GC-FTIR Analysis of Chemical Warfare Nerve Agents

By Jenni L. Briggs, PhD, PIKE Technologies, Madison, WI and Jim Hancock, Defense R&D Canada – Suffield, Alberta, Canada

Homeland security and defense organizations have a requirement for the rapid screening and identification of unknowns at the scene of an incident. Of particular concern would be the use of chemical warfare (CW) agents or toxic industrial chemicals.

For this application, laboratory identification methods need to provide reliable molecular information about the analyte. Infrared (IR) spectroscopy is one technique that can provide unique spectroscopic data as well as functional group information. The aims of this study were to investigate the separation via GC and subsequent detection by IR of chemical warfare nerve agents, and to determine the functional groups and spectral information of the agents.

Materials and Methods

A mixture of the following CW nerve agents (250 ng/µL per component in hexane) were prepared:

- Isopropyl methylphosphonofluoridate (GB)
- Pinacolyl methylphosphonofluoridate (GD)
- O-Ethyl N,N-dimethylphosphoramidocyanidate (GA)
- Cyclohexyl methylphosphonofluoridate (GF)

Figure 2. Optical path of the GC-FTIR Accessory.

The instrumentation consisted of a gas chromatograph, a PIKE Technologies GC-FTIR interface module and an FTIR spectrometer.

The GC was equipped with a resistively heated low thermal mass DB-1 column (30 m x 0.25 µm). The carrier gas was helium, flowing at 1.4 mL/min. The column was temperature programmed from an initial temperature of 40 °C, held for 1.5 minutes, then increased by 80 °C/min to 275 °C and held for 2 minutes. Splitless injections (1 µL) were made with an injector temperature of 250 °C.

The PIKE GC-FTIR interface consisted of a 120 mm x 1.0 mm gold plated light pipe with a narrow band (4000 - 650 cm⁻¹) MCT detector (Figure 2). Light pipe and transfer lines were maintained at 200 °C.

Figure 3. Gram-Schmidt chromatogram
Results

Samples provided to a laboratory for analysis would typically contain more than a single analyte and require a separation step prior to acquiring the IR spectrum. Gas chromatography (GC) is the technique of choice for the separation of volatile organic compounds and in combination with IR, GC-FTIR offers a powerful identification technique for the identification of nerve agents.

Figure 3 illustrates a Gram-Schmidt chromatogram for a mixture of the CW agent nerve agents GB, GD, GA and GF. Typical GC analysis of this mixture would take approximately 27 minutes. Using a low thermal mass column installed in the GC, the separation of the four nerve agents was complete in under 5 minutes.

At 250 ng per component, library searchable (S/N >10:1) were acquired for each nerve agent. Samples collected at the scene of an incident will not contain analytes at the trace levels but rather will likely be present at the high nanograms to microgram levels.

All four nerve agents contain a P-O functional group that was observed \(\sim 1000 \text{ cm}^{-1}\). Figure 4 illustrates the vapor phase spectrum acquired for GB, the most volatile of nerve agents. The IR spectrum for GD, which contains a pinacol group, exhibits more intense bands in the CH stretch region \(\sim 3000 \text{ cm}^{-1}\) than observed for GB, which contains an isopropyl group. Figure 6 illustrates the IR spectrum for GA; this nerve
agent contains a distinct cyanide group near 2200 cm⁻¹. The most intense CH stretch was observed for GF, which possess a cyclohexyl alkyl group, as shown in Figure 7.

Conclusions

• GC-FTIR was shown to be a rapid technique that could be used for both the screening and identification of samples suspected of containing nerve agents.

• Library searchable spectra were acquired which provided both molecular and functional group information.