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VAPOR-PHASE INFRARED ABSORPTIVITY COEFFICIENT OF O,S-DIETHYL METHYLPHOSPHONOTHIOATE

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14. ABSTRACT-LIMIT 200 WORDS We measured the vapor-phase absorptivity coefficient of O,S-diethyl methylphosphonothioate 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 nuclear magnetic spectroscopy. We describe the experimental method used to acquire the individual spectra that were used to produce the composite spectrum and summarize the statistical uncertainties in the data.					
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Infrared	Absorptivity coefficient	Quantitative	O,S-diethyl methylphosphonothioate		
FTIR	CAS 2511-10-6	Saturator cell	Vapor-phase		
VX	EA-5533	Vapor pressure	OSDEMP		
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EXECUTIVE SUMMARY

We measured the vapor-phase absorptivity coefficient of O,S-diethyl methylphosphonothioate (EA-5533) in the mid-infrared (IR). 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 gas chromatography (GC) and nuclear magnetic resonance spectroscopy. The concentration of the compound in the vapor was determined with a gravimetric method. The purity of the vapor was concurrently verified by thermal desorption GC. Nine 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: 2.6 % and Type-B: 2.8 % of the absorptivity coefficient. To our knowledge, this is the first time that the vapor-phase absorptivity coefficient of this compound has been measured in the mid-IR.

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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 January 2009.

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VAPOR-PHASE INFRARED ABSORPTIVITY COEFFICIENT OF O,S-DIETHYL METHYLPHOSPHONOTHIOATE

1. INTRODUCTION

We determined the high resolution vapor-phase absorptivity coefficient of the organophosphonothioate ester, O,S-diethyl methylphosphonothioate (OSDEMP) in the spectral range of 4000-550 cm^{-1} in units of $(\mu\text{mol/mol})^{-1}\text{m}^{-1}$ and made an initial computation of the uncertainties of the data. To our knowledge, the high resolution vapor-phase absorptivity coefficient of this compound has not previously been measured.

OSDEMP has the Chemical Abstracts Service (CAS) Registry Number 2511-10-6 and is indexed under the name: phosphonothioic acid, methyl-, O,S-diethyl ester. The molecular formula is $\text{C}_5\text{H}_{13}\text{O}_2\text{PS}$, and it has a formula weight of 168.19. Other synonyms for the compound include O,S-diethyl methylphosphonothioic acid; OSDEMP; and EA-5533. The calculated boiling temperature is 223 $^{\circ}\text{C}$.¹ The structure is shown in Figure 1.

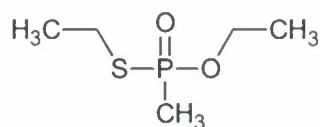


Figure 1. Structure of O,S-Diethyl Methylphosphonothioate (OSDEMP)

OSDEMP is an impurity in the nerve agent, O-ethyl-S-(2-diisopropylamino)ethyl methylphosphonothioate (VX), observed at an average concentration of 0.89 % in U.S. ton containers tested during the evaluation of technologies for disposal of U.S. chemical weapons stocks.² The compound has a significant toxicity in animal tests, with an LD_{50} reported of: rat: oral, 6.0 mg/kg; dog: iv, 5,620 $\mu\text{g}/\text{kg}$; mouse: iv, 1 mg/kg; and rabbit: iv, 2,480 $\mu\text{g}/\text{kg}$.³

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 for measuring the volatility of chemical warfare (CW) agent related compounds.⁴

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,⁵ as well as a variety of CW agent related compounds.^{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 boil off of a bulk liquid nitrogen tank, across an alumina wicking mechanism in a glass holder filled with the analyte. This results in a saturated vapor-liquid equilibrium of the analyte on the downstream side of the saturator cell results, with the concentration of the analytes dependent upon 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 controller (Brooks Instrument Co., Hatfield, PA) to maintain a constant flow to the saturator cell. A second mass flow controller was used 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 Model IFS/66V (Bruker Optics, Billerica, MA) 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 $15798\text{--}0\text{ cm}^{-1}$ 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 pathlengths of 4.057, 5.377, and 8.024 m. The temperature of the White cell was maintained at $23 \pm 0.1\text{ }^{\circ}\text{C}$ 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 Institutes of Standards and Technology (NIST) traceable digital barometers and thermometers, and all data were archived. Concentration-pathlength products (CL) were computed in units of $\mu\text{mol/mol(m)}$ (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 $1.0132 \times 10^5\text{ Pa}$ (760 Torr) using the ideal gas law.

2.2 Feedstock.

The material used to generate the vapor streams for the experiments was supplied by the Chemical Sciences Division at the U.S. Army Edgewood Chemical Biological Center (ECBC). An aliquot of the feedstock was analyzed by nuclear magnetic resonance (NMR) spectroscopy (^1H , ^{13}C , and ^{31}P). The phosphorous mole purity was 97.6%, including an

unidentified phosphorous acid at 0.5%. Analysis by gas chromatography-mass spectrometry (GC-MS) gave: O,S-diethyl methylphosphonothioate, 98.4%; O,O,S-triethyl phosphorothioate, 0.8%; O-ethyl-S-methyl methylphosphonothioate, 0.5%; dimethyl methylphosphonate, 0.2%; and two non-phosphorous impurities at a total of <0.2%. Examination of the vapor-phase spectra of the effluent from the saturator cell initially showed the presence of water vapor, with absorption bands nearly as intense as those from the OSDEMP. The material was purged for several days with 75 mL/min of dry nitrogen. Thereafter, samples of the effluent from the White cell analyzed by thermal desorption-gas chromatography (GC) indicated a purity of 98.1%. Because the phosphorous acid shown in the NMR analysis would not be sufficiently volatile to contribute to the vapor, this result was consistent with the results of NMR analysis. We used a purity of $98.1 \pm 0.5\%$ to calculate the ratio of OSDEMP in the vapor.

3. RESULTS AND DISCUSSION

3.1 Absorptivity Coefficient.

Four trials were run to obtain spectra at nine 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 23.5 °C for all three experiments.

Trace water vapor was observed in the first two spectra only, and the features were removed by spectral subtraction. Baseline corrections of spectra were performed with a linear subtraction. 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 81-661 $\mu\text{mol}/\text{mol}(\text{m})$ (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, 1047 and 720.6 cm^{-1} , were calculated using MatLab. At least for these two spectral lines, 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 Outliers⁹ (Figures 2 and 3).

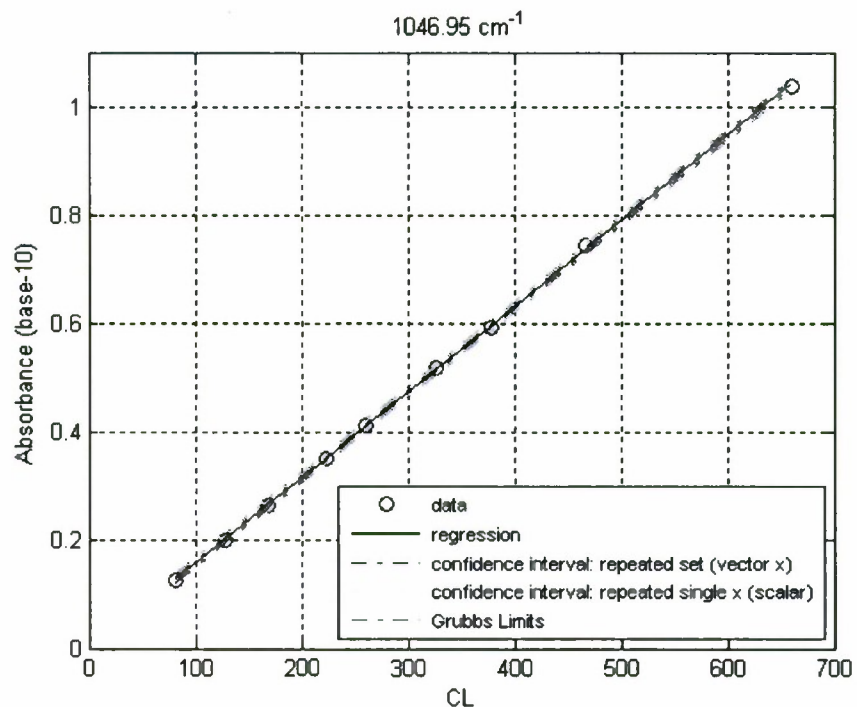


Figure 2. Beer's Law Plot of 1047 cm^{-1} Line in the Vapor-Phase Spectrum of O,S-Diethyl Methylphosphonothioate

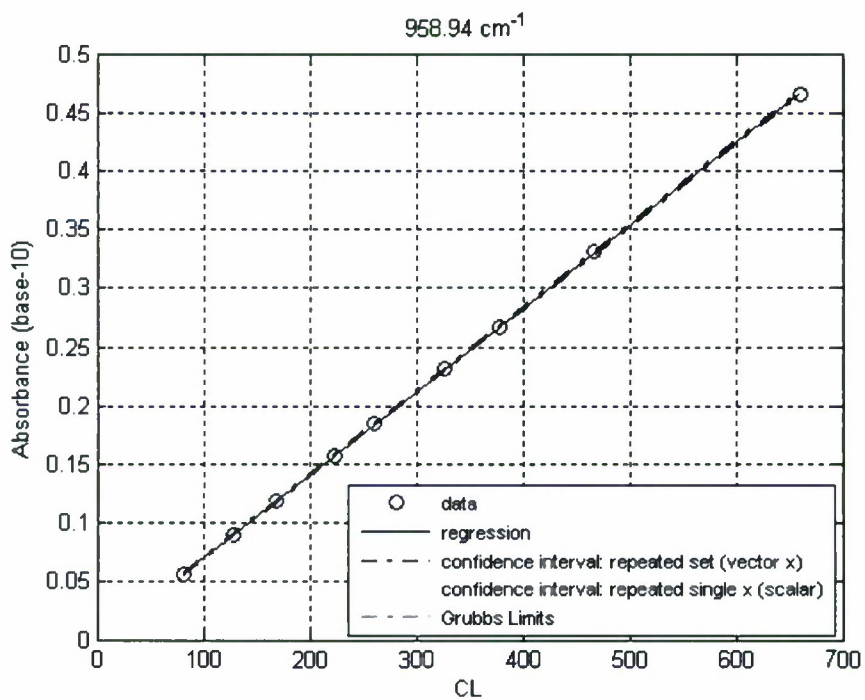


Figure 3. Beer's Law Plot of 959 cm^{-1} Line in the Vapor-Phase Spectrum of O,S-Diethyl Methylphosphonothioate

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 $A \leq 1.048$, 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 $(\mu\text{mol}/\text{mol})^{-1}\text{m}^{-1}$. To obtain α in $(\text{mg}/\text{m}^2)^{-1}$, multiply the values in the mantissa of Figure 4 by 0.1436. This factor is derived from eq 1 using the molecular weight of OSDEMP (168.19).

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

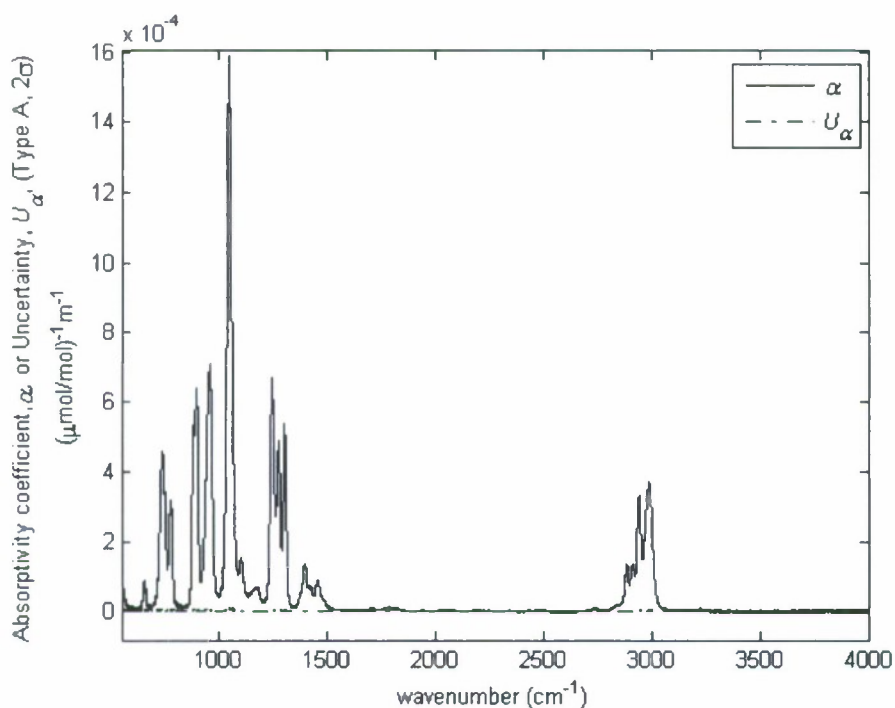


Figure 4. Absorptivity Coefficient and Statistical Uncertainty (Type-A, 2σ) for O,S-Diethyl Methylphosphonothioate

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

Table 1. Absorptivity Coefficient of O,S-Diethyl Methylphosphonothioate for Selected Bands

	Wavenumber cm^{-1}	2989.51	1246.40	1046.86	958.70
	Wavelength/ μm	3.345	8.023	9.552	10.431
Absorptivity coefficient	$(\mu\text{mol}/\text{mol})^{-1}\text{m}^{-1}$	3.660E-04	6.694E-04	1.580E-03	7.067E-04
	m^2/mg	5.256E-05	9.611E-05	2.268E-04	1.015E-04

In general, expanded Type-A uncertainties were approximately 1-2 % 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, $U_A, 2\sigma$) (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: $a = 5.75 \times 10^{-3}$, and $b = .58 \times 10^{-6}$ (Table 2).

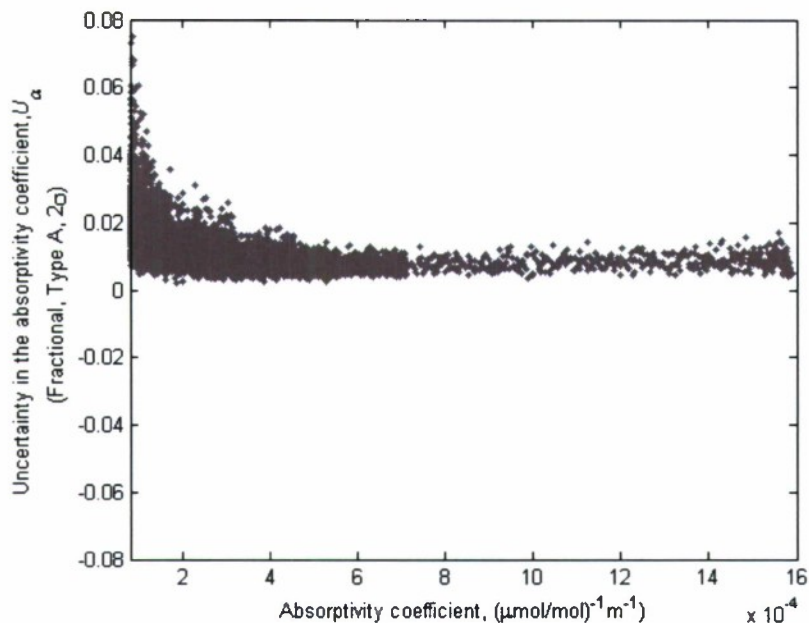


Figure 5. Absorption Coefficient (Abscissa) and Type-A Uncertainty (Fractional, 2σ) for O,S-Diethyl Methylphosphonothioate

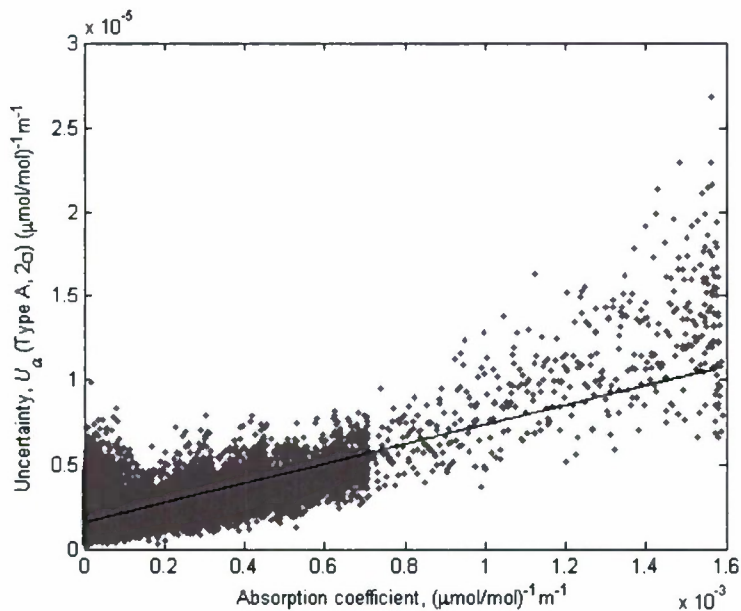


Figure 6. Absorption Coefficient (Abscissa) and Type A Uncertainty (2σ) for O,S-Diethyl Methylphosphonothioate

Table 2. Type-A Statistical Uncertainty for O,S-Diethyl Methylphosphonothioate Vapor-Phase Absorptivity Coefficient

Type-A Uncertainty $2\sigma \approx ma+b$	
Slope m	Intercept b
5.75×10^{-3}	1.58×10^{-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.

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

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 detector nonlinearity dominates at 0.01 (1σ).

Table 3. Uncertainties in Absorptivity Coefficient of O,S-Diethyl Methylphosphonothioate from ECBC Data Where $\alpha \geq 0.000079$ ($\mu\text{mol/mol})^{-1} \text{m}^{-1}$

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	0.0025	Purity of feedstock
Δ_B	0.028	Combined type B (2σ)
Δ_A	0.026	Type-A deviation (2σ)

3.2 Vapor Pressure.

A literature search indicated that the vapor pressure of O,S-diethyl methylphosphonothioate had previously been measured within a range of $t = (18 \text{ to } 167) \text{ }^\circ\text{C}$.

Measurements in the range of $t = (18.0 \text{ to } 43.8) \text{ }^\circ\text{C}$ were made using Knudsen effusion,¹ while those at higher temperatures were acquired using differential thermal analysis (DTA).^{*} The saturator cell technique has been used extensively at ECBC to measure the vapor pressure of a variety of CW agent related compounds^{10,11,12} and has been adopted as method of measuring vapor pressure by the American Society for Testing and Materials.¹³ Given the lack of vapor pressure measurements at temperatures $< 18 \text{ }^\circ\text{C}$ and the availability of a purged saturator cell filled with the compound, we believed that it would be useful to obtain additional data vapor pressure.

Vapor pressure data was obtained using the saturator cell at three temperatures: $t = (8, 13, \text{ and } 23.4) \text{ }^\circ\text{C}$. The measurement at $23.4 \text{ }^\circ\text{C}$ was run to give a point that would bracket the historical data. A carrier rate of $80 \text{ cm}^3 \cdot \text{min}^{-1}$ (referenced to $21.1 \text{ }^\circ\text{C}$) was used for all three determinations, with the carrier rate, pressure, and bath temperature recorded continuously in Labview. The data from the three vapor pressure measurements is shown in Table 4.

Table 4. Data from Measurements of Vapor Pressure of O,S-Diethyl Methylphosphonothioate in our Laboratory. P_{cell} = Pressure in the saturator cell (measured as ambient pressure using a digital barometer); $\Delta \text{ Mass}$ = change in mass of saturator cell during the experiment; P_{OSDEMP} = measured vapor pressure of the OSDEMP.

$t/^\circ\text{C} (T/\text{K})$	P_{cell}/Pa	$\Delta \text{ Mass}/\text{g}$	P_{OSDEMP}/Pa
8 (281.15)	132244	0.0742	3.19
13 (286.15)	131821	0.0817	5.20
23.4 (296.55)	130549	0.1027	13.03

The data from Table 4 were pooled with the data from references 1 and 10. The coefficients for the Antoine equation¹⁴ were computed from the least squares fit of the data points using MatLab. The computed vapor pressure curve, Antoine coefficients, and the raw data points used to fit the curve are shown in Figure 7. The experimental vapor pressure measurements from our work, as well as the literature data, and fractional deviations of the calculated values from the experimental measurements are shown in Table 5.

^{*}Savage, J.J. Edgewood Arsenal: EA Notebook No. 8068, p. 31, unpublished data, 2009.

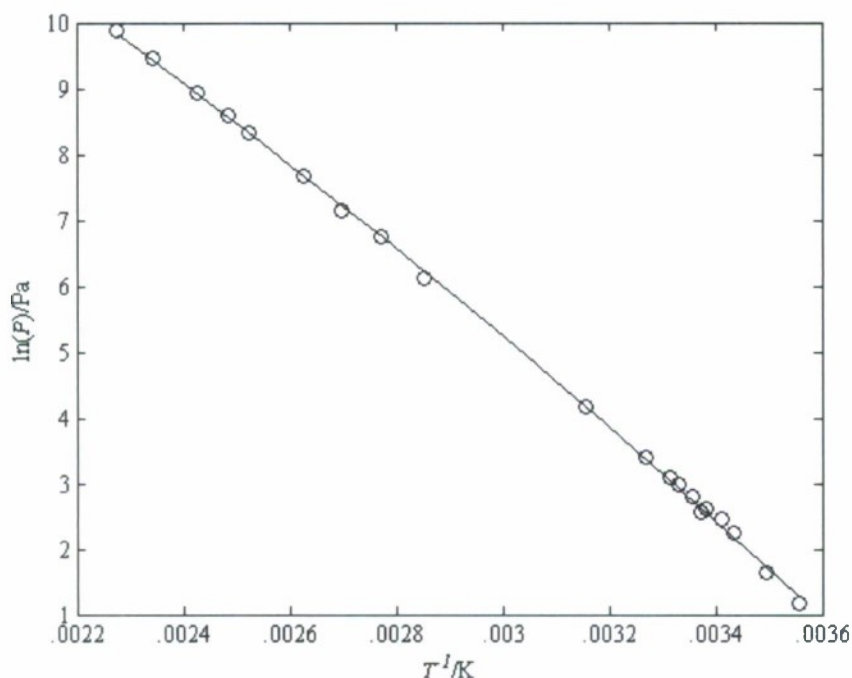


Figure 7. Vapor Pressure of O,S-Diethyl Methylphosphonothioate as a Function of the Inverse of the Absolute Temperature. The circles represent the experimental values of the vapor pressure from this work and refs 10 and 11. The line represents the best fit of the Antoine equation: $\ln(P)/Pa = a - b(c + T)$, where $a = 20.983$; $b = 4063.03$; and $c = -75.068$. For $P/Torr$, substitute $a = 16.094$.

The estimated uncertainty of the measurements in our work encompass the uncertainties in: (1) the moles of OSDEMP ($n_{analyte}$) (including its purity); (2) moles of carrier ($n_{carrier}$); (3) pressure in the saturator cell (P_{cell}); and (4) temperature of the water bath. The fractional uncertainty in the mass measured by the Sartorius analytical balance is $0.0002\text{ g}/0.0742\text{ g} \times 100 = 0.27\%$, and we used an uncertainty of 0.25% for the purity of the vapor (both at 1σ). The uncertainty in the number of moles of carrier gas was dominated by the uncertainty in the rate of the carrier, 0.5% for the Brooks mass flow controller used. The uncertainty in the digital barometer was 0.1% (P_{cell}). Determining the effect of temperature is a bit more complex. It can be estimated however by the effect of a change in temperature on the pressure. Although we were able to verify the temperature of the water bath to within 0.2 °C using a liquid in glass thermometer, the controller has a precision of ± 0.5 °C. At 23.4 °C, this represents an uncertainty of 5.0% of the vapor pressure; whereas at 8 °C, the uncertainty becomes 4.1%. The uncertainty in the temperature of the OSDEMP, therefore, dominates. The combined uncertainty, expanded to a confidence interval of 95% was calculated as follows: $(n_{analyte}^2 + n_{purity}^2 + P_{cell}^2 + T^2)^{1/2} \times 2 = 4.6\%$ (using a mean value of 4.55% for the uncertainty arising from the imprecision in the water bath).

Table 5. Data Used to Calculate the Antoine Equation for the Vapor Pressure of O,S-Diethyl Methylphosphonothioate, Calculated Values of Vapor Pressure, and Deviations

T/K	$P_{\text{expt}}/\text{Pa}$	P_{calc}	$(P_{\text{expt}}-P_{\text{calc}})/P_{\text{calc}} \times 100$
281.15	3.19	3.55	-10.3
286.15	5.20	5.67	-8.2
291.15	9.60	8.85	8.5
293.15	11.73	10.51	11.6
295.75	13.60	13.09	3.9
296.55	13.03	13.99	-6.8
297.85	16.53	15.57	6.2
300.15	20.00	18.76	6.6
301.85	22.13	21.48	3.0
305.95	30.00	29.53	1.6
316.95	65.33	65.73	-0.6
350.65	453.3	512.7	-11.6
360.65	846.6	859.1	-1.5
370.65	1280	1390	-7.9
380.65	2133	2180	-2.1
396.15	4133	4142	-0.2
402.15	5333	5224	2.1
412.15	7666	7552	1.5
426.65	12866	12415	3.6
439.65	19598	18747	4.5

As seen in Table 5, the experimental vapor pressure values measured in our work appear to be lower than those reported in reference 1, at least in the range $t = (8 \text{ to } 23.4) \text{ }^\circ\text{C}$. Because the differences are larger than the fractional uncertainty that we have calculated for our measurements, the reason for the apparent bias is not clear. Vapor pressure measurements that rely upon measurements of change in mass (i.e., saturator cell and Knudsen effusion) are sensitive to the presence of impurities with vapor pressures different from that of the primary analyte. The authors of reference 1 reported a purity of 97.9%, analyzed by GC only, for the material used in their tests. We found that, at least initially, water represented a significant fraction of the mass loss from the saturator cell because of its higher vapor pressure relative to the phosphonothioate. The water content of the OSDEMP was apparent only by the presence of the distinctive absorption bands in the vapor-phase IR spectra, as it was not measured by either GC or NMR during the initial tests of the purity. It is possible, therefore, that differences in water content or other volatile impurities may have caused the differences in the experimental values of the vapor pressure of the compound reported by the different researchers.

The calculated value of the vapor pressure of O,S-diethyl methylphosphonothioate at 25 °C is 16.0 Pa (0.120 Torr). Table 4 of reference 1 gives a value of 0.0571 Torr at 25 °C. Because the calculated value for the vapor pressure of OSDEMP using the Antoine coefficients in reference 1 is 0.126 Torr, this is apparently a typographical error.

4. CONCLUSIONS

The vapor-phase absorptivity coefficient of O,S-diethyl methylphosphonothioate was measured within the range 4000-550 cm^{-1} . Type-A uncertainties, expanded to 2σ , are $<2.6\%$ of the absorptivity coefficient at intensities $\geq 5\%$ of the most intense absorption feature, with a Type-B uncertainty of 2.8%.

The vapor pressure of the compound was also measured at $t = (8, 13, \text{ and } 23.4 \text{ }^\circ\text{C})$, and the Antoine coefficients were recalculated. The calculated vapor pressure of the compound at $25 \text{ }^\circ\text{C}$ is 16.0 Pa (0.120 Torr). This contrasts with the literature value of 0.126 Torr from reference 1. The calculated boiling temperature is $231.55 \text{ }^\circ\text{C}$. Because this value was calculated from measurements made at a maximum temperature of $166.5 \text{ }^\circ\text{C}$, the uncertainty is unknown.

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