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VAPOR-PHASE INFRARED ABSORPTIVITY COEFFICIENT OF 2-CHLOROVINYL DICHLOROARSINE (LEWISITE)

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We measured the vapor-phase absorptivity coefficient of the vesicant chemical warfare agent 2-chlorovinyl dichloroarsine (Lewisite) in the mid-infrared (4000-550 cm^{-1}) at a spectral resolution of 0.125 cm^{-1}. The Lewisite used in the feedstock was purified by fractional distillation and analyzed by nuclear magnetic resonance 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.

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EXECUTIVE SUMMARY

We measured the vapor-phase absorptivity coefficient of 2-chlorovinyl dichloroarsine [Lewisite (L)] in the mid-infrared. We used agent filled saturator cells suspended in a temperature controlled liquid bath to generate continuous streams of the compound diluted in nitrogen, which 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 spectroscopy. The concentration of L in the vapor was determined with a gravimetric method. Ten 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: 2.2% and Type-B: 3% of the absorptivity coefficient. We report a comparison of our data to that obtained by another laboratory using a different vapor generation method.

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PREFACE

The work described in this report was performed under the direction of the Detection Capability Officer, Defense Threat Reduction Agency Joint Science and Technology Office. This work was started and completed in May 2008.

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Acknowledgments

This work was performed under the direction of the Detection Capability Officer, Defense Threat Reduction Agency Joint Science and Technology Office.

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VAPOR-PHASE INFRARED ABSORPTIVITY COEFFICIENT OF 2-CHLOROVINYL DICHLOROARSINE (LEWISITE)

1. INTRODUCTION

We determined the high resolution vapor-phase absorptivity coefficients of the vesicant 2-chlorovinyl dichloroarsine (L, Lewisite) in the spectral range of 4000-550 cm^{-1} in units of $(\mu mol/mol)^{-1}m^{-1}$ and made an initial computation of the uncertainties of 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] Given the extensive use of vapor-phase infrared (IR) spectra for standoff detection of chemical warfare (CW) agents, the need for current data is thus apparent.

Lewisite has the Chemical Abstracts Service (CAS) Registry Number 541-25-3 and is indexed under the name, arsonous dichloride, (2-chloroethenyl)-. The molecular formula is $C_2H_2AsCl_3$, and it has a molecular weight of 207.35. Other synonyms for the compound include dichloro-(2-chlorovinyl)arsine, chlorovinylarsine dichloride, and EA-1034. The structure is shown in Figure 1.

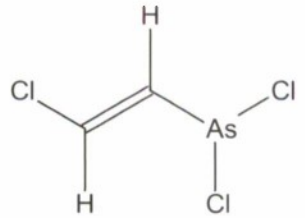

Figure 1. Structure of 2-Chlorovinyl Dichloroarsine (Lewisite).

Lewisite is vesicant CW agent that was first synthesized in 1918 although not employed in combat during WWI. The freezing and boiling points are -1.2 and 195.9 °C[2], respectively.

2. EXPERIMENTAL PROCEDURES

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 CW agent related compounds.[3]

The method, modified to generate continuous streams of chemical compounds for obtaining quantitative vapor-phase IR spectra, has been used to measure the absorptivity coefficients of benzene[4], as well as a variety of CW agent related compounds.[5] 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 boil off of a bulk liquid nitrogen tank, across a conical alumina wicking mechanism in a glass holder filled with the analyte. This produces a saturated vapor-liquid equilibrium 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 Instrument Model 5850S (Hatfield, PA) mass flow controllers 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 accuracies of approximately 1% or better of rate at flows ≥25% of full scale.

Spectra were obtained with a Bruker Model IFS/66V FTIR. 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 settings of 1.405, 2.727, and 5.377 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 CW agent 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 1.0132 X 10^5 Pa (760 Torr) using the ideal gas law.

2.2 Feedstock.

The material used to generate the vapor streams for the experiments was purified by fractional distillation to maximize the concentration of the *trans*-2-chlorovinyl isomer. The purity was determined to be ≥99% by ^1H and ^{13}C nuclear magnetic resonance spectroscopy (NMR).

3. RESULTS AND DISCUSSION

Three trials were run to obtain spectra at ten 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 three experiments.

Trace 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=-$\log_{10}(T)$].

The composite spectrum (absorptivity coefficient) was computed using spectra with concentration pathlength products ranging 98-975 μmol/mol(m) (corrected to 296 K and 101325 Pa). As an initial check of the quality of the data, Beer's Law plots of two spectral lines, 1212.5 and 720.6 cm^{-1}, were calculated using MatLab®. Results showed that the data appeared to be well fitted, with no points lying outside of the 95% confidence limits for either a repeated set or a repeated single x or the 95% confidence limits for a Grubbs Test for Outliers[6] (Figures 2 and 3).

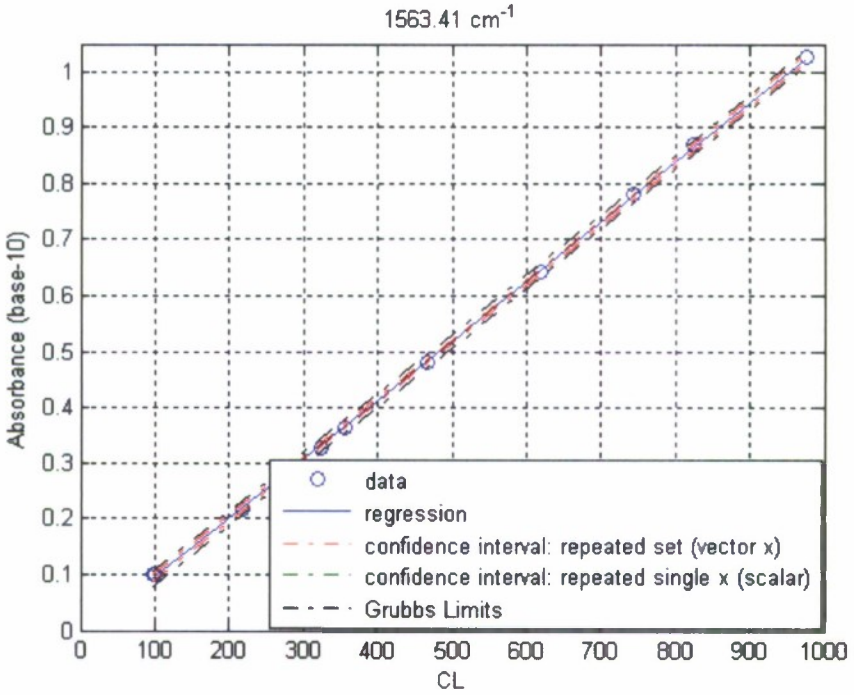

Figure 2. Beer's Law Plot of 1563.41 cm^{-1} Line in the Vapor-Phase Spectrum of 2-Chlorovinyl Dichloroarsine.

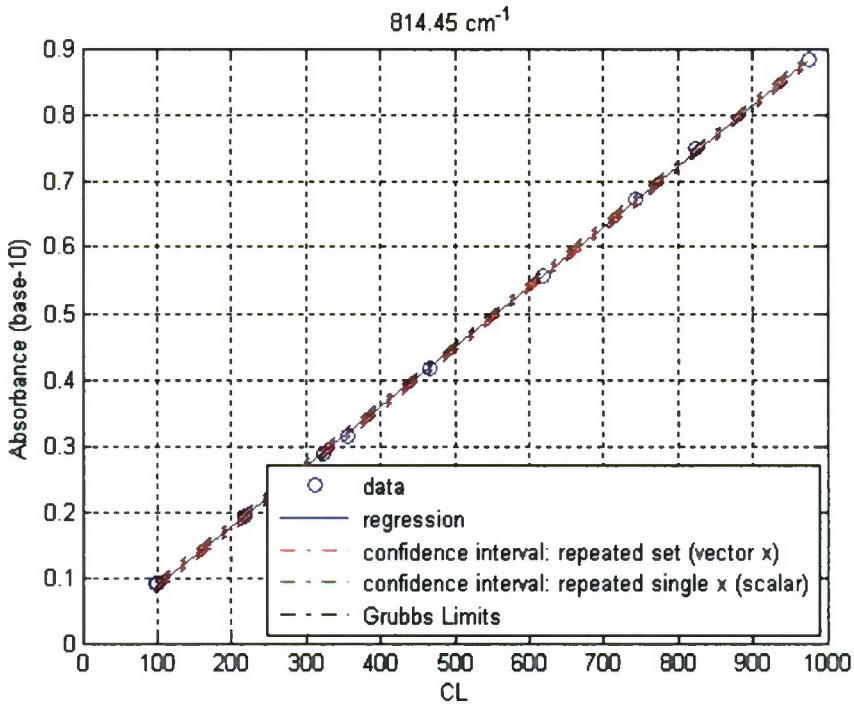

Figure 3. Beer's Law Plot of 814.45 cm^{-1} Line in the Vapor-Phase Spectrum of 2-Chlorovinyl Dichloroarsine.

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=-logT) >1.5 are normally assigned a weight of zero. Because all values recorded were for A≤1.026, 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 mantissa of Figure 4 by 0.1165. This factor is derived from eq 1 using the molecular weight of Lewisite (207.35).

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

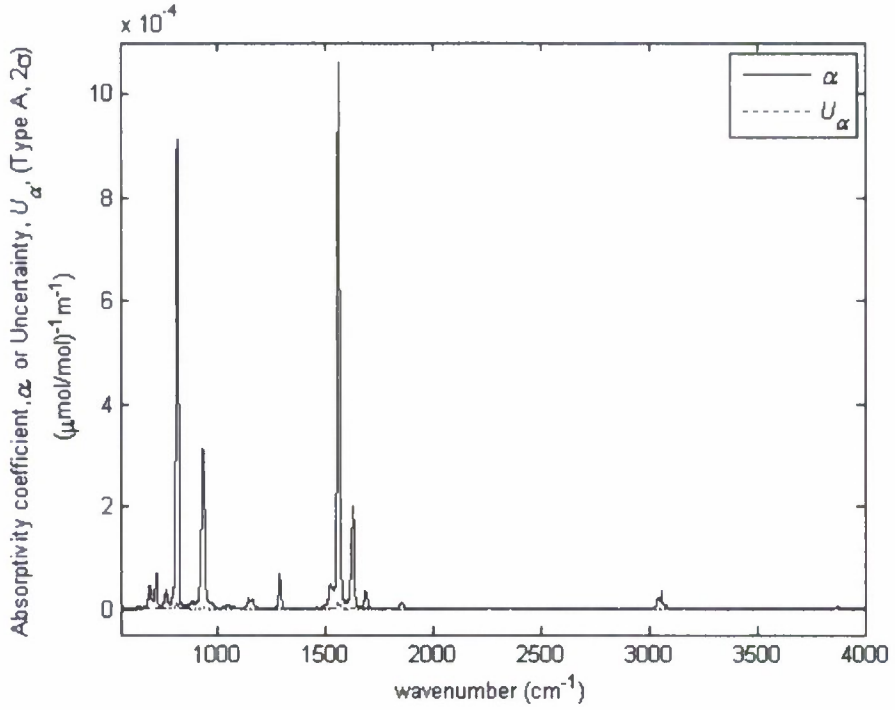

Figure 4. Absorptivity Coefficient and Statistical Uncertainty (Type-A, 2σ) for 2-Chlorovinyl Dichloroarsine.

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

Table 1. Absorptivity Coefficient of 2-Chlorovinyl Dichloroarsine for Selected Bands.

Wavenumber, cm^{-1} (Wavelength, μm)	Absorptivity coefficient, $(\mu mol/mol)^{-1}m^{-1}$ $[(mg/m^2)^{-1}]$
1563.40 (6.396)	1.061E-03 (1.24E-04)
931.16 (10.74)	3.147E-04 (3.667E-05)
814.30 (12.28)	9.075E-04 (1.06E-04)

In general, expanded Type-A uncertainties were 1-1.5% of the absorptivity coefficient, as seen in Figures 5 and 6. Figure 5 is a plot of absorptivity coefficients (abscissa) and fractional uncertainty (Type-A, U_A, 2σ) (mantissa). Figure 6 is a plot of the absorptivity coefficient and uncertainty and 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 7, the coefficients are $a= 9.79 \times 10^{-3}$ and $b=6.30 \times 10^{-7}$ (Table 2).

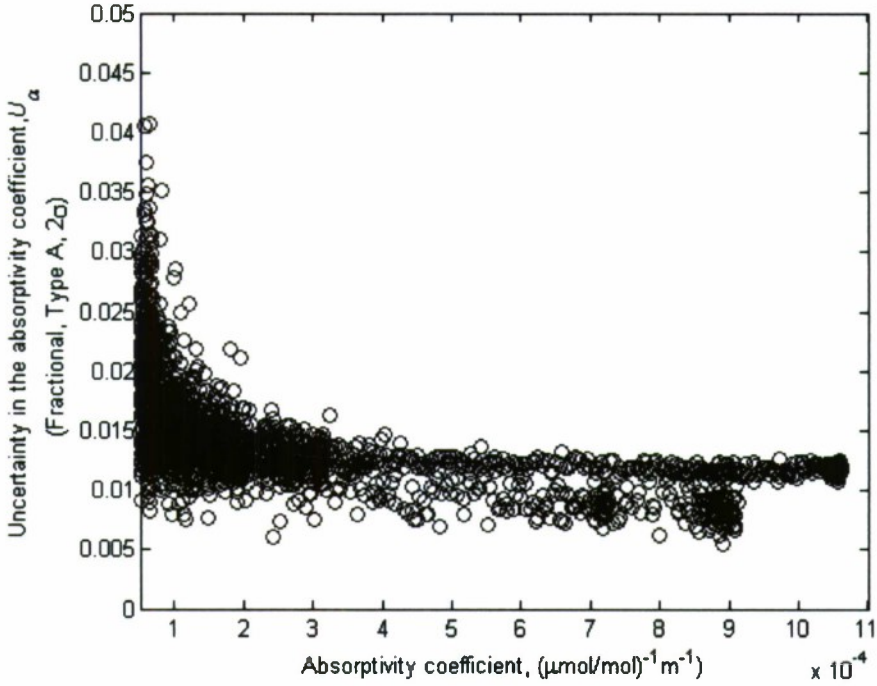

Figure 5. Absorption Coefficient (Abscissa) and Type-A Uncertainty (Fractional, 2σ) for Lewisite.

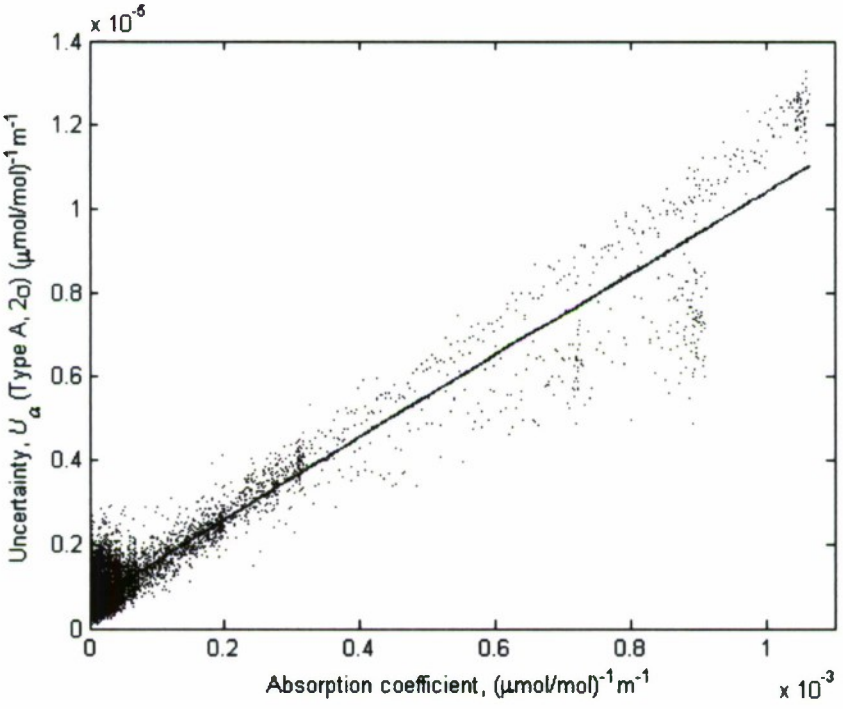

Figure 6. Absorption Coefficient (Abscissa) and Type A Uncertainty (2σ) for Lewisite.

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

Type-A Uncertainty $2\sigma \approx ma+b$	
Slope m	Intercept b
9.79×10^{-3}	6.30×10^{-7}

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.

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

The expanded uncertainty, Type-A + B, was computed with the following equation.

$$U_{A+B}=(\Delta_B^2+\Delta_A^2)^{1/2}*2 \quad (3)$$

The sources of uncertainty and their fractional values, as well as an explanation of the symbols in eq 1 are given in Table 4. Among the Type-B uncertainties, the purity of the vapor dominates at 0.015 (1σ).

Table 3. Uncertainties in Absorptivity Coefficient of Lewisite from ECBC Data where $\alpha \geq 0.000053$ $(\mu mol/mol)^{-1}m^{-1}$.

Symbol	Fractional deviation	Source
ΔL	0.005	Pathlength
ΔT	0.0006	Temperature of White cell
ΔP	0.0003	Pressure
$\Delta FTIR$	0.0005	Drift in spectrometer
ΔNL	0.01	Nonlinearity in detector
ΔMR	0.005	Mass rate
ΔD	0.005	Dilution rate
$\Delta purity$	0.0075	Purity of feedstock
Δ_B	0.015	Combined type B (1σ)
Δ_A	0.0094	Type-A deviation (1σ)
U_{A+B}	0.036	Combined type A+B, expanded to 2σ

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

2-chlorovinyl dichloroarsine for comparison to the data acquired at ECBC is that obtained by Pacific Northwest National Laboratory (PNNL) at the U.S. Army Dugway Proving Ground.[7] 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 Type-A and Type-B uncertainties.

As can be seen in Figure 7, the spectra from ECBC and PNNL are qualitatively and quantitatively similar. Within the range of frequencies <2000 cm^{-1} and absorptivity coefficients >0.0002 $(\mu mol/mol)^{-1}m^{-1}$, the positions of absorption features differ by <0.01 cm^{-1}, with good agreement even in the fine structure. This is illustrated in Figure 8, which shows an expanded view of the absorption band at 814 cm^{-1}, in which the fine structure is closely matched in the two spectra. When the ordinate scale is expanded in the fingerprint region, it is possible to see differences in the baselines of the two spectra (Figure 9). Several peaks in the PNNL spectrum exhibit a derivative-like appearance along the sides of the peaks at the baseline. Two peaks in vicinity of 1020 and 1380 cm^{-1} in the PNNL spectrum at are not seen in the spectrum from ECBC. Figure 10 shows an expanded view of the 3000 cm^{-1} region, associated with C-H stretch. Baseline shift on the red (lower wavenumber) side of the vinyl stretching bands above 3000 cm^{-1} may indicate aerosol scattering in the PNNL spectrum. Absorption features between 2900 and 3000 cm^{-1} may arise from a saturated impurity present in the feedstock used to generate the PNNL spectrum.

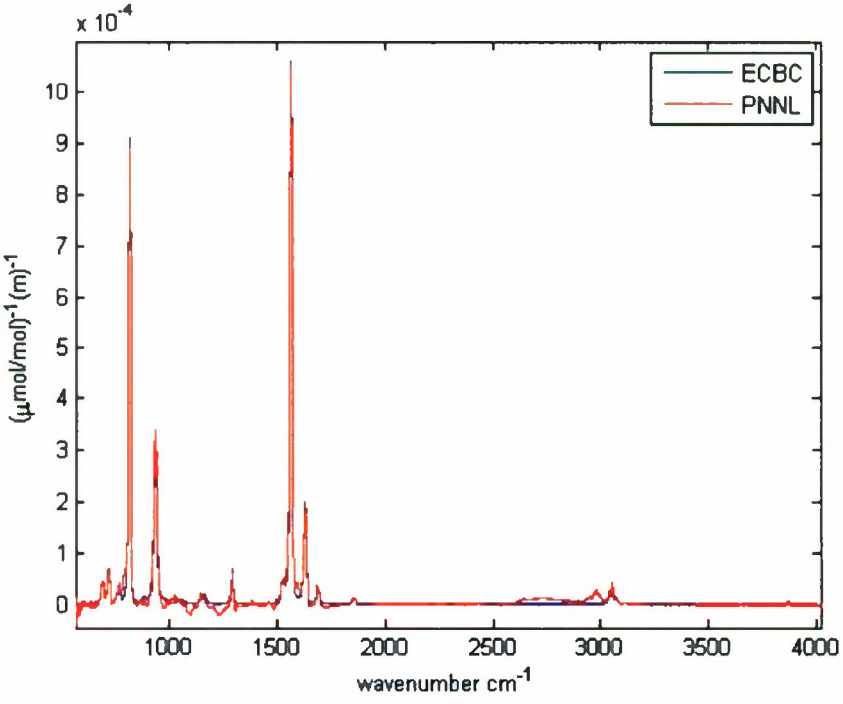

Figure 7. Absorptivity Coefficients of Vapor-Phase Lewisite from ECBC (in Blue) and PNNL (in Red). At frequencies <2000 cm^{-1} and absorptivity coefficients >0.0002 $(\mu mol/mol)^{-1}m^{-1}$, the spectra are qualitatively and quantitatively similar.

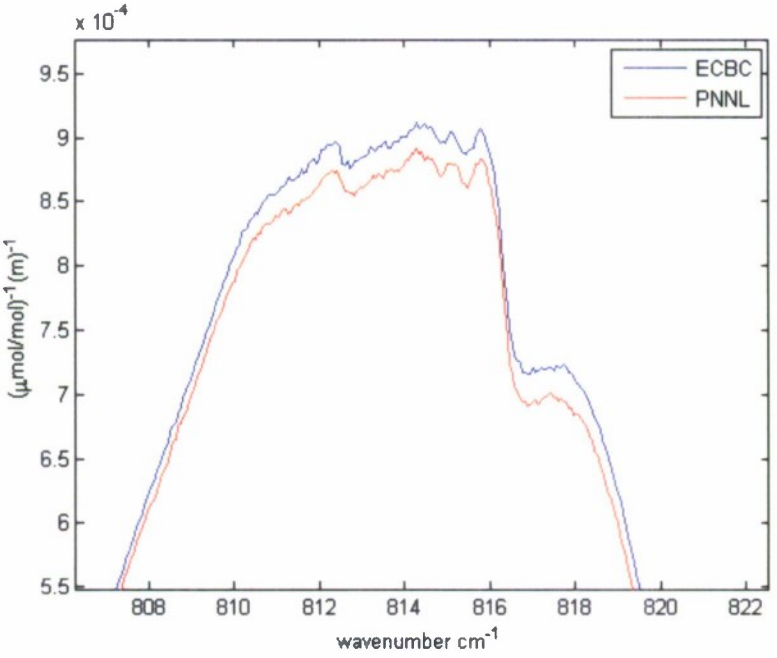

Figure 8. 814 cm^{-1} Absorption Band in the Spectra of Lewisite from ECBC and PNNL. Positions of absorption bands in the two spectra are in agreement to within <0.01 cm^{-1}.

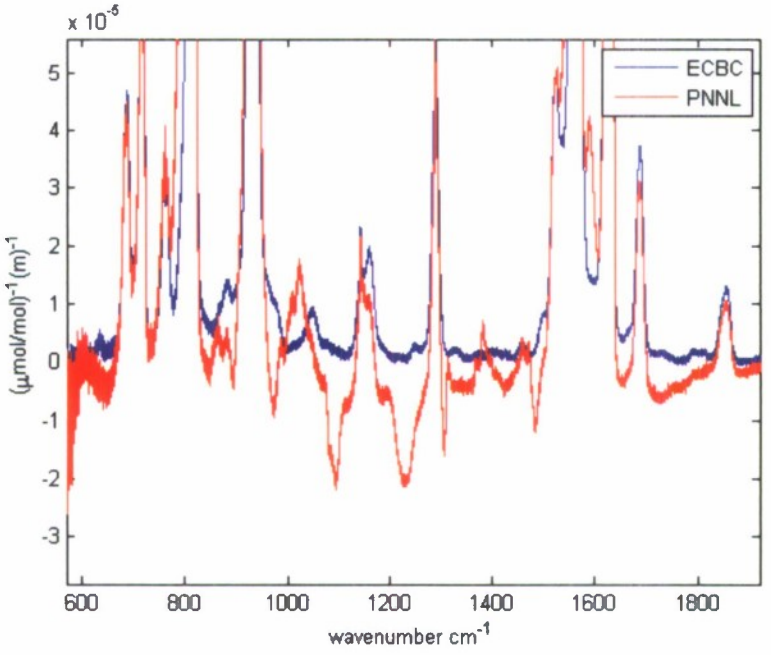

Figure 9. Absorptivity Coefficient Spectra of Lewisite from ECBC and PNNL. Spectra are zoomed into the fingerprint region, showing the derivative-like features in the baseline of the PNNL spectrum and the presence of several peaks not observed in the ECBC spectrum.

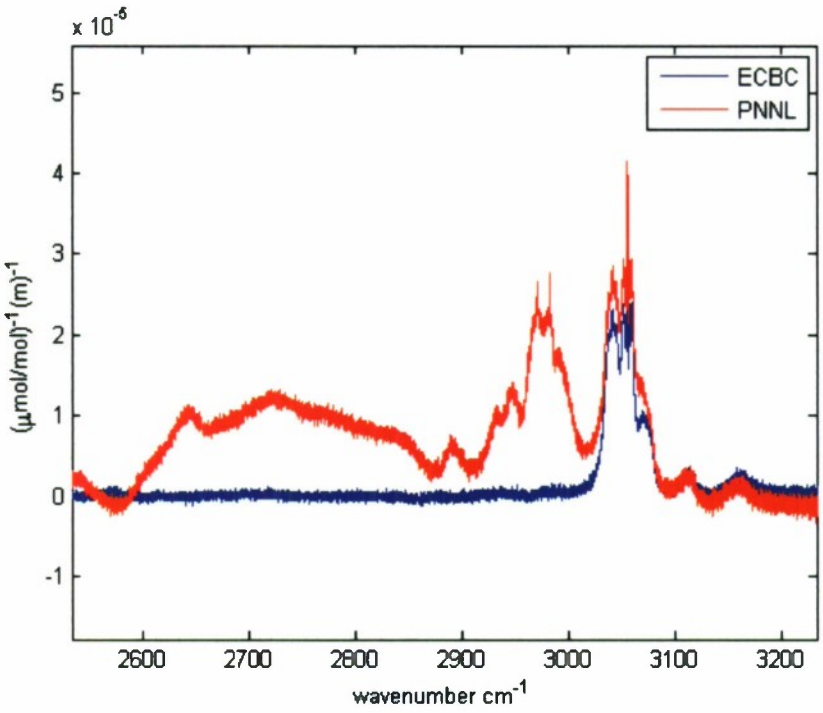

Figure 10. Spectra of Lewisite from PNNL and ECBC in the 3000 cm^{-1} Region (C-H stretch). The baseline in the PNNL spectrum appears to be shifted on the red side of the vinyl stretching bands. Peaks at frequencies <3000 cm^{-1} may indicate the presence of a saturated impurity in the feedstock used to generate the spectra.

Table 4. Comparison of Peak Heights in Vapor-Phase Absorptivity Coefficient Spectra of Lewisite from PNNL and ECBC. The peak heights for the PNNL spectrum shown in the table were obtained after normalizing to 23 °C (296.15 K) using the ideal gas law.

Frequency cm^{-1}	Peak Height				
	ECBC	PNNL	(PNNL-ECBC)/ECBC x 100	PNNL (after baseline correction)	(PNNL-ECBC)/ECBC x 100
3055.49	0.0000355	0.0000414	16.6	0.0000428	20.6
1627.68	0.000199	0.000186	-6.53	0.000190	-2.15
1563.43	0.001063	0.001056	-0.66	0.001059	0.38
1288.68	0.0000681	0.0000577	-15.3	0.0000632	-7.20
929.29	0.000312	0.000339	8.65	0.000341	9.29
814.30	0.000912	0.000892	-2.19	0.000894	-1.97

In evaluating the quantitative similarity of absorptivity coefficient spectra, we would generally compare their integrated areas because this method better accounts for differences in resolution. In this case, the baseline shifts and differences in peak shapes in

the PNNL spectrum, as well as the extra peaks in the 3000 cm^{-1} region, would reduce the meaningfulness of such a comparison. We chose instead to compare peak heights. Because the PNNL spectrum was acquired at a temperature of 33 °C (306.15 K), it was first necessary to normalize it to 23 °C (296.15 K) using the ideal gas law. We then did a multipoint baseline correction of the PNNL spectrum around the derivative-like features to bring the edges of the peaks to the baseline. A comparison of the maximum intensities of several peaks before and after baseline correction is shown in Table 4. Deviations are ≤2 % for the strongest absorption features and fractionally larger for the weaker bands. This was particularly in the 3000 cm^{-1} region, where the intensity of the weak vinyl C-H stretch at 3055.49 cm^{-1} is 16.6 % greater in the PNNL spectrum than in the ECBC spectrum. After baseline correction, the difference increased to 20.6%. The increase may have resulted from the presence of the impurity and the high degree of aerosol scattering in the PNNL spectrum, both of which were difficult to correct.

5. CONCLUSIONS

The vapor-phase absorptivity coefficient of 2-chlorovinyl dichloroarsine (Lewisite) was measured within the range 4000-550 cm^{-1}. Type-A uncertainties, expanded to 2σ, are 2.2 % of the absorptivity coefficient at intensities ≥5 % of the most intense absorption feature, with a Type-B uncertainty of 3 %.

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