) will be a zero. Therefore, all parameters should be considered together during an FT-IR measurement, and the system should be prepared to recognize false alerts that were triggered by parameters \((d \text{ and } \Delta T)\) and not the toxic gas concentration \((c)\).

Previously, most FT-IR research has been focused on the development of a compact detector for portable sensors,4 improvement in the detection limit,14 signal processing...
methods\textsuperscript{,15} or installation of FT-IR interferometers.\textsuperscript{12} However, as the FT-IR technology is intended to operate outdoors, much indoor-based sensor development research tends to require the development of a functional outdoor spectrum before commercialization and systemization can be achieved during the final production stages. Therefore, research into the real-world field interference is very important in the development and optimization of passive FT-IR remote sensor operation techniques. Field interferences, if unaddressed, could trigger false alerts, negating the usefulness of the entire sensor system. Ideally, to determine such interference effects, outdoor tests should be conducted to analyze the combined effects of outdoor conditions. However, outdoor testing has many limitations, including cost, national security, and chemical safety regulations. For these reasons, previous interference measurement data have only been obtained through indoor chamber experiments. Though this interference data are very convenient to obtain and can be helpful in predicting inference effects, these experiments have clear limitations in replicating realistic-usage scenarios.

Fortunately, for this study, we obtained permission to observe firing tests of 76 mm artillery shells at our outdoor facility. These detonations produced unique data illustrating how propellant detonation can hinder accurate measurement in the IR spectrum under realistic conditions. Accordingly, we collected outdoor measurements and analyzed the interference effect due to artillery smoke and the thermal effect due to detonation. We confirmed that among the toxic chemicals detected in the smoke, characteristic ammonia peaks were observed. Ammonia (NH\textsubscript{3}) is widely used in industrial systems and has been identified as a high-priority toxic industrial chemical by International Task Force ITF-25 and ITF-40.\textsuperscript{1} Therefore, we analyzed the ammonia spectra and evaluated a detection algorithm to score the change in ammonia concentration during artillery firing.

## RESULTS AND DISCUSSION

In this study, the IR spectrum (brightness temperature) of artillery smoke with different background conditions was measured using a passive FT-IR detector.\textsuperscript{16} Table 1 and Figure 1 provide an overview of the real-time procedure used to obtain the IR spectrum measurements.

### Table 1. Experimental Conditions for Each Background Condition

| Background condition | Atmospheric temperature (°C) | Background temperature (°C) | Distance from FT-IR detector (m) |
|----------------------|-----------------------------|-----------------------------|---------------------------------|
| Concrete             | 27                          | 27–30                       | 87                              |
| Forest               | 20                          | 20–22                       | 200                             |

As shown schematically in Figure 1, the artillery was set up on a concrete road and an FT-IR detector was installed on a hill 87 m from the artillery. When the FT-IR detector was aimed at the muzzle of the artillery barrel from the hill, the main detection background was the concrete road. The surface temperature of the concrete was measured using an IR thermal camera (FLIR), with the results described in Table 1, along with the temperature of another background condition, a forest 200 m away, selected for comparison. As described in Figure 1, gunsmoke was generated at the muzzle of the artillery and continuously moved toward the forest region. When we measured the IR spectrum against the forest background, the smoke coverage was found to be relatively larger than the initial smoke coverage due to gas diffusion. The commercial FT-IR detector (Block engineering, PORTHOS) used in this study had a field of view of 1.5°. This means that it could measure a 2.55 m diameter circular region at a distance of 100 m, so its measurement area was ~3.86 m\textsuperscript{2} for the concrete background and 20.4 m\textsuperscript{2} for the forest background. All measured spectra were taken from the artillery smoke without other interferences, considering these measurement diameters.

The commercial FT-IR system consisted of an FT-IR detector mounted on a tripod and linked to a laptop to provide real-time monitoring. Before the commencement of artillery fire, blackbody calibration was conducted to ensure accurate IR spectrum measurements. A total of 20 rounds of artillery munitions were then fired within 1 h under almost identical conditions. For the first 10 rounds, we measured the muzzle of the artillery (Figure 1a) against the concrete background, and for the second 10 rounds, we measured the diffused artillery smoke against the forest background (Figure 1b). Each measurement began 10 s before the artillery was fired and finished 10 s afterward. Most of the resulting smoke diffused in the direction shown in Figure 1 (right to left).

For measurement and analysis, we converted the observed FT-IR spectra into a detection algorithm score based on the generalized likelihood ratio test (GLRT). The GLRT is a widely known statistical detection algorithm typically used to analyze various chemical gases by comparison against a Z matrix, which consists of the FT-IR radiance information of various backgrounds, interferences, and target gases as follows

\[
\begin{pmatrix}
S_1 & \cdots & BG_{11} & BG_{m1} \\
S_2 & \cdots & BG_{12} & BG_{m2} \\
\vdots & \cdots & \vdots & \vdots \\
S_{n-1} & \cdots & BG_{1n-1} & BG_{mn-1} \\
S_n & \cdots & BG_{1n} & BG_{mn}
\end{pmatrix}
\]

where each background spectrum is included in the BG column and information describing the target gas spectrum is included in the S column. Among the various gas detection algorithms, the GLRT has the advantage of minimizing the effect of spectrum distortion due to interference and background FT-IR signals. This is accomplished by reverse-tracing the spectrum of the target gas through comparison with every background and interference spectrum in the Z matrix.
Prior to outdoor tests, the alarm threshold value ($\gamma$) for the ammonia GLRT algorithm was set to $\gamma = 3.0$. Using our customized signal processing program, we were then able to compare all of the GLRT scores included in the library (see Supporting Information eq S1 for further details).

## RESULTS AND DISCUSSION

Prior to the commencement of artillery fire, we measured the background IR spectrum for comparison with the IR spectrum of the artillery smoke. There were no ammonia interference signals in the IR spectra measured against backgrounds such as the sky, concrete, forest, or the seashore. Detailed information describing the background data is provided in Figure S1 of the Supporting Information. As shown in Figure 2a,b, the measured IR spectra showed no specific chemical peaks for the concrete or forest backgrounds, respectively, as confirmed by the expanded IR spectrum data from 900 to 1000 cm$^{-1}$ in Figure 2c,d. Additionally, we calculated the GLRT detection algorithm scores, shown in Figure 2e,f, which were all found to be less than 1.0.

During the field tests, 20 rounds were fired in 1 h, but a change in the wind direction meant that only 19 instances of artillery smoke were measured as described in the Supporting Information (Figure S2). From the first instance of artillery fire to the last, there were no observed changes in temperature and humidity. After firing, every measurement of artillery smoke immediately triggered an ammonia alert. As shown in Figure 3a, a pure ammonia cloud produces two characteristic IR absorption peaks at 930 and 967 cm$^{-1}$, representing the N–H band. In Figure 3b, an artillery smoke IR spectrum is plotted against the pre-firing IR spectrum for a concrete background. Comparing these data, significant ammonia peaks are clear at 930 and 967 cm$^{-1}$. For the forest background, the passive FT-IR measurements in Figure 3c also showed the same ammonia peaks after firing.

All artillery smoke caused an ammonia alert to be issued from both the PORTHOS FT-IR system and our customized GLRT-based analysis system. Note that the two characteristic peaks observed in the spectra are too clearly manifested to be false alerts. To confirm whether these ammonia detection behaviors are temporary, we analyzed the full IR spectrum of the artillery smoke. As shown in Figure 4a,b, the artillery smoke definitely has ammonia peaks in its accumulated FT-IR spectrum. Comparing Figure 4a,b, the significantly greater maximum intensity in Figure 4a is due to the initial temperature of the artillery smoke, which can be as high as 3000 °C depending on the gunpowder type and load. However, neglecting this single maximum intensity peak, the intensities of the other detected ammonia peaks are nearly the same.
Analyzing the change in the GLRT score offers another way to identify the existence of chemical gases. To demonstrate, we ran our customized GLRT detection algorithm analysis on every artillery smoke measurement, and the results indicated clear differences in detection scores against the concrete background and the forest background due to the diffusion of the smoke. The results are shown in Figure 5, in which the instance of artillery fire is marked as a dotted line. Against the concrete background, as shown in Figure 5a, the GLRT score sharply increases up to 5.44, then decreases rapidly within a few seconds. After this spike-shaped behavior, the remaining artillery smoke was dispersed as described by each graph. On average, ammonia peaks were observed for 5 s during which the GLRT score remained about 1.0. Although later changes in GLRT scores were dependent on wind velocity and direction, the observed initial spike-shaped GLRT score change was consistent for the concrete background. Because the detonation of the gunpowder rapidly transferred thermal energy into smoke, the temperature difference between the smoke and the background drastically increased at the artillery muzzle. As previously mentioned, the intensity of IR radiance detected by a passive FT-IR detector is highly dependent on the gas concentration, optical path length, and temperature difference. Therefore, we can reasonably assume that the spike-shaped GLRT score behavior is the result of a transfer of thermal energy from the detonated gunpowder.

We were also able to measure the IR spectrum of the diffused artillery smoke against the forest background. As shown in Figure 5b, the diffused ammonia GLRT score measured against the forest background is relatively smaller than against the concrete background. The GLRT score also varies widely between 0.54 and 5.23, and the detection time exhibits significant variation from 7 to 20 s, depending on the wind intensity and direction. Compared to observations against a concrete background, the GLRT score against the forest background did not show a spiked shape, instead exhibited mostly step-shaped responses.

We also plotted the measured FT-IR spectra against duration in Figure 6. The data were measured at a frequency of 3 Hz, meaning that each data point covers a time period of 0.33 s. When the propellant was detonated, the flat IR spectrum (bottom) suddenly changed and ammonia peaks were clearly developed (red dotted box). For a few seconds following detonation, relatively weak ammonia peaks remained before the IR spectrum recovered to the flat baseline (top). This indicates that a momentary transfer of thermal energy

Figure 4. Continuous spectrum data for artillery smoke against (a) a concrete background, where the smoke rapidly dissipated or moved away, but had a maximum brightness temperature of 60 and (b) a forest background, in which the spectra are longer than those against the concrete background, but the maximum intensity is relatively smaller.

Figure 5. GLRT score vs time against the (a) concrete background and the (b) forest background. Artillery smoke continuously moved from the concrete to the forest background because of the wind. The GLRT score of ammonia is clearly manifested as a spike when measured against the concrete background, while against the forest background, the GLRT ammonia score peak is relatively smooth, indicating long-term detection.
from the propellant to the ammonia in the artillery smoke enhanced its spectral intensity, as described in eq 1.

To accurately determine the actual ammonia concentration in the air without the influence of the heat transfer, we would need to collect samples from the artillery smoke, but unfortunately access to the artillery equipment was not permitted during these experiments. Theoretically, the total amount of ammonia generated by artillery firing is dependent on the loaded propellant amount and type, as a TNT-based propellant could easily produce such ammonia during detonation (see Supporting Information eq S2). However, the various FT-IR measurements and analyses in this study verified that considerable ammonia was produced by artillery fire, indicating that protection protocols and the interference effect of artillery smoke and various backgrounds should be considered during artillery operations.

CONCLUSIONS

In this study, we successfully measured and analyzed a series of FT-IR spectra in the vicinity of field artillery firing exercises considering various experimental conditions such as background, presence of artillery smoke, and different measurement distances. We found that a significant transfer of heat from propellant detonation could be a reason for the strong ammonia detection alert from the passive FT-IR detector immediately following firing, even though the total released ammonia was found to be relatively rare; then the smoke moved away and dissipated. By analyzing the ammonia peaks detected using a real-time GLRT statistical algorithm score, we confirmed that the GLRT score shape is related to the background condition. Even though the thermal energy transfer from detonation is the dominant factor determining the detection of ammonia in artillery smoke, it is obvious that this is not a false alarm: ammonia is indeed generated by a propellant detonation. Though in these experiments air sampling was not allowed, using the FT-IR detector and the results of the GLRT scoring, we successfully demonstrated that ammonia is produced from propellant detonation and that it is necessary to separate the effects of ammonia concentration from the effects of thermal energy transfer in interpreting the data gathered by FT-IR sensor systems.
(13) Beil, A.; Baum, R.; Johnson, T. J. Detection of chemical agents in the atmosphere by passive IR remote sensing. *Proc. SPIE* **1999**, *3856*, 44−56.

(14) Zhang, Z.; Clewes, R. J.; Howle, C. R.; Reid, D. T. Active FTIR-based stand-off spectroscopy using a femtosecond optical parametric oscillator. *Opt. Lett.* **2014**, *39*, 6005−6008.

(15) Gautam, R.; Vanga, S.; Ariese, F.; Umaphy, S. Review of multidimensional data processing approaches for Raman and infrared spectroscopy. *EPJ Tech. Instrum.* **2015**, *2*, 1−38.

(16) Deutsch, E. R.; Kotidis, P.; Zhu, N.; Goyal, A. K.; Ye, J.; Mazurenko, A.; Norman, M.; Zafiriou, K.; Baier, M.; Connors, R. Active and passive infrared spectroscopy for the detection of environmental threats. *Proc. SPIE* **2014**, *9106*, 1−10.