FT-IR Analysis of Chemical Warfare Agents*

Ernest H. Braue, Jr. 1,** and Michael G. Pannella 2

1 Department of Chemistry, The Pennsylvania State University, Mont Alto, PA 17237, USA
2 US Army Medical Research Institute of Chemical Defense, Building E-3100, Aberdeen Proving Ground, MD 21010-5425, USA

Abstract. The qualitative and quantitative FT-IR analyses of dilute aqueous solutions of GA (tabun), GB (sarin), GD (soman), and VX were evaluated using the CIRCLE CELL TM. Infrared spectra were recorded using a Nicolet 60SX FT-IR spectrometer fitted with a liquid nitrogen-cooled MCTA detector. The CIRCLE CELL TM used a high pressure micro-flow-through sampling accessory fitted with a ZnSe internal reflection element. Peak heights were evaluated with the Nicolet SUPER QUANT program after spectral subtraction of the solvent. The $P=0$ stretching absorption band, centered around 1240 cm $^{-1}$ for the G-type agents and 1180 cm $^{-1}$ for VX, produced good quantification. At a concentration of 2.0 mg/ml for the G-type agents and 1.0 mg/ml for VX, quantitative analysis produced coefficients of variation of 3 % or less. The detection limit was observed to be around 0.1 mg/ml.

Key words: infrared spectroscopy, CIRCLE CELL TM, chemical warfare agents.

The CIRCLE CELL TM, manufactured by Spectra-Tech, Inc. [1] is a version of the cylindrical internal reflection (CIR) technique developed by Wilks [2, 3]. This cell has become a popular FT-IR accessory because it

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** To whom correspondence should be addressed
facilitates the collection of IR spectra from aqueous solutions. In previous work from this laboratory, we described a detailed study on the quality of quantification possible in aqueous solutions with the use of the CIRCLE CELL™ [4, 5]. We now report the qualitative and quantitative analysis of dilute solutions of the chemical warfare agents tabun (GA), sarin (GB), soman (GD), and VX.

Due to the toxic nature of many of the compounds of interest used in our laboratory, we designed, with the help of Spectra-Tech, Inc. [1], two specially sealed accessories useful for recording the IR spectrum of these chemicals. The first is a sealed CIRCLE CELL™ used for liquids and the second is a sealed chamber large enough to accommodate most of the typical FT-IR sampling accessories.

Experimental Methods

1. A Nicolet 60SX FT-IR spectrometer utilizing an MCT-A detector was used to record all spectra. Instrumental parameters were optimized to give the best results. Spectra recorded were the result of 200 co-added interferograms at 4.0 cm⁻¹ resolution. Happ-Genzel apodization was used in the subsequent Fourier transform.

2. The CIRCLE CELL™ used the high-pressure, flow-through, micro-boat sampling accessory fitted with a ZnSe internal reflection element. The inlet and outlet tubes were terminated with a LUER-LOK fitting outside the sampling compartment. The temperature inside the sampling accessory was maintained at 10°C by using a circulating water bath. A 1-ml gas-tight Hamilton syringe was filled with 350 μl of sample in an approved fume hood. The liquid sample was transported to the FT-IR in a sealed container and injected into the CIRCLE CELL™ through the LUER-LOK fitting. Using this sampling technique the position of the CIRCLE CELL™ remained fixed and the purge to the instrument remained uninterrupted.

3. Saline solutions of chemical warfare agents, in the concentration range 0.1 to 2.0 mg/ml, were prepared from neat chemicals by standard laboratory techniques. Solutions of the hydrolyzed agents were obtained by letting the 2.0 mg/ml agent solutions stand at room temperature for several days. Semi-automated spectrum recorded and data analysis was accomplished with the help of written macro programs. At the beginning of each day a background spectrum of the empty CIRCLE CELL™ was recorded. A saline spectrum followed by five sample spectra were recorded at each concentration for each agent. After recording the saline spectrum and between recording each of the five agent samples, the CIRCLE CELL™ was flushed with a flow of nitrogen. This was necessary to avoid air bubbles being trapped inside the CIRCLE CELL™ during filling. The pure agent spectra were obtained after spectral subtraction of the saline spectrum. Quantification was accomplished using the Nicolet SUPER QUANT software package by calculating the maximum peak height for the isolated P=0 stretching absorbance band (1240 cm⁻¹ for G-type agents and 1180 cm⁻¹ for VX).