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VAPOR-PHASE INFRARED ABSORPTIVITY COEFFICIENTS OF THREE 2-(DIALKYLAMINO)ETHANETHIOL COMPOUNDS

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The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorizing documents.

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We measured the vapor-phase absorptivity coefficient of 2-(diisopropylamino)ethanethiol, 2-(diethylamino)-ethanethiol, and 2-(dimethylamino)ethanethiol in the mid-infrared (4000-550 cm^{-1}) at a spectral resolution of 0.125 cm^{-1}. The material used in the feedstock was synthesized at the U.S. Army Edgewood Chemical Biological Center, and the purity was verified by gas chromatography and NMR spectroscopy. In this report, we describe the experimental method used to acquire the individual spectra that were used to produce the composite spectra and summarize the statistical uncertainties in the data.

15. SUBJECT TERMS

Infrared	Quantitative	Saturator cell
FTIR	VX thiol	Vapor-phase
VX	Vapor	Absorptivity coefficient

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EXECUTIVE SUMMARY

We measured the vapor-phase absorptivity coefficient of 2-(diisopropylamino)-ethanethiol, 2-(diethylamino)ethanethiol, and 2-(dimethylamino)ethanethiol in the mid-infrared. We used chemical 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 gas chromatography (GC) and NMR spectroscopy. The concentration of the compound in the vapor was determined with a gravimetric method, and the purity of the vapor was concurrently verified by thermal desorption GC. Spectra at varying 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: <3% and Type-B: 3% of the absorptivity coefficient for all three compounds. To our knowledge, this is the first time that the vapor-phase absorptivity coefficients of these compounds have been measured in the mid-infrared.

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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 in August 2008 and completed in September 2008.

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VAPOR-PHASE INFRARED ABSORPTIVITY COEFFICIENTS OF THREE 2-(DIALKYLAMINO)ETHANETHIOL COMPOUNDS

1.   INTRODUCTION

In this report, we discuss the high resolution vapor-phase absorptivity coefficients of three 2-(dialkylamino)ethanethiol compounds in the spectral range of 4000-550 cm^{-1} in units of $(\mu mol/mol)^{-1}m^{-1}$, as well as the uncertainties of the data. To our knowledge, the high resolution vapor-phase absorptivity coefficients of these compounds have not previously been measured.

The V-type nerve agents are a class of highly toxic, persistent phosphonothioic acid esters, within which a 2-(dialkylamino)ethanethiolate functional group comprises the nucleophilic part of the molecule (Figure 1).[1] The primary products of hydrolysis of a V-type agent are the corresponding O-alkyl alkylphosphonic acid and the 2-(alkylamino)ethanethiol. They are commonly found in the bulk nerve agents. Surveillance of ton containers filled with O-ethyl-S-2-(diisopropylamino)ethyl methylphosphonothioate (US VX) showed an average mass fraction of 0.89%.[2] The free base thiol compounds can also be reacted with alkylphosphonic dichlorides and an alcohol to synthesize a crude mixture of nerve agent and related toxic compounds.[3] Our work with the 2-(diisopropylamino)ethanethiol indicated that the compound has a vapor pressure of approximately 60 Pa at 25 °C, contrasted with a vapor pressure of 0.117 Pa for US VX at the same temperature.[4] Even low concentrations of the thiols can likely contribute significantly to the spectra of the vapor from the V agents and having the absorptivity coefficients of these compounds is important in predicting the spectral signatures of the agents.
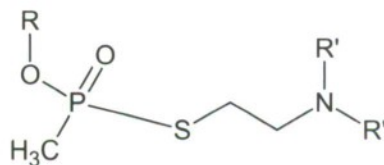
Figure 1. O-Alkyl-S-2-(dialkylamino)ethyl Alkylphosphonothioate, V-Type Nerve Agent. Shown is the methylphosphonothioate. The thiolate functional group (right half of the molecule with the P-S bond exaggerated) can be formed from R' = C_1, C_2, or C_3. The present work studied the absorptivity coefficients of the thiol compounds in which R' = methyl, ethyl, and isopropyl.

We studied the variants of the thiol identified in Table 1. The thiols shown in the table are incorporated into US VX (R = ethyl, R' = isopropyl), Russian VX (R = isobutyl, R' = ethyl), and Vx (R = ethyl, R' = methyl). The properties of the fourth compound in the series, with R = n-propyl, was not studied during this work.

Table 1. 2-(Dialkylamino)ethanethiols Studied during the Present Work. A fourth possible variant, R' = n-propyl was not studied.

R'	FORMULA	FW[a]	NAME(S)	CAS RN[b]
Methyl	$C_4H_{11}NS$	105.20	2-(Dimethylamino)ethanethiol Vx thiol	108-02-1
Ethyl	$C_6H_{15}NS$	133.26	2-(Diethylamino)ethanethiol RVX thiol	100-38-9
Isopropyl	$C_8H_{19}NS$	161.31	2-(Diisopropylamino)ethanethiol Ethanethiol, 2-[bis(1-methylethyl)amino]- VX thiol	5842-07-9

[a]Formula weight
[b]Chemical Abstracts Service registry number

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 the U.S. Army Edgewood Chemical Biological Center (ECBC) for measuring the volatility of chemical warfare agent (CWA) related compounds.[5]

The method, modified to generate continuous streams of chemical compounds for obtaining quantitative vapor-phase infrared spectra, has been used to measure the absorptivity coefficients of benzene[6] and a variety of CWA related compounds.[7,8,9] The experimental setup, data collection, and post-processing are described in more detail in Literature.[5,6] The saturator passes a stream of nitrogen carrier gas, obtained from the boiloff of a bulk liquid nitrogen tank, across an alumina wicking mechanism in a glass holder filled with the analyte. A saturated vapor-liquid equilibrium of the analyte on the downstream side of the saturator cell results with the concentration of the analyte determined by the temperature of the liquid phase. By suspending the saturator cell in a constant temperature bath (Julabo, Allentown, PA), the concentration of the analyte can be predicted by its vapor pressure at the temperature of the bath. The bath was maintained at 22 °C (Vx thiol) and 23 °C (RVX and VX thiols). The apparatus used in the Quantitative Fourier transform infrared (FTIR) Laboratory uses a Brooks (Brooks Instrument Co., Hatfield, PA) Model 5850S mass flow controller 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 $\geq$25% of full scale.

Spectra were obtained with a Bruker (Bruker Optics, Billerica, MA) Model IFS/66V FTIR spectrometer. The instrument is equipped with both 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

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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 pathlengths of 2.727, 4.057, 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. The ratio of single beam spectra of the CWA to spectra of clean, dry nitrogen was determined. 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 NIST traceable digital barometers and thermometers, and all data were archived. Concentration-pathlength products (CL) were computed in units of μmol/mol(m) (ppm-m). A digital barometer 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 barometer 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 materials used to generate the vapor streams for the experiments were supplied by the Chemical Sciences Division at ECBC. Aliquots of the feedstock materials were analyzed by NMR spectroscopy (^{1}H and ^{13}C), GC-mass spectrometry (MS), and GC-FTIR. The effluent from the White cell was sampled periodically by thermal desorption (TD)-GC. The analysis results of the feedstock chemicals are summarized in Table 2.

Table 2. Results of Purity Analysis of V-Related Thiol Feedstock Compounds

THIOL	PURITY FOUND			IMPURITIES[b]
	NMR (%)	GC-MS[a] (%)	TD-GC (%)	(%)
Dimethyl	>99	99.2	99.4	1,2-Dimethylaziridine (0.7) Methanol (0.1)[c]
Diethyl	>99	100.0	99.2	None observed
Diisopropyl	>99	99.95	99.1	Isopropylamine (0.05)

[a]Reported as area fraction, which also included the area of the corresponding disulfide compound.
[b]Area fraction by GC-MS.
[c]Area fraction by GC-FTIR, 1.7%.

All of the V-related thiol compounds dimerize readily to the corresponding 2-(dialkylamino)ethyl disulfide. The reaction can be minimized by keeping them dry and refrigerated and keeping exposure to the air as short as possible. The disulfides were not seen by NMR. Dimerization inevitably occurs, however, when they are analyzed by GC, probably in the heated injector. The disulfide compounds were also seen in the TD-GC analysis of the vapor effluent. Because of the low volatilities of the disulfides, it is extremely unlikely that they would be observed in the vapor from the saturator cell, even if present in the liquid-phase. This means

that dimerization must have occurred on the sorbent tube of the TD apparatus. For this reason, the areas of the disulfide compounds were summed with the thiols when computing the purities.

Methanol was observed in the spectra of the Vx thiol. Before acquiring the spectra that were used to compute the composite spectrum (absorptivity coefficient), it was purged at a low flow rate (<50 mL/min), and the effluent was monitored by taking infrared spectra periodically at low resolution until the alcohol could no longer be detected.

2.3   Data Treatment

Trace water vapor was observed in the effluent from all three compounds, which decreased over time. The features were removed by spectral subtraction. Baseline corrections of spectra were performed with a linear subtraction, with the baseline correction in no case exceeding 0.001 A $[A = -\log_{10}(T)]$.

As an initial check of the quality of the data, Beer's Law plots of two spectral lines were calculated for each compound using MatLab. This ensured that the data were well fitted, with no points lying outside the 95% confidence limits for either a repeated set or a repeated single x. Simultaneously the MatLab also checked for outliers using a Grubbs Test.[10]

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 $A < 1.5$, all data were weighted at 1. The absorptivity coefficient (α) was computed in $(\mu mol/mol)^{-1}m^{-1}$. Equation 1 can be used to derive α in $(mg \cdot m^{-2})^{-1}$.

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

Type-B uncertainty (expanded to $P = 0.95$) was computed using eq 2:

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

In eq 2, the symbols represent the fractional uncertainty in the following parameters: L, the optical pathlength of the White cell; T, the temperature of the White cell; P, the sample pressure; FTIR, the drift in the spectrometer; NL, detector nonlinearity; MR, mass rate; D, dilution rate; Purity, the purity of the vapor.

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3.   RESULTS AND DISCUSSION

3.1   Absorptivity Coefficient of 2-(Dimethylamino)ethanethiol

        Four trials were run to obtain spectra at 11 CL. 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 22 °C for all four trials.

        Beer's Law plots were computed for lines at 2783.5 cm^{-1} and 1056.1 cm^{-1}
(Figures 2 and 3). The data were well fitted, with little scattering evident.
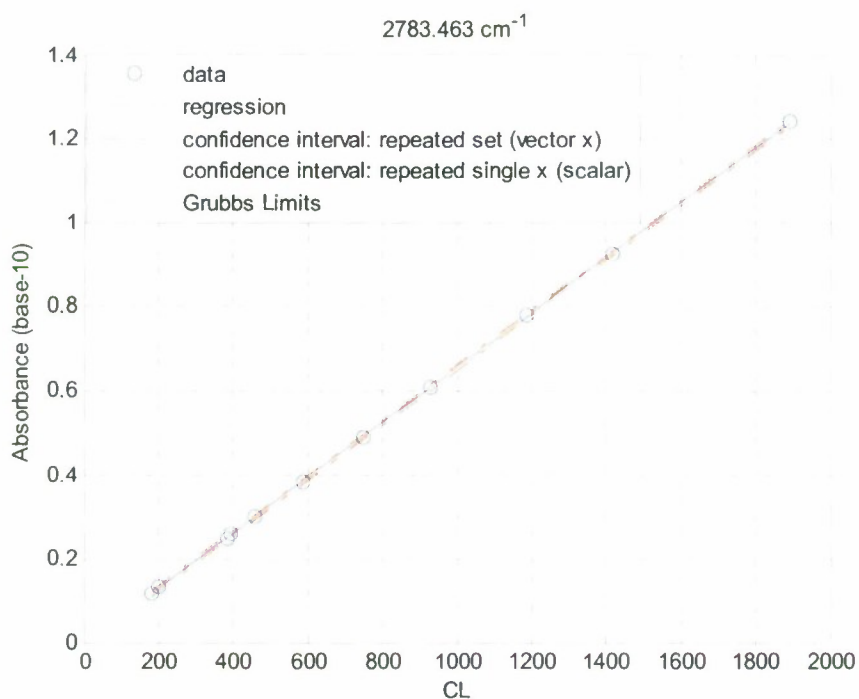
Figure 2. Beer's Law Plot of 2783.5 cm^{-1} Line in the Vapor-Phase Spectrum
of 2-(Dimethylamino)ethanethiol

1056.145 cm^{-1}
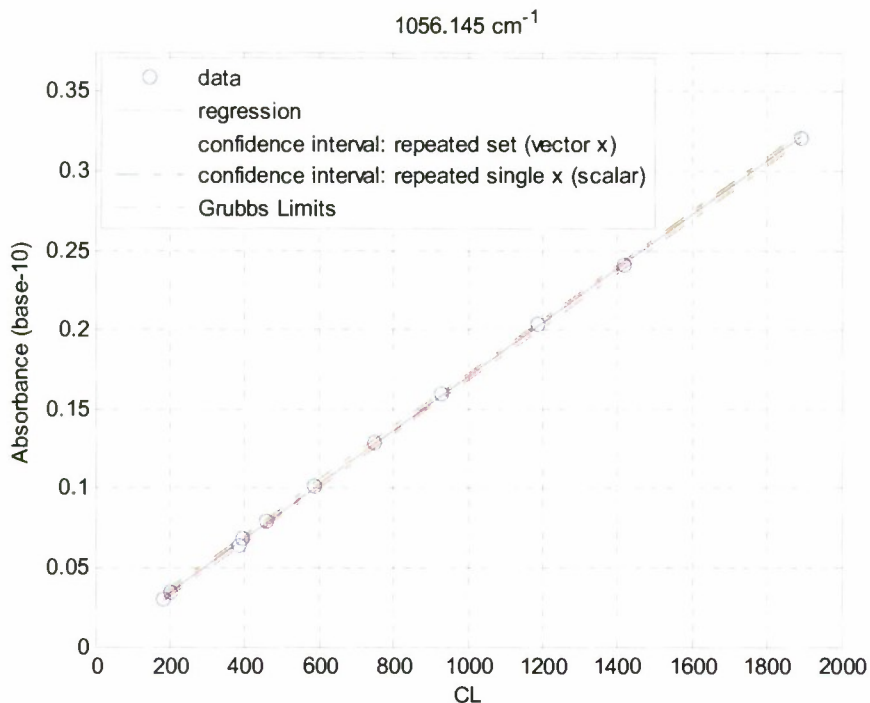
Figure 3. Beer's Law Plot of 1056.1 cm^{-1} Line in the Vapor-Phase Spectrum
of 2-(Dimethylamino)ethanethiol

The composite spectrum (absorptivity coefficient) was computed using spectra
with CL ranging from 181 to 1890 μmol/mol(m) (corrected to 296 K and 101325 Pa). Figure 4
is the plotted absorptivity coefficient (α) and Type-A uncertainty for the computed spectral
range. The figures are plotted with α in (μmol/mol)$^{-1}$m^{-1}. To obtain α in (mg·m^{-2})$^{-1}$, multiply the
values in the ordinate scale of Figure 4 by 0.2296.

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

Table 3 provides the absorptivity coefficients in $(\mu mol/mol)^{-1}m^{-1}$ and $(mg/m^2)^{-1}$ for selected bands in wavenumber (cm^{-1}) and micrometers (μm).

Table 3. Absorptivity Coefficient of 2-(Dimethylamino)ethanethiol for Selected Bands
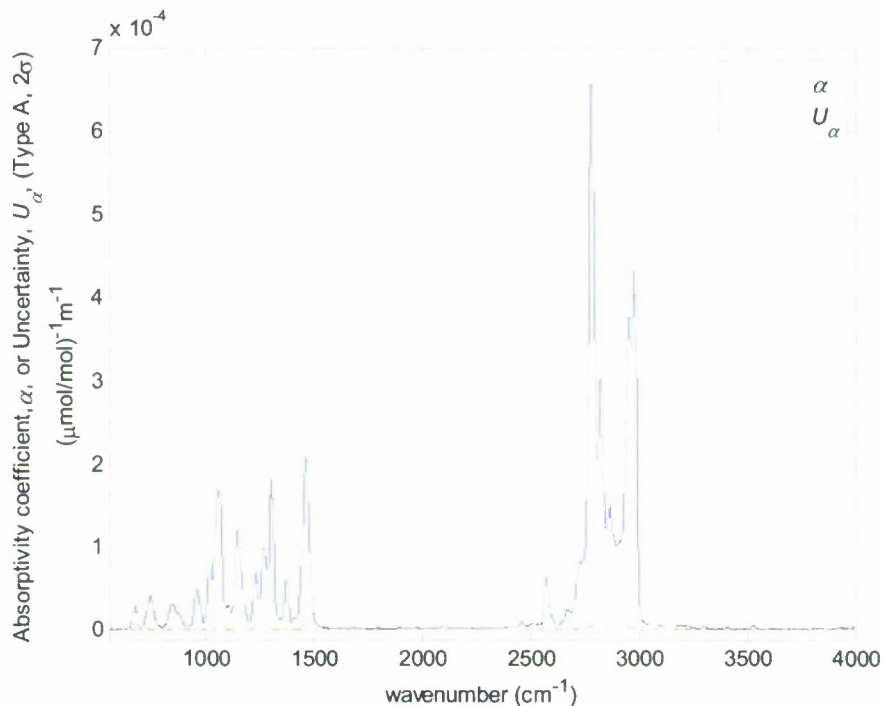
	Wavenumber/ cm^{-1}	2446.06	2059.26	1363.98	989.01
	Wavelength/μm	3.394	4.856	7.331	10.111
Absorptivity coefficient	$(\mu mol/mol \cdot m)^{-1}$	1.692×10^{-3}	2.659×10^{-3}	2.975×10^{-4}	6.328×10^{-5}
	m^2/mg	2.893×10^{-4}	4.547×10^{-4}	5.088×10^{-5}	1.082×10^{-5}

In general, expanded type-A uncertainties were approximately 0.5 to 1% of the absorptivity coefficient, as seen in Figures 5 and 6. Figure 5 is a plot of absorptivity coefficient and fractional uncertainty (Type-A, U_A, 2σ). 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 $a = 5.05 \times 10^{-3}$, and $b = 3.31 \times 10^{-7}$ (Table 4).
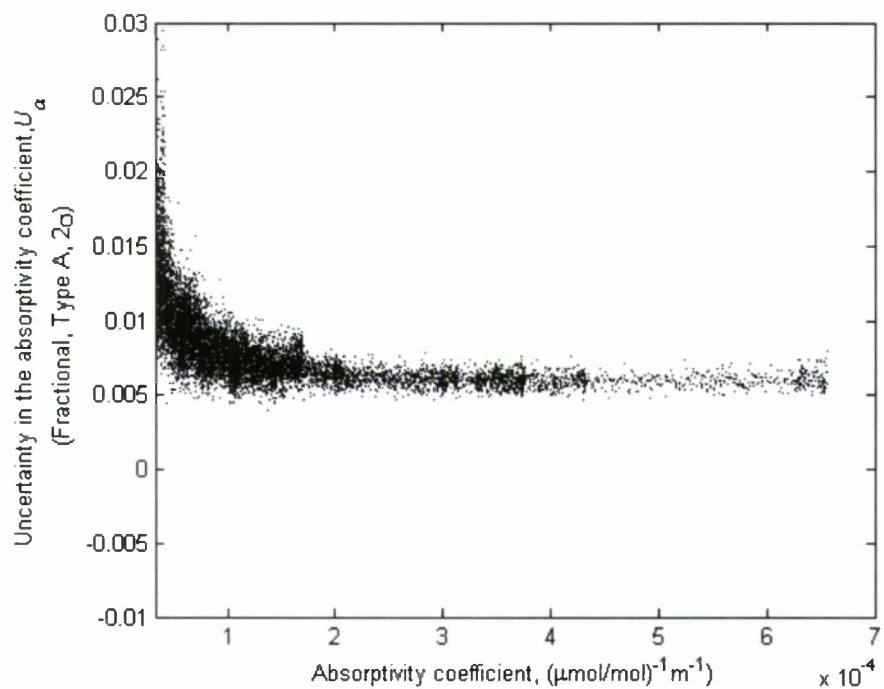
Figure 5. Absorption Coefficient and Type-A Uncertainty (Fractional, 2σ)
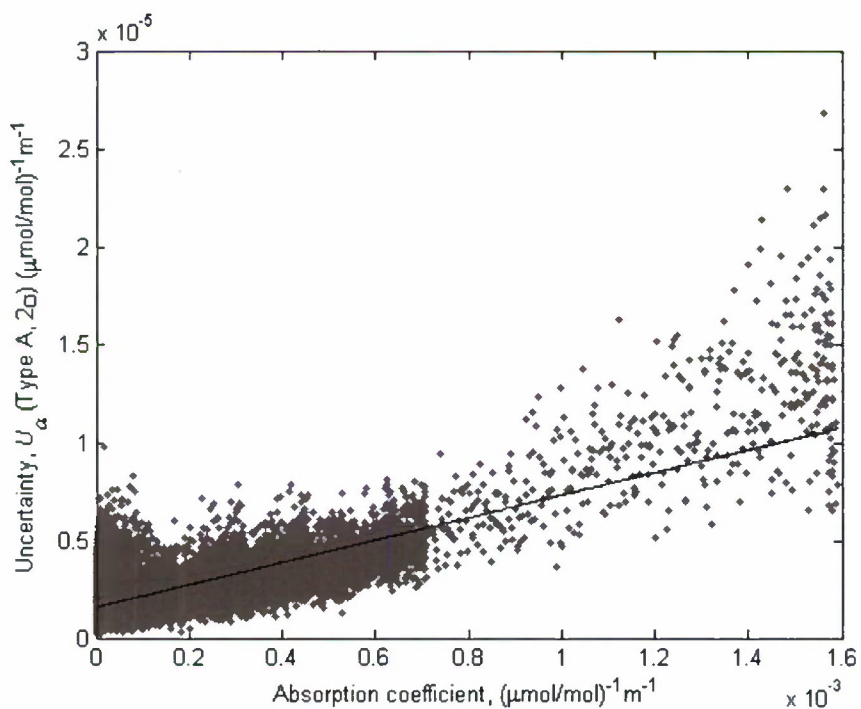for 2-(Dimethylamino)ethanethiol

Figure 6. Absorption Coefficient and Type-A Uncertainty (2σ)
for 2-(Dimethylamino)ethanethiol

Table 4. Type-A Statistical Uncertainty for 2-(Dimethylamino)cthanethiol
Vapor-Phase Absorptivity Coefficient

Type-A Uncertainty $2\sigma \approx ma + b$	
Slope m	Intercept b
5.05×10^{-3}	3.31×10^{-7}

The sources of uncertainty and their fractional values are given in Table 5. Among the Type B uncertainties, the detector nonlinearity dominates at 0.01 (1σ).

Table 5. Uncertainties in Absorptivity Coefficient of 2-(Dimethylamino)ethanethiol
where $\alpha \geq 0.000033$ (μmol/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	0.005	Mass rate
ΔD	0.005	Dilution rate
Δpurity	0.005	Purity of vapor
Δ_B	0.028	Combined type B (2σ)
Δ_A	0.015	Type-A deviation (2σ)

3.2   Absorptivity Coefficient of 2-(Diethylamino)ethanethiol

Four trials were run to obtain spectra at 11 CL. 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 22 °C for all four trials.

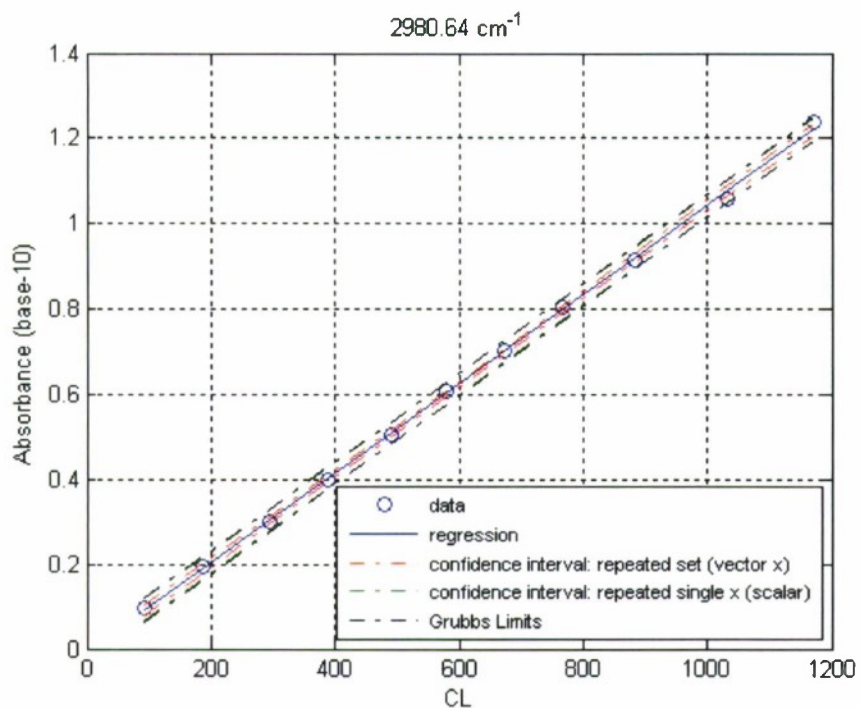Beer's Law plots were computed for lines at 2783.5 cm^{-1} and 1056.1 cm^{-1} (Figures 7 and 8).

Figure 7. Beer's Law Plot of 2980.6 cm^{-1} Line in the Vapor-Phase Spectrum of 2-(Diethylamino)ethanethiol
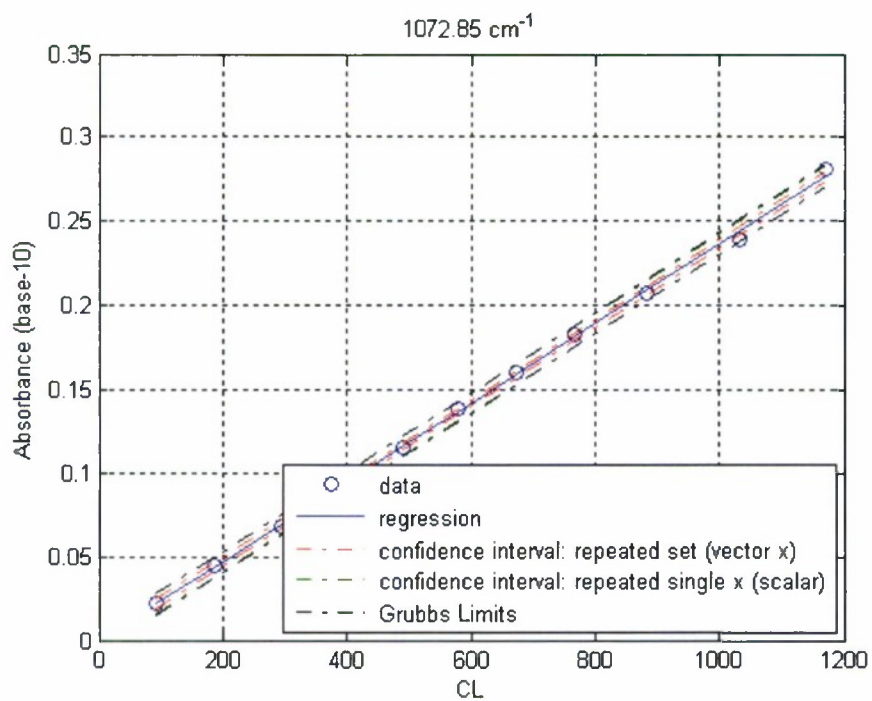

Figure 8. Beer's Law Plot of 1072.85 cm^{-1} Line in the Vapor-Phase Spectrum of 2-(Diethylamino)ethanethiol

The composite spectrum (absorptivity coefficient) was computed using spectra with CL ranging from 93 to 1171 μmol/mol(m) (corrected to 296 K and 101325 Pa). Figure 9 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 $(mg\cdot m^{-2})^{-1}$, multiply the values in the ordinate scale of Figure 4 by 0.1812.
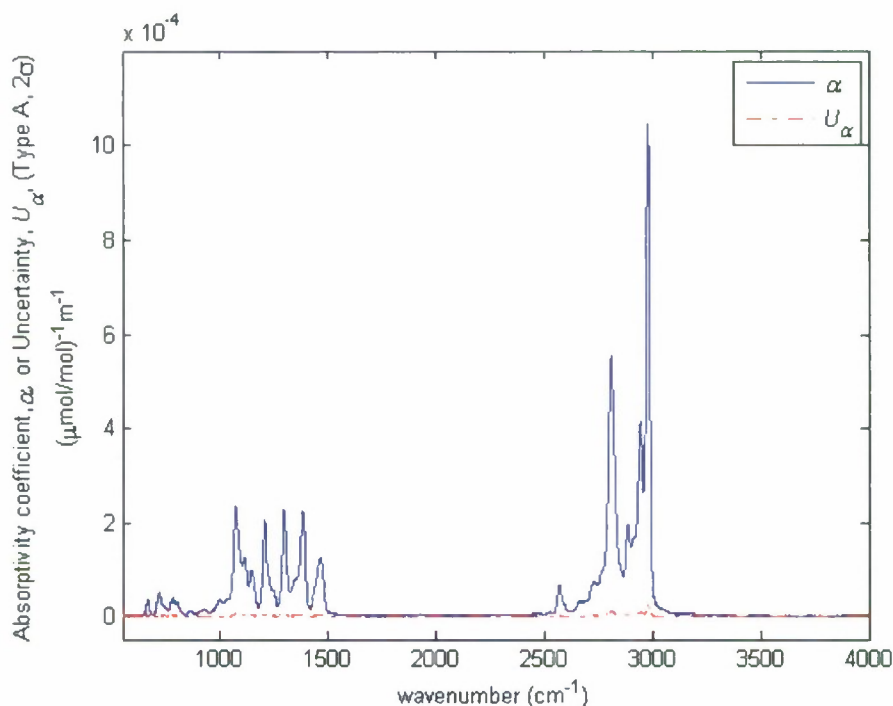

Figure 9. Absorptivity Coefficient and Statistical Uncertainty (Type-A, 2σ)
for 2-(Diethylamino)ethanethiol

Table 6 provides the absorptivity coefficients in $(\mu mol/mol)^{-1}m^{-1}$ and $(mg/m^2)^{-1}$ for selected bands in wavenumber (cm^{-1}) and micrometers (μm).

Table 6. Absorptivity Coefficient of 2-(Diethylamino)ethanethiol for Selected Bands

	Wavenumber/ cm^{-1}	2980.65	2809.14	1297.51	1072.18
	Wavelength/μm	3.355	3.560	7.707	9.327
Absorptivity coefficient	$(\mu mol/mol\cdot m)^{-1}$	1.044×10^{-3}	5.534×10^{-4}	2.291×10^{-4}	2.343×10^{-4}
	m^2/mg	1.893×10^{-4}	1.003×10^{-4}	4.152×10^{-5}	4.246×10^{-5}

Figure 10 is a plot of absorptivity coefficient and fractional uncertainty (Type-A, U_A, 2σ). In general expanded type-A uncertainties were approximately 2% of the absorptivity coefficient, as seen in Figures 11 and 12. Figure 11 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 11, the coefficients are $a = 1.85 \times 10^{-2}$, and $b = 4.24 \times 10^{-7}$ (Table 7).
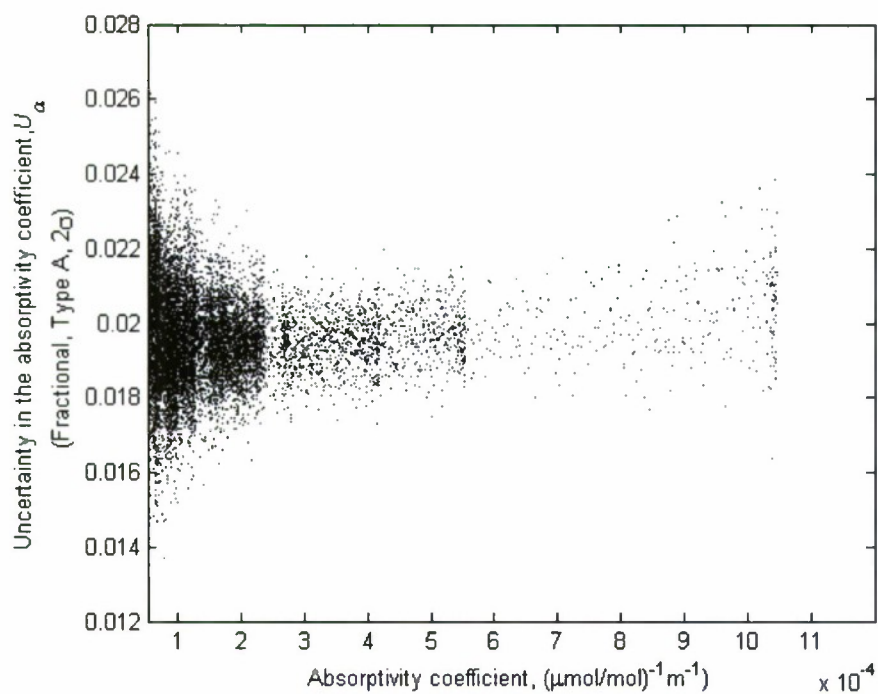
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Figure 10. Absorption Coefficient and Type-A Uncertainty (Fractional, 2σ) for 2-(Diethylamino)ethanethiol
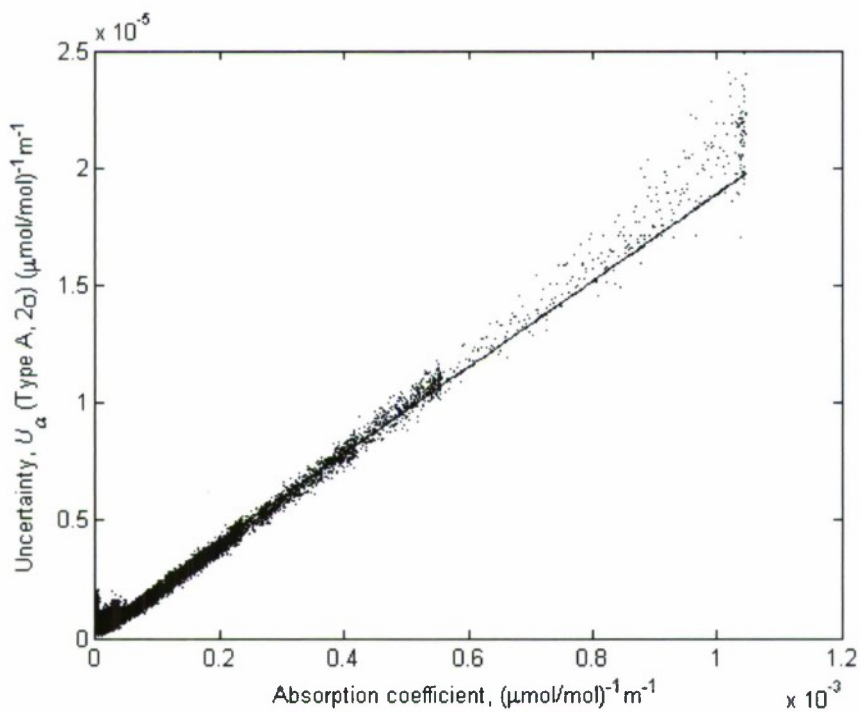

Figure 11. Absorption Coefficient and Type-A Uncertainty (2σ) for 2-(Diethylamino)ethanethiol

Table 7. Type-A Statistical Uncertainty for 2-(Diethylamino)ethanethiol
Vapor-Phase Absorptivity Coefficient

Type-A Uncertainty $2\sigma \approx ma + b$	
Slope m	Intercept b
1.85×10^{-2}	4.24×10^{-7}

The sources of uncertainty and their fractional values are given in Table 8. Among the Type B uncertainties, the detector nonlinearity dominates at 0.01 (1σ).

Table 8. Uncertainties in Absorptivity Coefficient of 2-(Diethylamino)ethanethiol
where $\alpha \geq 0.0000523$ $(\mu mol/mol)^{-1}m^{-1}$

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	0.005	Mass rate
ΔD	0.005	Dilution rate
$\Delta purity$	0.0075	Purity of vapor
Δ_B	0.031	Combined type B (2σ)
Δ_A	0.027	Type-A deviation (2σ)

3.3   Absorptivity Coefficient of 2-(Diisopropylamino)ethanethiol

Four trials were run to obtain spectra at 12 CL. The constant temperature bath was maintained at 23 °C for all four trials.

Beer's Law plots were computed for lines at 2974.4 cm^{-1} and 1165.9 cm^{-1} (Figures 12 and 13). The data were well fitted, with little scattering evident.

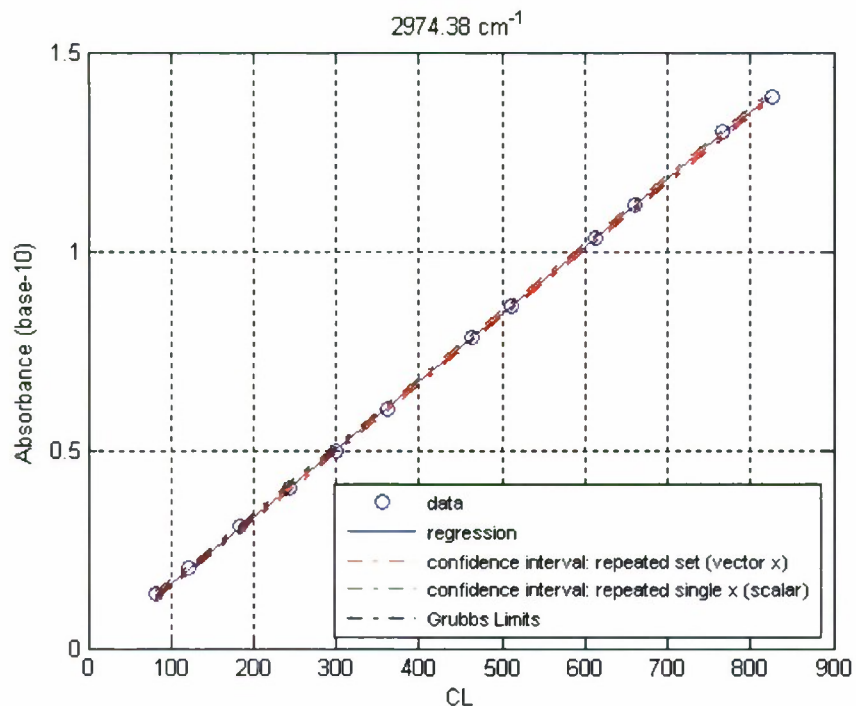Figure 12. Beer's Law Plot of 2974.4 cm^{-1} Line in the Vapor-Phase Spectrum
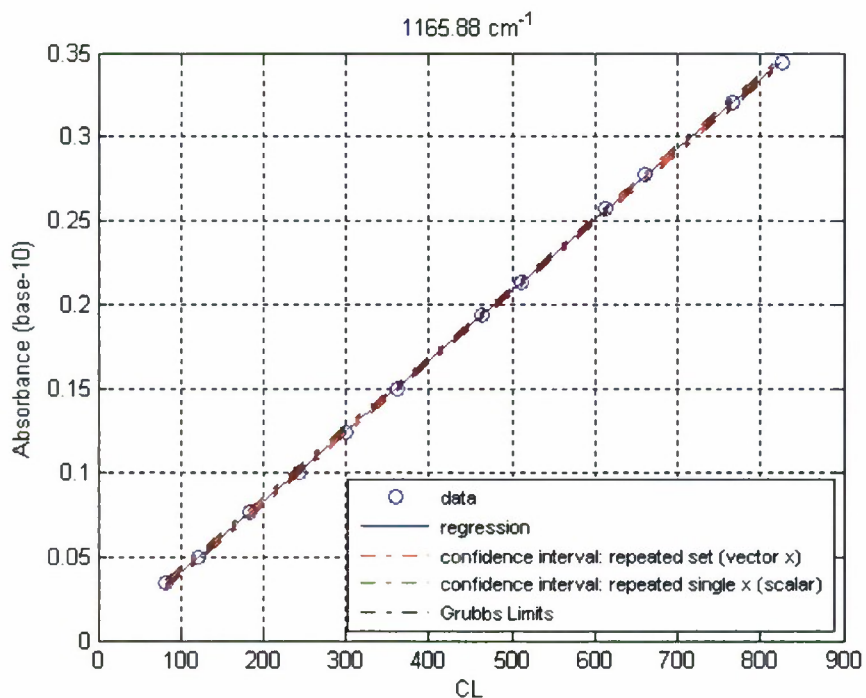of 2-(Diisopropylamino)ethanethiol

Figure 13. Beer's Law Plot of 1165.9 cm^{-1} Line in the Vapor-Phase Spectrum
of 2-(Diisopropylamino)ethanethiol

The composite spectrum (absorptivity coefficient) was computed using spectra
with CL ranging from 83 to 826 μmol/mol(m) (corrected to 296 K and 101325 Pa). Figure 14 is

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the plotted absorptivity coefficient (α), and Type-A uncertainty for the computed spectral range. The figures are plotted with α in (μmol/mol)$^{-1}$m^{-1}. To obtain α in (mg·m^{-2})$^{-1}$, multiply the values in the ordinate scale of Figure 14 by 0.1497.
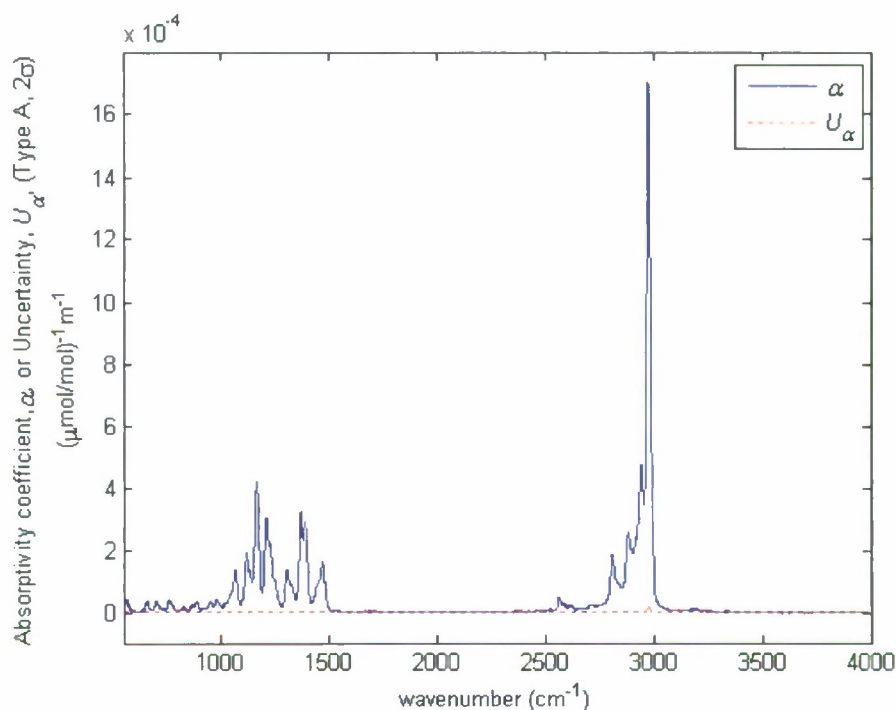

Figure 14. Absorptivity Coefficient and Statistical Uncertainty (Type-A, 2σ) for 2-(Diisopropylamino)ethanethiol

Table 9 provides the absorptivity coefficients in (μmol/mol)$^{-1}$m^{-1} and (mg/m²)$^{-1}$ for selected bands in wavenumber (cm^{-1}) and micrometers (μm).

Table 9. Absorptivity Coefficient of 2-(Diisopropylamino)ethanethiol for Selected Bands

	Wavenumber/ cm^{-1}	2974.26	1369.40	1210.00	1165.83
	Wavelength/μm	3.362	7.302	8.264	8.578
Absorptivity coefficient	(μmol/mol·m)$^{-1}$	1.697×10^{-4}	3.262×10^{-4}	3.026×10^{-4}	4.199×10^{-4}
	m²/mg	2.540×10^{-4}	4.883×10^{-5}	4.530×10^{-5}	6.286×10^{-5}

In general expanded type-A uncertainties were approximately <1% of the absorptivity coefficient, as seen in Figures 15 and 16. Figure 15 is a plot of absorptivity coefficient and fractional uncertainty (Type-A, U_A, 2σ). Figure 16 is a plot of the absorptivity coefficient and uncertainty and 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 16, the coefficients are $a = 5.14 \times 10^{-3}$, and $b = 8.83 \times 10^{-7}$ (Table 10).
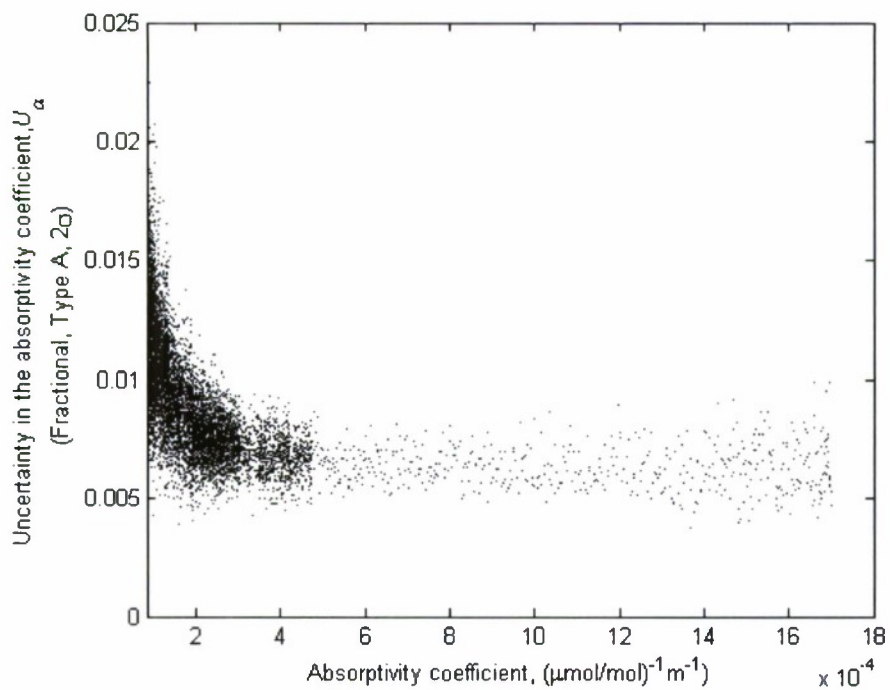
Figure 15. Absorption Coefficient and Type-A Uncertainty (Fractional, 2σ) for 2-(Diisopropylamino)ethanethiol
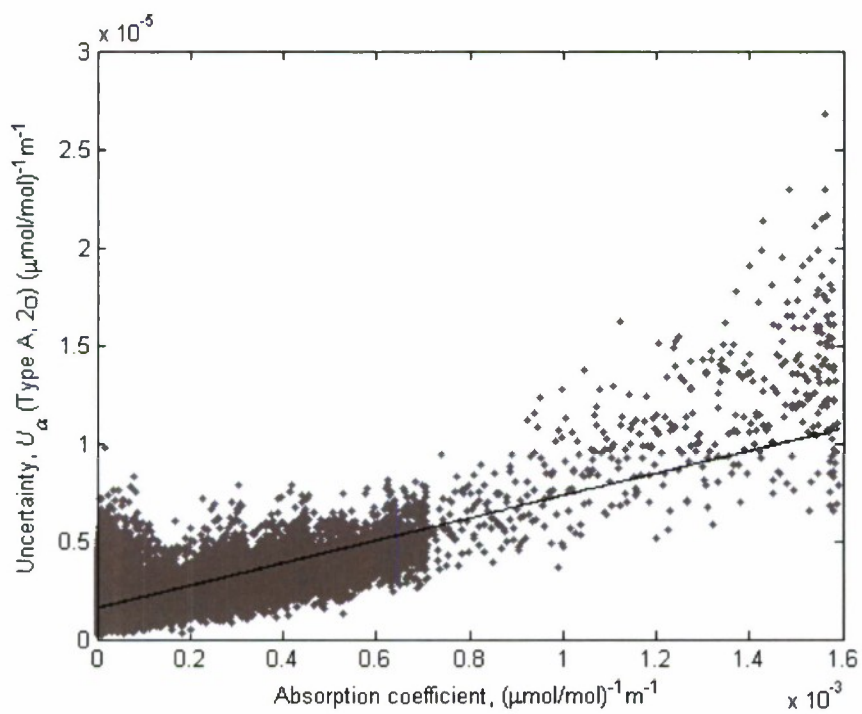

Figure 16. Absorption Coefficient and Type-A Uncertainty (2σ) for 2-(Diisopropylamino)ethanethiol

Table 10. Type-A Statistical Uncertainty for 2-(Diisopropylamino)ethanethiol
Vapor-Phase Absorptivity Coefficient

Type-A Uncertainty $2\sigma \approx ma + b$	
Slope m	Intercept b
5.14×10^{-3}	8.83×10^{-7}

The sources of uncertainty and their fractional values are given in Table 11. Among the Type B uncertainties, the detector nonlinearity dominates at 0.01 (1σ).

Table 11. Uncertainties in Absorptivity Coefficient of
2-(Diisopropylamino)ethanethiol where $\alpha \geq 0.000085$ $(\mu mol/mol)^{-1}m^{-1}$

Symbol	Fractional deviation	Source
ΔL	0.005	Pathlength
ΔT	0.0006	Temperature of White cell
ΔP	0.002	Pressure
ΔFTIR	0.0005	Drift in spectrometer
ΔNL	0.01	Nonlinearity in detector
ΔMR	0.005	Mass rate
ΔD	0.005	Dilution rate
Δpurity	0.005	Purity of feedstock
Δ_B	0.029	Combined type B (2σ)
Δ_A	0.016	Type-A deviation (2σ)

4.   CONCLUSIONS

The vapor-phase absorptivity coefficient of three thiol compounds related to V-type nerve agents were measured within the range 4000-550 cm^{-1}. Type-A uncertainties, expanded to 2σ, were <3% of the absorptivity coefficient at intensities ≥5% of the most intense absorption feature for all three compounds, while Type-B uncertainties were <3%.

To our knowledge the work discussed in this report represents the first time the high resolution vapor-phase absorptivity coefficients of these compounds have been measured in the mid-infrared.

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