Trace Level Analysis of Chemical Warfare Agents (CWAs) Related Chemicals by GC-IR Solid Phase System

ABSTRACT

The DiscovIR-GC® solid phase GC-FTIR system provides 10 ng detection limits per component in the 16-component Organization for the Prohibition of Chemical Weapons (OPCW) test mixture,\(^1\) a significant improvement over the 250 ng detection limit of a gas phase light pipe! The high-resolution solid phase GC-IR spectra at trace level (5ppm) provides:

- unique information of organophosphorous functional groups and isomers for many CWA-related organophosphorous compounds
- compatibility with various IR database searches for component identification
- identification of trace-level unknowns of active CWAs along with their precursors, derivatives, degradation and hydrolysis products from complex environmental samples such as soil, water, decontaminated waste, etc.

INTRODUCTION

The trace-level analysis of CWAs and their main degradation products and precursors has received much attention in recent literature. This attention is triggered by repeated reports on the actual or alleged use of CWAs, either in military operations or terrorist attacks. In addition, the emission of CWAs into the environment due to spills or other accidents at CWA storage facilities also causes concerns. The analytical investigation of the possible use of CWAs on a battlefield or after a terrorist attack, monitoring the destruction of CWAs or the cleanup of CWA storage facilities all requires unambiguous identification of various CWA-related chemicals, often at trace levels in a complex environmental matrix. The OPCW demands that the identified compounds must be confirmed by at least two different analytical techniques, one of which must be spectrometric. The coupled technology of solid phase GC-FTIR has received increased attention as its detection limits (ng level) are approaching those routinely reported during GC-MS analysis. This is a significant improvement of IR detector sensitivity when compared with a gas phase light pipe IR detector which only has ~250 ng detection limits.\(^2\) This application note demonstrates the strong technical capability of the DiscovIR-GC to gain high quality IR spectra of individual components in the 16-component OPCW test mix at 5 ppm levels for identifying CWA-related chemicals, particularly organophosphorous functional groups and isomers through IR database matching.

EXPERIMENTAL

Sample

The OPCW test mix is a 16-component mixture which is routinely used to calibrate GC and GC-MS systems and QC tests in the OPCW lab in The Hague, Netherlands. It also is used as GC-based instrument performance check mixture by the CWC\(^3\) Member States’ laboratories in their routine analysis of CWA sample\(^4\) (ex. OPCW Proficiency Tests). The mixture consists of nine normal alkanes (C\(_8\) ~C\(_{24}\) with even carbon numbers) for Retention Index calibration and seven CWA-related compounds for MS isotopic fragments and column performance check up. The standard concentration of the OPCW test mixture is 10 ppm in CH\(_2\)Cl\(_2\) which was diluted to the 5 ppm with CH\(_2\)Cl\(_2\) for the GC-IR analysis.

Data Acquisition & Processing

The GC-IR data discussed in this application note were acquired by Ms. Pingfeng Liu in the OPCW lab in The Hague, Netherlands using their newly-installed DiscovIR-GC detector. The data were then processed by Spectra Analysis Instruments’ application team.
**GC Conditions**

GC System: Agilent 6890 GC with CTC Analytics COMBI PAL Autosampler  
Column: HP-5MS, 30 m x 0.25 mm I.D. x 0.25 μm film thickness  
Column Oven: 40°C (2 min.), 10°C/min. to 280°C (5 min.)  
Carrier Gas: Helium, constant flow at 0.9 ml/min.  
Injection Volume: 2.0 μL splitless time 1 min.  
Injector Temp.: 280°C  
Sample Conc. 5μg/mL (5 ppm) per component in CH₂Cl₂ of OPCW Test Mix with total of 16 components  
Run Time: 31 minutes

**FTIR Detection**

DiscovIR-GC Solid Phase FTIR Detector  
Transfer Line Temp.: 280°C  
Disk Temperature: -50°C  
Disk Speed: 3 mm/min.  
Chamber Vacuum: 2.2 X 10⁻⁴ torr  
IR Detector Resolution: 8 cm⁻¹

**RESULTS**

The figure below is the infrared chromatogram of the solutes deposited on the ZnSe sample collection disk. The DiscovIR-GC collected time-ordered IR spectra every 0.5 seconds through the whole chromatographic separation. As a default, the DiscovIR-GC creates a max band chromatogram using the highest intensity of all IR bands across the mid-IR range (4000-650 cm⁻¹) at each elution time, which is similar to the MS response. Using Data Workup software from the DiscovIR-GC system, we can easily screen through all the IR spectra snapshots at each peak noticing that all nine peaks labeled as C8-C24 in green have very simple and similar IR spectra. The other seven peaks labeled A-G in red have different IR spectra and need to be identified one by one using IR database searches.
The figure below is a screenshot of the DiscovIR-GC monitor displaying the max band chromatogram in the top panel. The middle panel shows the IR spectrum (red) of Peak A at the red marker while the bottom panel displays the IR spectrum (blue) of C10 at the blue marker. The blue IR spectrum is a simple one with only five IR bands and is assigned as one \((\text{C}_{10}\text{H}_{22})\) of nine normal alkanes. All nine peaks labeled as C8-C24 in green (figure on previous page) can now be assigned as \(\text{C}_n\text{H}_{2n+2}\) normal alkanes with a descending order of volatility from early to late GC elution times.

The following figure is an IR spectrum overlay of three alkanes \((\text{C}_{10}\text{H}_{22}, \text{C}_{16}\text{H}_{34}, \text{C}_{22}\text{H}_{46})\) at the three selected peaks C10, C16 and C22.
The IR spectrum (below) of Peak A at 8.74 minutes is shown in red and can be used to search against IR spectral libraries for its identification. All commercial transmission IR libraries, online IR search services and in-house IR databases can be used to identify various unknowns including CWA related chemicals. The DiscovIR-GC system uses the GRAMS software platform which comes with a Spectral ID function for IR spectral matching. The blue spectrum in the figure below is the best match from Spectra Analysis Instruments’ small in-house IR database, identifying Peak A as Phosphoric Acid Trimethyl Ester (Trimethylphosphate) with low Hit Quality Index (HQI) at 0.19. HQI is used to rate the library matching with a lower number indicating a closer match (0 indicating a perfect match).

Similarly in the following figure, Peak D is identified as Tri-n-butylphosphate by matching its IR spectrum (red) at 20.05 min. with the top match (blue) from the in-house IR database with low HQI at 0.09.
Similarly in the next figure, Peak F is identified as Malathion by matching its IR spectrum (red) at 23.98 min. with the top match (blue) from the in-house IR database with low HQI at 0.15.

By using Spectral ID matching with the in-house IR database, all 16 peaks can be readily identified as shown in the figure below.

**A**: Trimethylphosphate  
**B**: 2,6-Dimethylphenol  
**C**: 5-Chloro-2-methylaniline  
**C8-C24**: n-Alkanes w/ even carbon numbers  
**D**: Tri-n-butylphosphate  
**E**: Dibenzothiophene  
**F**: Malathion  
**G**: Methylstearate
The DiscovIR-GC software is designed to process GC-IR data in many different ways such as plotting selected band chromatograms, which can classify the unknown peaks in a mixture according to a selected functional group (e.g. phosphorous ester P-O-C) corresponding to its IR absorption. The following figure is a screenshot of the DiscovIR-GC monitor displaying the selected band chromatogram in the top panel based on 1040 cm\(^{-1}\) band for P-O-C functionality, indicating that only three components A, D and F out of the 16 components are organophosphorous ester compounds. The middle panel shows the snapshot IR spectrum (red) of Peak A at 8.74 min. corresponding to the red marker while the bottom panel displays the snapshot IR spectrum (blue) of Peak F at 23.98 min. corresponding to the blue marker.

As you can see from the figure on the following page, Component A has a P=O functional group that has a unique IR absorption at 1280 cm\(^{-1}\). With a simple click on this IR band followed by the data processing button "Band", a band chromatogram based on 1280 cm\(^{-1}\) can be easily displayed as in the top panel. The middle panel shows the IR spectrum (red) of Peak A at 8.74 min. corresponding to the red marker while the bottom panel displays the snapshot IR spectrum (blue) of Peak D at 20.06 min. corresponding to the blue marker. The top panel clearly indicates that only two components A and D out of the 16-component mixture contain a P=O functional group. Component F is not included in this classification because it only has a P=S functional group instead of a P=O as in the Components A and D. This demonstrates the strong technical capability of the DiscovIR-GC to differentiate organophosphorous functional groups in a complex mixture at trace levels (10 ng). Detector sensitivity is also significantly better when compared to a gas phase light pipe IR detector which only has a 250 ng detection limit.\(^2\) The DiscovIR-GC has some room to further improve the sensitivity to \(~0.5\) ng if a multiple layer deposition technique is used with the repeated GC injections.
The GC-IR analysis of the 16-component OPCW test mix at trace levels (5 ppm) gave high quality IR spectra of each component which are database searchable to identify a broad range of CWA-related chemicals:

- nine normal alkanes C8-C24 (all with even carbon numbers)
- three organophosphorous compounds with different functional groups
  - A (Trimethylphosphate) and D (Tri-n-butylphosphate), both with P=O functionality
  - F (Malathion) with P=S functionality (not P=O)
- three aromatic compounds B (2,6-Dimethylphenol), C (5-Cholor-2-methylaniline) and E (Dibenzothiophene)
- one ester G (Methylestearate)

These high-resolution IR spectra provide unique information of organophosphorous functional groups and isomers for many CWA-related chemicals, and are IR database searchable with both large commercial IR libraries and in-house IR databases for component identification. The low detection limit of 10 ng per component with the DiscovIR-GC is a significant improvement of IR detector sensitivity compared with a gas phase light pipe IR detector at 250-500 ng detection limits.

The solid phase GC-IR is a powerful method that is used in the identification of trace-level unknowns of active CWAs, their precursors, by-products, and derivatives, and any degradants or hydrolysis products that might be in environmental samples containing a complex matrix such as soil, water, decontaminated waste, etc.

CONCLUSIONS

ACKNOWLEDGEMENT

Many thanks to Ms. Pingfeng Liu at the OPCW lab in The Hague, Netherlands for sharing the data acquired from their DiscovIR-GC unit using its OPCW test mix.

REFERENCES

[1] Standard concentration of the OPCW Test mixture is 10ppm in CH2Cl2.