EDGEWOOD

CHEMICAL BIOLOGICAL CENTER

U.S. ARMY RESEARCH, DEVELOPMENT AND ENGINEERING COMMAND

ECBC-TR-732

VAPOR-PHASE ABSORPTIVITY COEFFICIENT OF ETHYL N,N-DIMETHYLPHOSPHORAMIDOCYANIDATE

Barry R. Williams
Melissa S. Hulet

SCIENCE APPLICATIONS
INTERNATIONAL CORPORATION
Gunpowder, MD 21010-0068

Alan C. Samuels
Ronald W. Miles, Jr.

RESEARCH AND TECHNOLOGY DIRECTORATE

January 2010

Approved for public release;
distribution is unlimited.

20100204378

ABERDEEN PROVING GROUND, MD 21010-5424

REPORT DOCUMENTATION PAGE	*Form Approved* *OMB No. 0704-0188*

1. REPORT DATE *(DD-MM-YYYY)* XX-01-2010	**2. REPORT TYPE** Final	**3. DATES COVERED** *(From - To)* Aug 2005 - Sep 2005

4. TITLE AND SUBTITLE Vapor-Phase Absorptivity Coefficient of Ethyl N,N-dimethylphosphoramidocyanidate	**5a. CONTRACT NUMBER**
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S) Williams, Barry R.; Hulet, Melissa S. (SAIC); Samuels, Alan C.; and Miles, Ronald W., Jr. (ECBC)	**5d. PROJECT NUMBER** None
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) SAIC, P.O. Box 68, Gunpowder, MD 21010-0068 DIR, ECBC, ATTN: RDCB-DRD-P, APG, MD 21010-5424	**8. PERFORMING ORGANIZATION REPORT NUMBER** ECBC-TR-732
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Defense Threat Reduction Agency, Joint Science and Technology Office for Chemical and Biological Defense, 8725 John J. Kingman Road, Fort Belvoir, VA 22060-6201	**10. SPONSOR/MONITOR'S ACRONYM(S)** DTRA JSTO-CBD
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT-LIMIT 200 WORDS

We measured the vapor-phase absorptivity coefficient of the chemical warfare agent ethyl N,N-dimethylphosphoramidocyanidate (GA) in the mid-infrared (4000-550 cm^{-1}) at a spectral resolution of 0.125 cm^{-1}. The GA used in the feedstock was purified by fractional distillation and analyzed by nuclear magnetic resonance and gas chromatography/mass spectrometry to verify its purity. We describe the experimental method used to acquire the individual spectra that were used to produce the composite spectrum, summarize the statistical uncertainties in the data, and provide a comparison to similar data from another laboratory.

15. SUBJECT TERMS

Infared	Absorptivity coefficient	Quantitative	O-ethyl-N,N-dimethylphosphoramidocyanidate
FTIR	Saturator cell	GA	Vapor-phase
Tabun			

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON** Sandra J. Johnson
a. REPORT U	**b. ABSTRACT** U	**c. THIS PAGE** U	UL	22	**19b. TELEPHONE NUMBER** *(include area code)* (410) 436-2914

Blank

EXECUTIVE SUMMARY

We measured the vapor-phase absorptivity coefficient of ethyl N,N-dimethylphosphoramidocyanidate (GA, Tabun) in the mid-infared. We used agent filled saturator cells suspended in a temperature controlled liquid bath to generate continuous streams of the compound diluted in nitrogen. These were sent to a variable path White cell and measured using a high resolution research grade Fourier transform infrared spectrometer. The purity of the feedstock was verified by nuclear magnetic resonance (NMR) spectroscopy and gas chromatography/mass spectrometry. The mass of GA in the vapor was determined with a gravimetric method, and the ratio was verified with thermal desorption gas chromatography. Thirteen spectra at different concentration-pathlength products were processed line by line through least squares analysis using MatLab to produce the absorptivity coefficient of the compound and the statistical uncertainty in the data. Uncertainties in the data, expanded to a confidence interval of 2σ (*P*=0.95), are Type-A: 2.4% of the absorptivity coefficient [4.3% of the absorptivity coefficient at intensities $\geq 1.2 \times 10^{-4}$ $(\mu mol/mol)^{-1}m^{-1}$] and Type-B: 4.8% of the absorptivity coefficient. We report a comparison of our data to that obtained by another laboratory using a different vapor generation method.

Blank

PREFACE

The work described in this report was authorized under the direction of the Detection Capability Officer, Defense Threat Reduction Agency Joint Science and Technology Office. This work was started in August 2005 and completed in September 2005.

The use of either trade or manufacturers' names in this report does not constitute an official endorsement of any commercial products. This report may not be cited for purposes of advertisement.

This report has been approved for public release. Registered users should request additional copies from the Defense Technical Information Center; unregistered users should direct such requests to the National Technical Information Service.

Acknowledgments

We thank Dr. David McGarvey (Chemical Sciences Division) and Dr. William Creasy (SAIC) for their analysis of GA by nuclear magnetic resonance spectroscopy and high resolution mass spectrometry.

Blank

CONTENTS

1. INTRODUCTION 9

2. EXPERIMENTAL METHODS 9

2.1 Instrumental Details 9
2.2 Feedstock 10

3. RESULTS AND DISCUSSION 12

4. INTERLABORATORY COMPARISON 18

5. CONCLUSIONS 19

LITERATURE CITED 21

FIGURES

1. Structure of GA 9

2. Vapor-Phase Spectra of Effluent from GA Experiments (Green) and Triethyl Phosphate (Red) 11

3. Beer's Law Plot of 1043.6 cm^{-1} Line in Spectra of GA 13

4. Beer's Law Plot of 1328.9 cm^{-1} Line in Spectra of GA 13

5. Absorptivity Coefficient and Statistical Uncertainty (Type-A, 2σ) for GA 14

6. Absorption Coefficient (Abscissa) and Type-A Uncertainty (Fractional, 2σ) for GA 15

7. Absorptivity Coefficient Spectra from ECBC (Red), PNNL (Olive), and Barrett & Dismukes (Aqua) 16

8. Absorption Coefficient (Abscissa) and Type A Uncertainty (Fractional, $2\ \sigma$) for GA 16

TABLES

1. Absorptivity Coefficient of GA for Selected Bands 15

2. Type-A Statistical Uncertainty for GA Vapor-Phase Absorptivity Coefficient ... 17

3. Uncertainties in Absorptivity Coefficient of GA-Tabun from ECBC Data where $\alpha \geq 0.00012\ (\mu mol/mol)^{-1}m^{-1}$ 17

4. Comparison of Integrated Absorption Coefficients of GA in Spectra from ECBC and PNNL/Dugway 18

VAPOR-PHASE ABSORPTIVITY COEFFICIENT OF ETHYL N,N-DIMETHYLPHOSPHORAMIDOCYANIDATE

1. INTRODUCTION

We determined the high resolution vapor-phase absorptivity coefficients of the nerve agent, ethyl N,N-dimethylphosphoramidocyanidate (GA, Tabun) in the spectral range of 4000 to 550 cm^{-1} in units of $(\mu mol/mol)^{-1}m^{-1}$ and computed the uncertainties in the data. Previous efforts at the U.S. Army Edgewood Chemical Biological Center (ECBC) to obtain the absorptivity coefficients of this compound dated back to the 1960's and were performed at lower resolution on a grating spectrometer.[1]

The compound has the Chemical Abstracts Service (CAS) Registry Number 77-81-6 and is indexed under the name: phosphoramidocyanidic acid, dimethyl-, ethyl ester. The molecular formula is $C_5H_{11}N_2O_2P$, and it has a formula weight of 162.13. Other synonyms for the compound include dimethylaminoethoxy-cyanophosphine oxide; dimethylamidoethoxyphosphoryl cyanide; ethyldimethylaminocyanophosphonate; dimethylphosphoramidocyanidic acid, ethyl ester; ethyl phosphorodimethylamidocyanidate, EA 1205; and Tabun. The structure is shown in Figure 1.

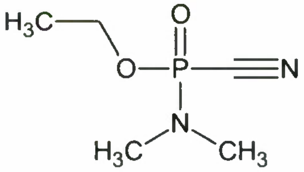

Figure 1. Structure of Ethyl Dimethylphosphoramidocyanidate (GA)

Ethyl dimethylphosphoramidocyanidate (GA) is a nerve agent that was first synthesized in Germany in 1938. The vapor pressure of the compound is 0.057 Torr at 25 °C, and the calculated boiling temperature is 247.5 °C.[2]

2. EXPERIMENTAL METHODS

2.1 Instrumental Details.

The system used to generate the continuous vapor stream was an adaptation of the saturator cell method developed at ECBC for measuring the volatility of chemical warfare agent (CWA) related compounds.[3]

The method, modified to generate continuous streams of chemical compounds for obtaining quantitative vapor-phase infrared (IR) spectra, has been used to measure the absorptivity coefficients of benzene[4], as well as a variety of CWA related compounds.[5,6,7,8] References 4 and 5 describe the experimental setup, as well as the data collection and post-processing in more detail. The saturator passes a stream of nitrogen carrier gas, obtained from the boiloff of a bulk liquid nitrogen tank, across a cylindrical alumina wicking mechanism closed at one end in a glass holder filled with the analyte. The result is a saturated vapor-liquid equilibrium of the analyte on the downstream side of the saturator cell, with the concentration of the analyte determined by the temperature of the liquid phase. By suspending the saturator cell in a constant temperature bath, the concentration of the analyte can be predicted by its vapor pressure at the temperature of the bath. The apparatus used in the Quantitative Fourier transform infrared spectrometer (FTIR) Laboratory uses a Brooks Model 5850S mass flow controllers (Brooks Instrument Co., Hatfield, PA) to maintain a constant flow to the saturator cell, along with a second mass flow controller to add diluent to the stream, providing an additional means of adjusting the concentration of the compound delivered to the White cell of the FTIR. Linearity of the S series mass flow controllers is adjusted using a second order polynomial, resulting in uncertainties of approximately 1 % or better of rate at flows ≥25 % of full scale.

Spectra were obtained with a Bruker Model IFS/66V FTIR (Bruker Optics, Billerica, MA). The instrument is equipped with deuterated triglycine sulfide and mercury-cadmium-telluride (HgCdTe) detectors and is capable of obtaining spectra with a maximum spectral resolution of 0.1125 cm^{-1} (unapodized). The interferograms were recorded from 15798-0 cm^{-1} with a resolution of 0.125 cm^{-1}. Absorbance (log base-10) spectra were processed with boxcar apodization and 2X zero filled to obtain a data spacing of 0.0625 cm^{-1}. The instrument is equipped with a variable path White cell. The experimental data used path lengths of 2.727 to 10.66 m. The temperature of the White cell was maintained at 23±0.1 °C through the use of a thermostatically controlled chamber enclosing the spectrometer and cell. Data were acquired at a speed of 60 KHz (HeNe laser zero crossing frequency) using the HgCdTe detector. Single beam spectra of the CWA were ratioed against spectra of clean, dry nitrogen. To minimize the effects of nonlinearity in the detector, the interferograms were processed using the proprietary Opus nonlinearity correction function. All interferograms were archived enabling further post-processing of data.

Temperature and pressure data were recorded using National Institute of Standards and Technology (NIST) traceable digital manometers and thermometers, and all data were archived. Concentration-pathlength products (CL) were computed in units of [μmol/mol (m) (ppm-m)]. A differential pressure manometer had previously been used to measure the dynamic pressure in the White cell with gas flowing into the cell, and the ambient pressure was plotted versus the differential pressure. The resulting equation was used to correct the readings from the ambient pressure manometer to the pressure in the White cell. The concentration-pathlength data were corrected to 296 K and 1.01325×10^5 Pa (760 Torr) using the ideal gas law.

2.2 Feedstock.

The feedstock used in the experiments was obtained through the CASARM program under lot number GA-U-2101-CTF0N at a stated purity of 97.7% [obtained by gas chromotogrpahy-thermal conductivity detector (GC-TCD) only]. Analysis by of the neat material diluted in solvent by gas chromotography-mass spectrometry (GC-MS) indicated 3.4% triethyl phosphate (TEPO), as well <1% each of O-ethyl-N,N-dimethyl phosphoramidofluoridate, O,O'-diethyl-N,N-dimethyl phosphoramidate, and diethyl methylphosphonate as impurities. The feedstock was analyzed by ^{31}P NMR using independent techniques: an internal standard and diluted in deuterated chloroform giving a mean mole purity of 94.2%, with 1.3% triethyl phosphate, and several additional phosphorous compounds at <1 mol %. Samples of the vapor stream were collected with sorbent tubes for analysis by gas chromatography (GC). A GC with a flame ionization detector (GC-FID) coupled directly to the effluent of the White cell yielded a purity of 94.3%. A sorbent tube analyzed off-line by GC-MS confirmed the presence of several of the impurities observed in the liquid sample; O,O'diethyl N,N-dimethyl phosphoramidate was not seen. Although the spectrum of triethyl phosphate is similar to that of GA, comparison with a quantitative vapor-phase spectrum of the compound with the spectrum of the GA showed that the TEPO has a band of medium intensity at 920 cm^{-1} that is not present in the GA. By overlaying the vapor-phase spectrum of the TEPO with that of the GA, it was possible to show that the TEPO probably contributes little to the composite spectrum (Figure 2). No vapor-phase spectra of the other impurities were available.

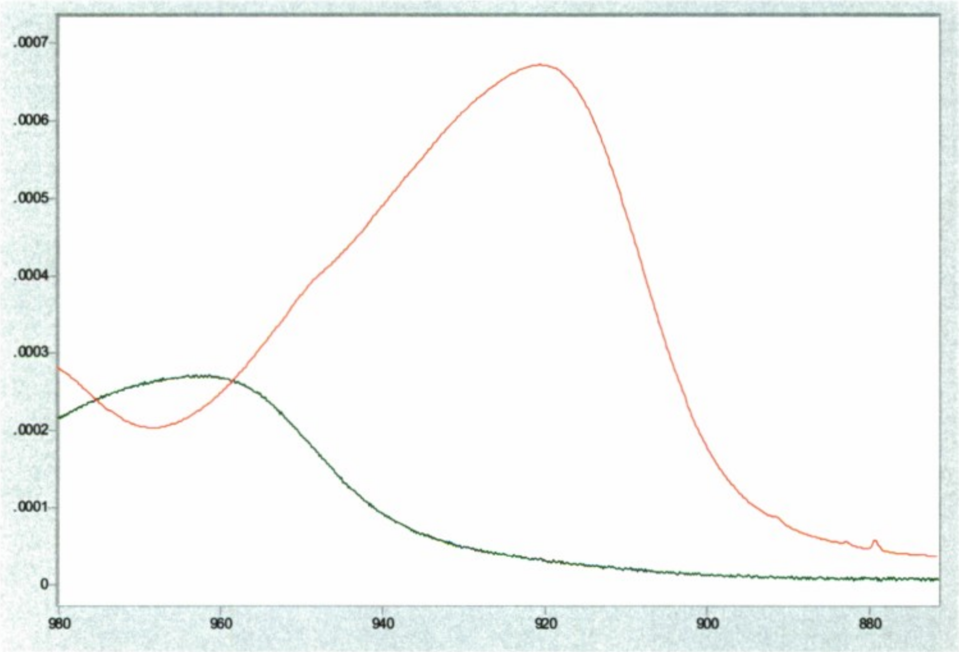

Figure 2. Vapor-Phase Spectra of Effluent from GA Experiments (Green) and Triethyl Phosphate (Red). Although present in the feedstock, triethyl phosphate was not Observed in the spectra.

A possible explanation for the failure to observe triethyl phosphate in the vapor from the GA may lie in the difference in their respective vapor pressures. The vapor pressure of triethyl phosphate is 0.106 Torr at 25 °C*, significantly higher than that of GA at that temperature (0.057 Torr). There would be a tendency, therefore, for the compound to purge from the GA over time.

---

*Brozena, A. *Vapor Pressure of Triethyl Phosphate (TEPO)*, U.S. Army Armament Research & Development Command: Picatinny Arsenal, NJ, unpublished data, January 2010.

3. RESULTS AND DISCUSSION

Six trials were run to obtain spectra at thirteen concentration-pathlength products. A trial is defined as filling and weighing the saturator cell, suspending it in the bath, applying a stream of nitrogen for a measured time, acquiring several spectra, stopping the nitrogen and removing it from the bath, and reweighing the saturator cell after drying the exterior surfaces and re-equilibrating to room temperature. The constant temperature bath was maintained at 24.0 °C for all experiments.

One month elapsed between the first three trials and the final three, during which time, the saturator cells were kept at room temperature in a locked fume hood. After restarting analyses on 19 September, the initial spectra that were acquired showed features of a possible impurity. By subtracting out a ratioed spectrum of GA acquired during the earlier set of analyses, the spectrum of the impurity was recovered and identified as hydrogen cyanide (HCN). It is likely that the compound arose as a hydrolysis product from reaction of the GA with trace water. The impurity apparently purged from the cells within a few hours. However, with the spectral features no longer visible in the spectra, the mass loss arising from the HCN contributed to anomalous concentration-pathlength calculations of the spectra acquired that day, including those in which the hydrogen cyanide could no longer be seen. The data from that day were, therefore, not included in the composite absorptivity calculations for the GA. Because the phosphorous byproduct of the hydrolysis of GA, O-ethyl N,N-dimethyl phosphoramidic acid, is not volatile by the saturator cell method and does not contribute to the mass loss or the spectra, the presence of the impurity in the feedstock could be ignored.

As an initial check of the quality of the data, Beer's Law plots of two spectral lines, 1043.6 and 1328.9 cm^{-1}, were calculated using MatLab. Calculations for these two spectral lines showed that the data appeared to be well fitted. There were no points lying outside of the 95% confidence limits for either a repeated single CL or the 95% confidence limits for a Grubbs Test for Outliers (Figures 3 and 4).

Trace water vapor was observed in several spectra. The concentration, which decreased over time, was computed using the absorptivity coefficients and the features of the water vapor were removed by spectral subtraction. Baseline corrections of the spectra were performed with a linear subtraction. The baseline correction in no case exceeded 0.001 A [A=-$\log_{10}(T)$].

Water vapor and hydrogen chloride were observed in several spectra. The concentrations of the compounds in the vapor, which decreased over time, were computed using their absorptivity coefficients, and the features of the impurities were removed by spectral subtraction. Baseline corrections of the spectra were performed with a two point linear subtraction using a MatLab algorithm written in-house. The baseline correction in no case exceeded 0.001 A [A=-$\log_{10}(T)$].

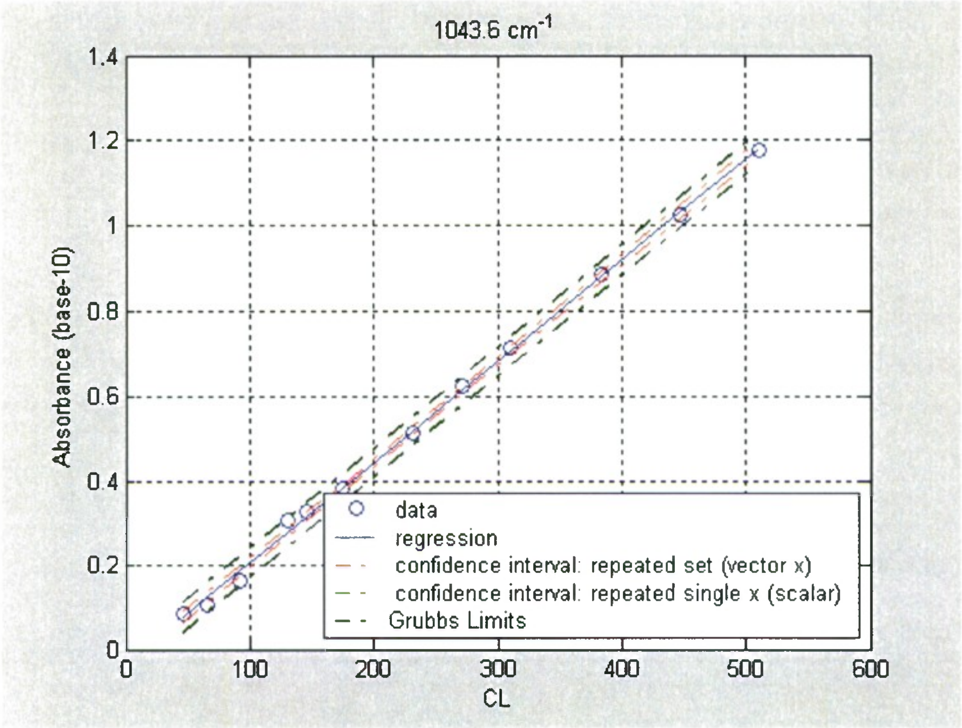

Figure 3. Beer's Law Plot of 1043.6 cm^{-1} Line in Spectra of GA.

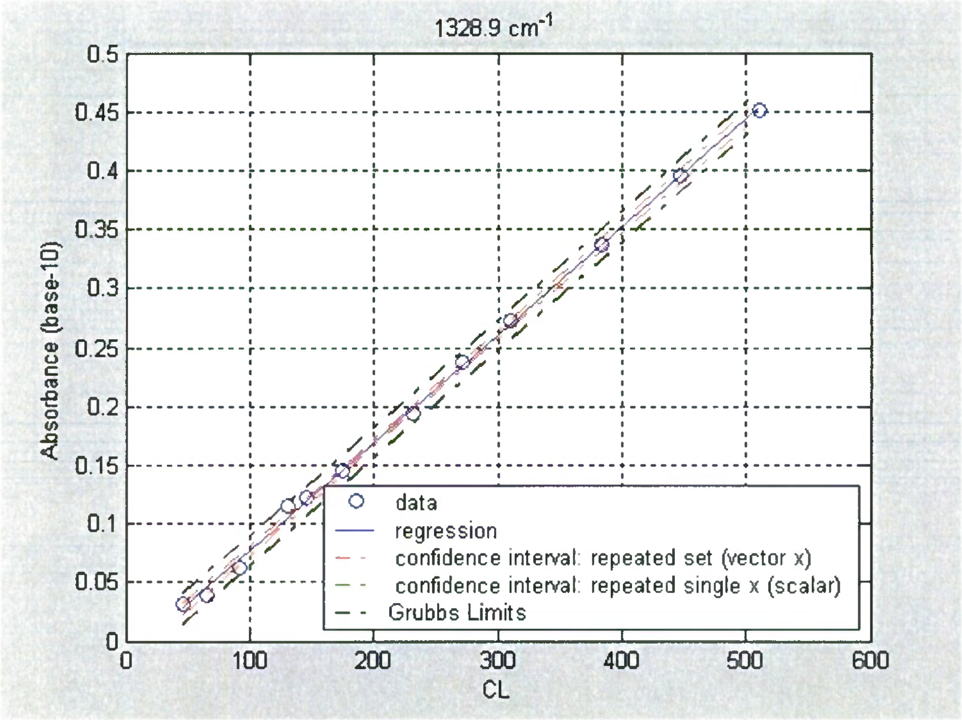

Figure 4. Beer's Law Plot of 1328.9 cm^{-1} Line in Spectra of GA.

The composite spectrum (absorptivity coefficient) and statistical uncertainty (Type-A, 2 σ) were computed within MatLab using spectra with concentration-path length products ranging 46 to 272 μmol/mol(m) (corrected to 296 K and 101325 Pa). The absorptivity coefficient (α) and uncertainty (Type-A, 2σ) were computed line by line within the spectral range of 4000-550 cm^{-1} using a MatLab program written in-house. Values of (A=-log$T$) >1.5 are normally assigned a weight of zero. Because all values recorded were for A≤1.185, all data were weighted at 1. Figure 4 is the plotted absorptivity coefficient (α) and Type-A uncertainty for the computed spectral range. The figures are plotted with α in $(\mu mol/mol)^{-1}m^{-1}$. To obtain α in $(mg/m^2)^{-1}$, multiply the values in the ordinate scale of Figure 5 by 0.14895. This factor is derived from eq 1 using the molecular weight of Lewisite (162.13).

$$\frac{m^2}{mg}\left(\frac{24.15}{mw}\right)=\frac{mol}{\mu mol(m)} \qquad (1)$$

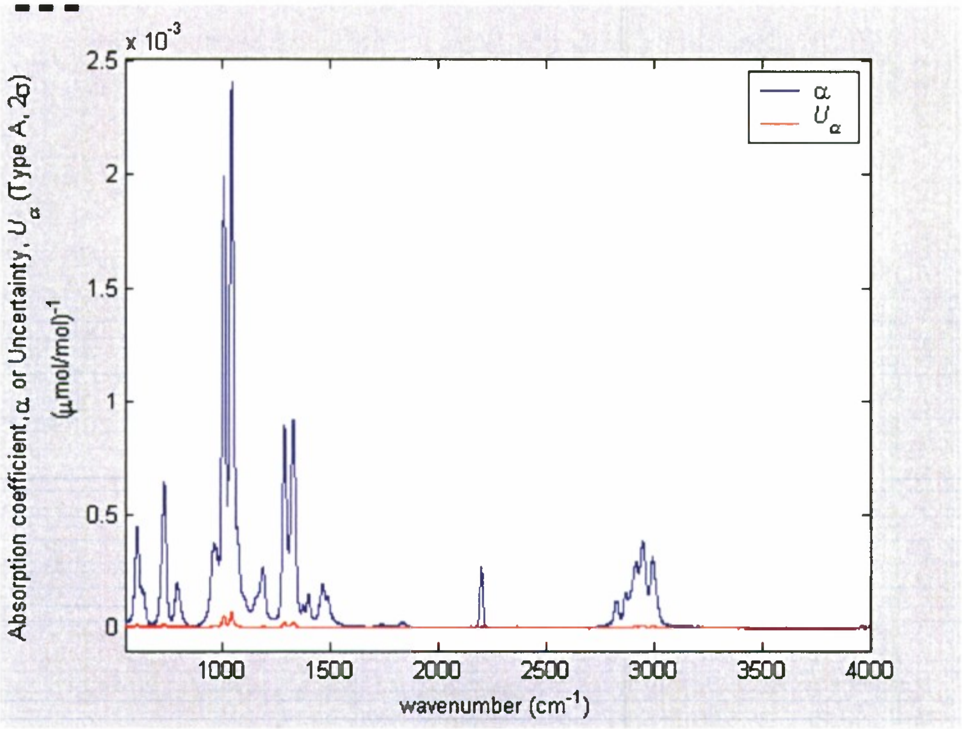

Figure 5. Absorptivity Coefficient and Statistical Uncertainty (Type-A, 2σ) for GA.

Table 1 provides the absorptivity coefficients in $(\mu mol/mol)^{-1}m^{-1}$ and $(mg/m^2)^{-1}$ for selected bands in units of wave number and micrometers (μm).

Table 1. Absorptivity Coefficient of GA for Selected Bands

Wave number, cm^{-1} (Wavelength, μm)	Absorptivity coefficient, $(\mu mol/mol)^{-1}m^{-1}$ $[(m^2/mg)^{-1}]$
1007.0 (9.93)	1.98×10^{-3} (2.95×10^{-4})
1043.8 (9.58)	2.39×10^{-3} (3.56×10^{-4})
1328.8 (7.53)	9.155×10^{-4} (1.36×10^{-4})

In general expanded Type-A uncertainties were 2 to 3% of the absorptivity coefficient, as seen in Figures 6 and 7. Figure 7 is a plot of absorptivity coefficients (abscissa) and fractional uncertainty (Type-A, $U_{A,}$ 2σ) (mantissa). Figure 7 is a plot of the absorptivity coefficient and uncertainty. Figure 7 also includes a best fit of the data points obtained by least squares, which is an approximation of $U_A.\approx ax+b$. For the fitted line in Figure 8 the coefficients are a= 2.32×10^{-2} and b=2.38×10^{-6} (Table 2).

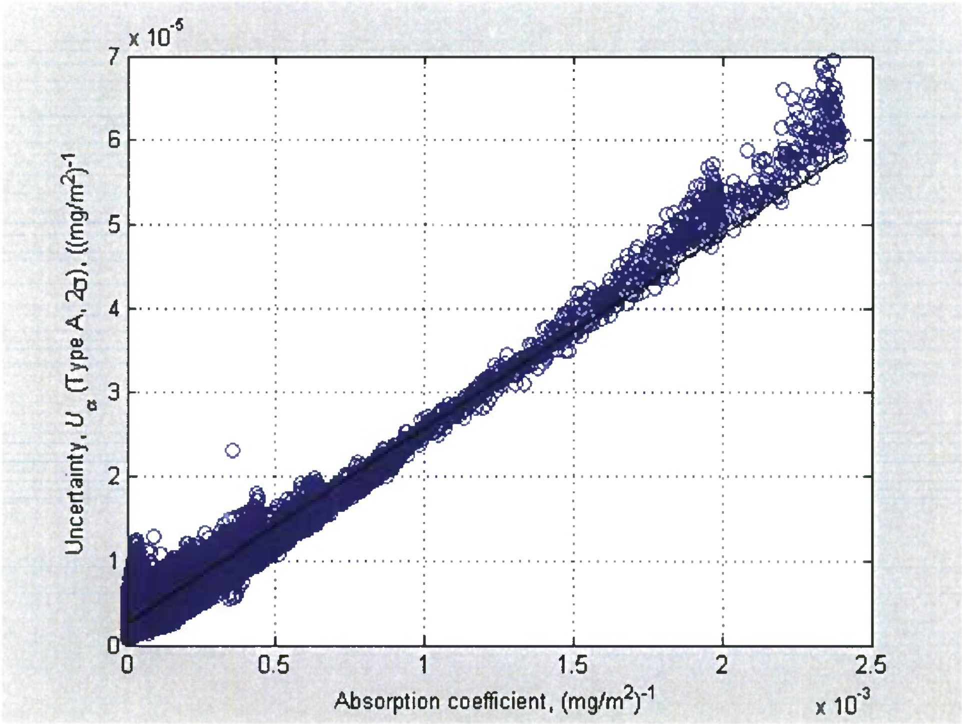

Figure 6. Absorption Coefficient (Abscissa) and Type A Uncertainty (Fractional, 2σ) for GA. The line indicates the "best fit" obtained by least squares.

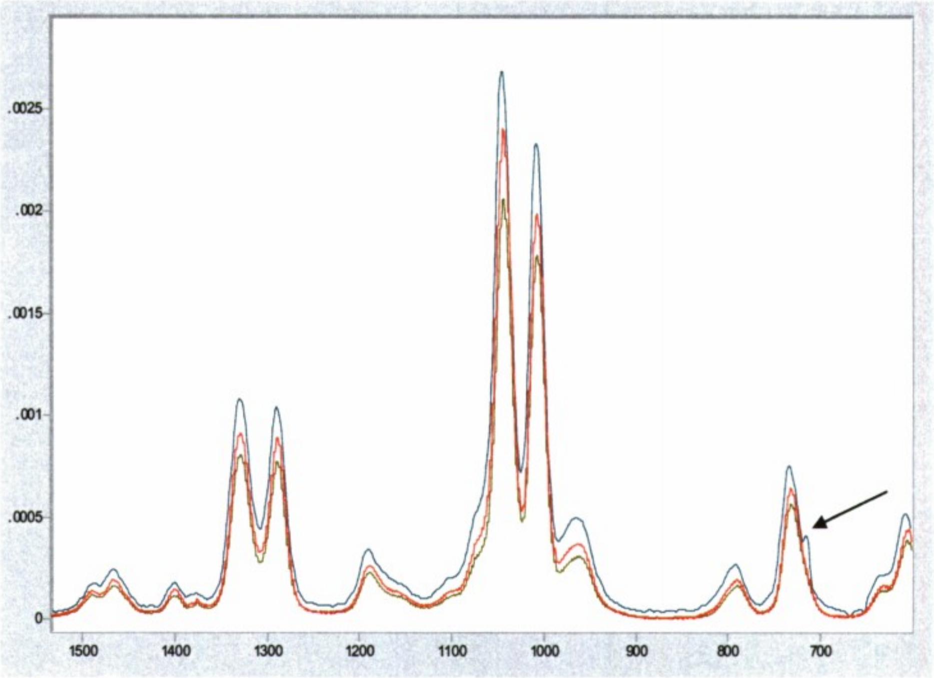

Figure 7. Absorptivity Coefficient Spectra from ECBC (Red), PNNL (Olive), and Barrett & Dismukes (Aqua). The arrow indicates the presence of a possible impurity in the spectrum from Barrett and Dismukes.

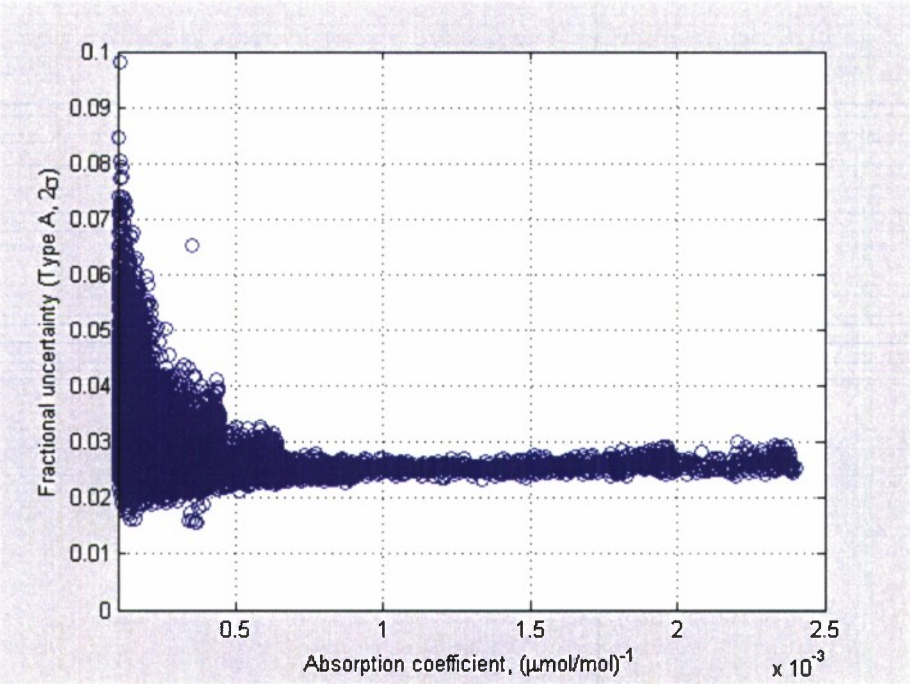

Figure 8. Absorption Coefficient (Abscissa) and Type-A Uncertainty (Fractional, 2σ) for GA.

Table 2. Type-A Statistical Uncertainty for GA Vapor-Phase Absorptivity Coefficient

Type-A Uncertainty $2\sigma \approx ma+b$	
Slope m	Intercept b
2.32×10^{-2}	2.38×10^{-6}

Type-B estimated standard errors, along with their sources, as well as the combined Type-A and B uncertainties, are provided in Table 3. The expanded combined Type-B uncertainty was computed using eq 2:

$$\Delta_B=(\Delta L^2+\Delta T^2+\Delta P^2+\Delta FTIR^2+\Delta NL^2+\Delta MR^2)^{1/2} \times 2 \qquad (2)$$

The sources of uncertainty and their fractional values, as well as an explanation of the symbols in Equation 1, are given in Table 4. The Type-A uncertainty of 4.3% (2σ), indicated in Table 3, is valid for values of the absorptivity coefficient ≥ 0.00012 $(\mu mol/mol)^{-1}m^{-1}$ ($\alpha \geq 5$ % of the peak of maximum intensity). For the most intense features, the Type-A uncertainty averages 2.4% of the absorptivity coefficient. Among the Type B uncertainties, the dilute rate and vapor purity dominate at 0.015 (1σ).

Table 3. Uncertainties in Absorptivity Coefficient of GA-Tabun from ECBC Data where $\alpha \geq 0.00012$ $(\mu mol/mol)^{-1}m^{-1}$

Symbol	Fractional deviation	Source
ΔL	0.005	Pathlength
ΔT	0.0006	Temperature of White cell
ΔP	0.002	Pressure
$\Delta FTIR$	0.0005	Drift in spectrometer
ΔNL	0.01	Nonlinearity in detector
ΔMR	0.002	Mass rate
ΔD	0.015	Dilution rate
$\Delta purity$	0.015	Purity of vapor
Δ_B	0.048	Combined type B (2σ)
Δ_A	0.043	Type-A deviation (2σ)

Table 4. Comparison of Integrated Absorption Coefficients of GA in Spectra from ECBC and PNNL/Dugway

Spectral Region (cm^{-1})	Integrated Areas PNNL	 ECBC	Deviation (PNNL-ECBC)/ ECBC X 100
3116-2699	0.03597	0.0408	-0.118
1661-550	0.2067	0.2376	-0.130
3200-550	0.2530	0.2907	-0.130
1130-884	0.1003	0.1160	-0.135
1661-856*	0.1064	0.1216	-0.125

*Excluding 1007 cm^{-1} region

4. INTERLABORATORY COMPARISON

Comparison of data between laboratories, especially when obtained using different methods, can be useful in assessing the experimental methods and for validating the accuracy of the data. One other source for the high resolution absorptivity coefficient of GA for comparison to the data acquired at ECBC is that obtained by Pacific Northwest National Laboratory (PNNL) (Dugway Proving Ground, UT).[9] The PNNL database includes a detailed discussion of experimental methods and statistical processing. Each absorptivity coefficient spectrum is provided with a metadata file listing physical data for the compound, temperature and pressure range, number of individual spectra included in the fit of the absorptivity coefficient, and uncertainties: Type-A (4.5%) and Type-B (≤10%) for GA. The original quantitative vapor-phase IR database from Barrett and Dismukes provided an additional source of data for comparison.[10] Statistical uncertainties were computed for each compound in the data set. Compounds measured in the vapor-phase used a continuous flow system comprised of a bubbler system with nitrogen as a carrier gas. The vapor concentration was measured using a bubbler system with gas chromatography. A reference temperature and pressure for the data were not provided. For purposes of the comparison in this report, we assumed that the White cell used to acquire the data was maintained at room temperature, ~23 °C, and the sample pressures were normalized to 101325 Pa.

Our spectrum is shown overlaid with the spectra from PNNL/Dugway and Barrett and Dismukes in Figure 7. Table 4 contains comparisons of the integrated areas of several spectral regions in our spectrum vis-à-vis the PNNL/Dugway data. The mean Δ in the major areas of the fingerprint and C-H stretch regions is about 12.8%. This likely arises, at least in part, from variations in the optical pathlengths of the White cells used to compute the concentration-pathlength products of the samples. The model and manufacturer of White cell is the same for both laboratories. The pathlengths of the cell used in the PNNL/Dugway experiments was determined by disassembling and measuring the physical distances between mirrors. The GA data used a pathlength stated to be 5.60 m. We measured the pathlengths of our cell using laser time-of-flight, establishing a pathlength of 5.377 m at the same micrometer setting. This results in a Δ of $(5.6-5.377)/5.377 \times 100 = 4.1\%$. When used to compute the concentration-pathlength products of the individual samples, the longer pathlength in the cell used by PNNL/Dugway has the effect of increasing each concentration-pathlength product by 4.1%. Absorptivity coefficient is computed as $\alpha = A/CL$, where L is pathlength, the computed value of α varies in inverse proportion to the optical pathlength. An increase in pathlength without a proportional change in either absorbance or concentration results in a linear decrease in the computed value of α.

An additional explanation is that differences noted arise at least in part from variations in the concentrations of impurities in the two sets of data. The purity of the material used in the experiments by PNNL/Dugway was not given. A simple test was used to show that the qualitative differences between the spectra are in general not large. The PNNL/Dugway spectrum was multiplied by 1.1385 and subtracted from our spectrum. The residual area was only 0.07% of the area of our spectrum. The primary difference noted, however, was that the ratio of the intensities of the bands at 1044 cm^{-1} and 1007 cm^{-1} is 1.151 in the PNNL spectrum and 1.209 in ours. These are the bands associated with the $P\text{-}O\text{-}CH_2CH_3$ functional group in the GA molecule, which is also found in a number of the common impurities found in the agent.

The PNNL/Dugway spectra were acquired using a syringe pump with diluent at 20 $L\cdot min^{-1}$. The highest flow rate of agent used with the syringe pump was 12.0 $\mu L\cdot min^{-1}$. Using $d_{25°C} = 1.07\ g\cdot cm^{-3}$, this corresponds to a mass rate of 12.9 $mg\cdot min^{-1} \times 1000\ L\cdot m^{-3} \times 20\ L\cdot min^{-1} = 645\ mg\cdot m^{-3}$. The volatility of GA at 25 °C is 497 $mg\cdot m^{-3}$.[11] The resulting supersaturation of GA could have caused condensation of material in the transfer lines.

The integrated absorptivity coefficient in the spectrum from Barrett and Dismukes is approximately 24% higher than in the newer data. At least one band, apparently arising from an impurity with an absorption band in the vicinity of 715 cm^{-1}, is present in the earlier data that cannot be seen in the current spectra. This is indicated in fig 8 with an arrow.

5. CONCLUSIONS

We used a saturator cell system to acquire vapor-phase spectra of the nerve agent, ethyl dimethylphosphoramidocyanidate. These were used to compute the vapor-phase absorptivity coefficient at 0.125 cm^{-1} resolution. Uncertainties are Type-A=4.3% and Type-B=4.8% of the absorptivity coefficient for absorptivity coefficient $\geq$ 5% of the peak of maximum intensity.

Blank

LITERATURE CITED

1. Barrett, W.J.; Dismukes, E.B. *Infrared Spectral Studies of Agents and Field Contaminants - Report No. 2;* Southern Research Institute: Birmingham, AL, December 1969; (AD-506 023).

2. Samuel, J.B.; Penski, E.C.; Callahan, J.C. *Physical Properties of Standard Agents, Candidate Agents, and Related Compounds at Several Temperatures*, ARCSL-SP-83015, U.S. Army Armament Research and Development Command: Aberdeen Proving Ground, MD, June 1983; UNCLASSIFIED Report (AD-C033 491).

3. Tevault, D.E.; Keller, J.; Parsons, J. Vapor Pressure of Dimethyl methylphosphonate (AD-E491 779). In *Proceedings of the 1998 ERDEC Scientific Conference on Chemical and Biological Defense Research*, 17-20 November 1998; ECBC-SP-004; Berg. D.A., Compiler; U.S. Army Edgewood Chemical Biological Center: Aberdeen Proving Ground, MD, 1999; UNCLASSIFIED Report (AD-A375 171).

4. Williams, B.R.; Ben-David, A.; Green, N.; Hulet, M.S.; Miles, R.W.; Samuels, A.C. *Validation and Support of a Quantitative Vapor-Phase Infrared Instrument Facility and Generation of a Library of Chemical Warfare and Related Materials by Fourier Transform Infrared Spectroscopy*; ECBC-CR-076; U.S. Army Edgewood Chemical Biological Center: Aberdeen Proving Ground, MD, 2006; UNCLASSIFIED Report (AD-A471 712).

5. Williams, B.R.; Samuels, A.C.; Miles, R.W.; Hulet, M.S.; Ben-David, A. ECBC Quantitative Vapor-Phase Infrared Spectral Database. In *Proceedings of the 2006 Scientific Conference on Chemical & Biological Defense Research,* 13-15 November 2006, SOAR-07-20, January 2007.

6. Williams, B.R.; Samuels, A.C.; Miles, R.W.; Hulet, M.S. *Vapor-Phase Absorptivity Coefficient of Cyclohexyl Isothiocyanate;* ECBC-TR-637; U.S. Army Edgewood Chemical Biological Center: Aberdeen Proving Ground, MD, 2008; UNCLASSIFIED Report (AD-A465 730).

7. Williams, B.R.; Samuels, A.C.; Miles, R.W.; Hulet, M.S.; Berg, F.J.; McMahon, L.; Durst, H.D. *Vapor-Phase Absorptivity Coefficient of Bis-(2-Chloroethyl) Suflide;* ECBC-TR-638; U.S. Army Edgewood Chemical Biological Center: Aberdeen Proving Ground, MD, 2008; UNCLASSIFIED Report (AD-A487 002).

8. Williams, B.R.; Samuels, A.C.; Miles, R.W.; Hulet, M.S. *Vapor-Phase Absorptivity Coefficient of 2-Chlorovinyl Dichloroarsine;* ECBC-TR-667; U.S. Army Edgewood Chemical Biological Center: Aberdeen Proving Ground, MD, 2009; UNCLASSIFIED Report (AD-A493 633).

9. *DOE/PNNL Infrared Spectral Library, Release 11.0*, [DVD-ROM], Pacific Northwest National Laboratory: Richland, WA, September 2006.

10. Barrett, W.J., Dismukes, E.B. *Infrared Spectral Studies of Agents and Field Contaminants - Report No. 1*; Southern Research Institute, Birmingham, AL, December 1969; UNCLASSIFIED Report (AD-395 378).

11. *Potential Military Chemical/Biological Agents and Compounds; FM 3-11.9*; Department of Defense: Washington, DC, January 2005; UNCLASSIFIED Report.