



# EDGEWOOD CHEMICAL BIOLOGICAL CENTER

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## SELECTED PHYSICAL PROPERTIES OF O-ETHYL S-[(2-DIETHYLAMINO) ETHYL] METHYLPHOSPHONOTHIOATE (VM)

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<b>14. ABSTRACT:</b> The physical properties of <i>O</i> -ethyl <i>S</i> -[(2-diethylamino) ethyl] methylphosphonothiolate (VM), which is structurally similar to <i>O</i> -ethyl <i>S</i> -[(2-diisopropylamino) ethyl] methylphosphonothiolate (VX) and <i>O</i> -isobutyl <i>S</i> -[(2-diethylamino) ethyl] methylphosphonothiolate (RVX), were investigated to address concerns regarding reliability of the literature data. These physical properties include vapor pressure, density, viscosity, surface tension, and flash point. Correlations as a function of temperature were derived, where possible, and comparisons were made to literature data for VM, VX, and RVX.					
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Heat of vaporization				Surface tension	
Physical properties				Melting point	
Chemical Abstracts Service (CAS)				Vapor pressure	
Differential scanning calorimetry (DSC)				Viscosity	
<i>O</i> -ethyl <i>S</i> -[(2-diethylamino) ethyl] methylphosphonothiolate (VM), CAS no. 21770-86-5				Volatility	
<i>O</i> -ethyl <i>S</i> -[(2-diisopropylamino) ethyl] methylphosphonothiolate (VX), CAS no. 50782-69-9				Flash point	
<i>O</i> -isobutyl <i>S</i> -[(2-diethylamino) ethyl] methylphosphonothiolate (RVX), CAS no. 159939-87-4				Boiling point	
Denuder–liquid chromatography–mass spectrometry (denuder–LC–MS)					
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## **PREFACE**

The work described in this report was authorized under Defense Threat Reduction Agency project number CB3662. The work was started in February 2012 and completed in September 2012. This work is documented in U.S. Army Edgewood Chemical Biological Center (ECBC; Aberdeen Proving Ground, MD) laboratory notebook no. 10-0041.

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# SELECTED PHYSICAL PROPERTIES OF *O*-ETHYL *S*-[(2-DIETHYLAMINO) ETHYL] METHYLPHOSPHONOTHIOATE (VM)

## 1. INTRODUCTION

To combat emerging chemical and biological (CB) threats, modeling and simulation efforts can be very useful tools to help facilitate prediction of downwind hazard and environmental fate, evaluation of protective equipment and filter performance, and selection of lower toxicity materials to mimic the behavior of highly toxic materials. Proper assessment of these processes requires the use of physical property data. Because these modeling efforts are only as good as the imported data, it is critical to have accurate, validated physical property information on these materials of interest.

*O*-ethyl *S*-[(2-diethylamino) ethyl] methylphosphonothiolate (VM), also known as EA 1664, is a low-volatility material that is similar in structure, but somewhat less stable than *O*-ethyl *S*-[(2-diisopropylamino) ethyl] methylphosphonothiolate (VX) and *O*-isobutyl *S*-[(2-diethylamino) ethyl] methylphosphonothiolate (RVX). The chemical structures of these materials are shown in Figure 1.

Currently, the physical property data available in the literature for VM consist of density, viscosity, surface tension, and several reduced-pressure boiling points that were measured in the late 1950s at the Army Chemical Center, MD using samples of unstated purity.<sup>1</sup> More recent data include vapor pressure measured in the ambient range using the denuder–liquid chromatography–mass spectrometry (denuder–LC–MS) technique<sup>2</sup> and quantitative solubility data.<sup>3</sup> A 1983 compilation by Samuel et al.<sup>4</sup> contains a value for the flash point<sup>5</sup> of VM that we judge to be questionable and a value for the vapor pressure at 25 °C from an unidentified source.

Initial attempts to determine the ambient temperature vapor pressure for VM at the U.S. Army Edgewood Chemical Biological Center (ECBC; Aberdeen Proving Ground, MD) using the modified ASTM International (West Conshohocken, PA) saturator, Dynatherm gas chromatographic method<sup>6</sup> (Dynatherm Analytical Instruments from CDS Analytical, Inc.; Oxford, PA) were unsuccessful due to thermal instability of the compound during the desorption portion of the experiment.<sup>7</sup>

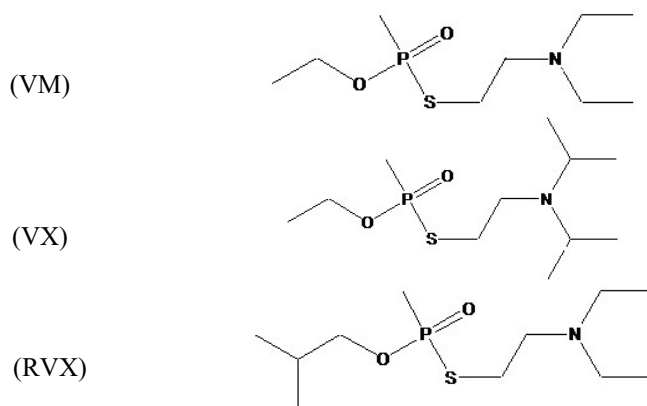


Figure 1. Chemical structures of VM, VX, and RVX.

To address uncertainties associated with the VM literature data, the Chemical Analysis and Physical Properties Branch of the Research and Technology Directorate at ECBC investigated selected physical properties of VM samples of known purities. These physical properties included density, viscosity, surface tension, flash point, and high-temperature vapor pressure measured using differential scanning calorimetry (DSC). The new density, viscosity, surface tension, and flash point data are compared to the literature data herein. New DSC vapor pressure data were combined with recent ambient denuder–LC–MS data and fitted to a single, consolidated Antoine equation over the experimental range. Calculated vapor pressures, heats of vaporization, and volatilities as functions of temperature are presented as well as a comparison of the physical properties of VM to those of VX and RVX.

## 2. EXPERIMENTATION

### 2.1 Materials

Table 1 provides sample information for the four different lots of VM that were used for this work. All of these samples were synthesized in ECBC laboratories.

Table 1. VM Sample Information

Property	Lot Number	Purity (%)
Vapor Pressure, Density, Viscosity, Surface Tension	04-0057-68 (Bottle 1)	99
Vapor Pressure	04-0046-101.1	96
Flash Point (Sample 1)	04-0057-68 (Bottle 2)*	80
Flash Point (Sample 2)	04-0046-101.2	96
Flash Point (Sample 3)	04-0046-102.1	95

\*This sample was recovered after density, viscosity, and surface tension measurements. Purity was retested before flash point testing and found to be 80%.

## **2.2 Methods**

### **2.2.1 Vapor Pressure by DSC**

The vapor pressure of VM was determined using DSC in accordance with ASTM E 1782, *Standard Test Method for Determining Vapor Pressure by Thermal Analysis*.<sup>8</sup> For this work, a TA Instruments (New Castle, DE) Q10P Differential Scanning Calorimeter was used. Before sample measurements were performed, the DSC was calibrated using ASTM E 967, *Standard Test Method for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers*.<sup>9</sup> The vapor pressure measurement consists of heating a small specimen of the test material in the DSC cell through the boiling point at a controlled rate, while the pressure (vacuum) in the cell is held constant. At the boiling point, the vaporized specimen escapes from the sample pan through a small orifice (“pinhole”) in the lid of the sample pan. The energy associated with the transition of the specimen from liquid to vapor is recorded as a sharp boiling endotherm. The boiling point is taken at the intersection of tangents to the endotherm at the onset of boiling. The experimental pressure, which is measured using a mercury manometer, is the pressure in the cell as the specimen boils. This process is repeated with new specimens at a series of different pressures.

The DSC method was originally recommended for use with hermetic-type sealable sample pans that have a single 50–75  $\mu\text{m}$  pinhole in the lid for pressures between 5 kPa and 2 MPa (37 to 15000 Torr). At lower pressures, boiling endotherms broaden, which complicates accurate determination of extrapolated onset temperatures from the intersection of tangents to the curve. Peak-broadening reflects the loss of equilibrium and self-pressurization as the rate of specimen vaporization inside the pan exceeds the rate at which molecules exit through the pinhole. The use of larger pinholes at lower pressures has been shown to restore peak sharpness that is consistent with a return to equilibrium boiling conditions.<sup>10</sup> Recent quantitative studies with 1-octanol<sup>11</sup> have demonstrated that accurate results comparable to those above 5 kPa can be achieved at pressures as low as 0.2 kPa (1.5 Torr), if pinholes up to 350  $\mu\text{m}$  are used.

### **2.2.2 Density Method**

Liquid density was determined at 25, 35, and 50  $^{\circ}\text{C}$  in accordance with ASTM D 4052, *Standard Test Method for Density and Relative Density of Liquids by Digital Density Meter*,<sup>12</sup> using an Anton Paar, Inc. (Ashland, VA) model DMA 58 Digital Density Meter. This measurement is based on the change in frequency of an oscillating U-tube due to the presence of the test sample. Before sample measurements were obtained, the instrument was calibrated using air and distilled water at the experimental temperature, and proper instrument operation was validated by determining the density of toluene, which is the National Institute of Standards and Technology (NIST; Gaithersburg, MD) density standard.

### **2.2.3 Viscosity Method**

Viscosity was determined at 25, 35, and 50  $^{\circ}\text{C}$  in accordance with ASTM D 445, *Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (the Calculation of Dynamic Viscosity)*<sup>13</sup> using a Cannon-Manning semi-micro viscometer and

Cannon CT-1000 constant temperature bath (Cannon Instrument Company; State College, PA). The flow rate of a liquid under gravity is measured through a calibrated glass capillary viscometer, which was calibrated by the manufacturer.

#### **2.2.4 Surface Tension Method**

Surface tension measurements were conducted at 25 °C using a Krüss (Hamburg, Germany) K12 tensiometer with an external Lauda RM-6 circulating bath (Lauda-Brinkman, LP; Delran, NJ) in accordance with ASTM D 1331, *Standard Test Methods for Surface and Interfacial Tension of Solutions of Paints, Solvents, Solutions of Surface-Active Agents, and Related Materials*.<sup>14</sup> This is a force measurement in which the normal force acting on the liquid surface allows the liquid to conform to its smallest surface area. For this work, a small rectangular glass plate is lowered parallel to the liquid surface. The liquid is then raised until it just touches the bottom edge of the plate. Force on the plate increases due to wetting of the liquid against the plate. If the contact angle between the liquid and the plate is zero due to perfect wetting, then the surface tension is determined.<sup>15</sup> Proper operation of the tensiometer was validated using diethyl oxalate.

#### **2.2.5 Flash Point Method**

Flash point is defined as the lowest temperature at which the vapor above a liquid specimen ignites when an ignition source (test flame) is applied. This property can be determined using a number of different methods. For this work, flash point was determined in accordance with ASTM D 6450, *Standard Test Method for Flash Point by Continuously Closed Cup (CCCFP) Tester*,<sup>16</sup> using the Grabner flash point high-temperature (FLPH) Miniflash tester (Grabner Instruments; Vienna, Austria). Prior to sample measurements, proper operation of the instrument was validated using *n*-dodecane.

The ASTM International method used for this work defines the occurrence of a flash as the temperature at which the ignited vapor above the specimen causes an instantaneous pressure increase ( $\Delta p$ ) of at least 20 kPa inside the closed test chamber. The Miniflash tester, however, identifies a flash as the temperature at which the pressure exceeds a set threshold (default threshold of 20 kPa).<sup>17</sup> This condition is inconsistent with the ASTM International requirement for  $\Delta p \geq 20$  kPa. For example, if a sample has a baseline pressure higher than zero, the detected pressure increase may exceed the 20 kPa threshold without producing a value of  $\Delta p \geq 20$  kPa. To address this concern, the instrument flash point threshold pressure was set to 50 kPa so that data could be collected beyond the default threshold to facilitate determination of a flash that is consistent with the ASTM requirements.

The output of the continuously closed cup instrument typically consists of a sharp, well-defined pressure increase when testing flammable, high-purity samples. This is illustrated in Figure 2 by the pressure profile for a 99.5 mol % pure sample of *n*-dodecane, which has a flash point of 79 °C that was measured using the continuously closed cup method.

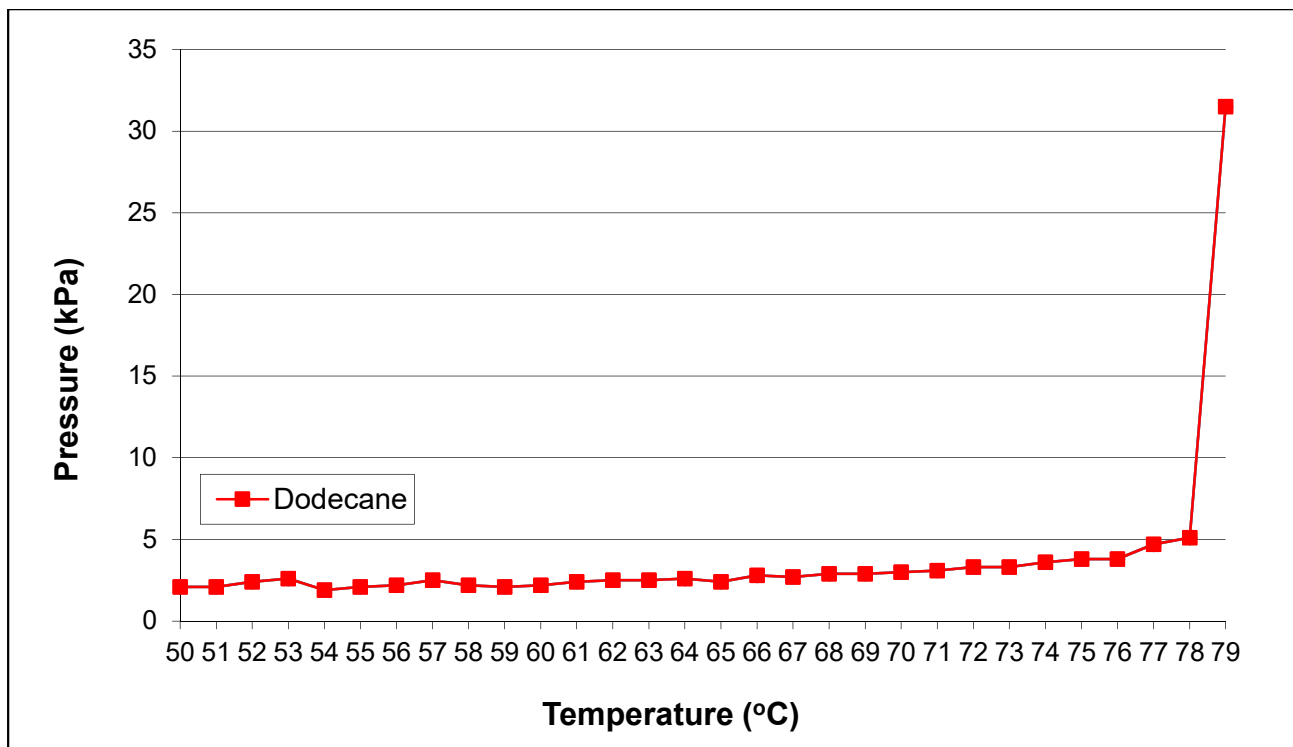


Figure 2. Flash point pressure profile of *n*-dodecane.

### 3. RESULTS AND DISCUSSION

#### 3.1 Vapor Pressure

DSC measurements were completed on two VM samples (Table 1) over the pressure range from 2 to 200 Torr. The results from the first sample [lot no. 04-0057-68 (bottle 1)] exhibited significant scatter due to thermal degradation during data measurement. Results obtained using the second sample (lot no. 04-0046-101.1) were marginally better; five moderately sharp boiling endotherms were produced below 40 Torr at temperatures between 113 and 175 °C. Specimen degradation was observed at higher pressures, as indicated by broad and erratic boiling endotherms above 180 °C. The results from the second sample are listed in Table 2, along with the denuder–LC–MS results measured by Jenkins et al.<sup>2</sup> between –9.8 and 40 °C.

Table 2. Experimental Vapor Pressure Data for VM

Temperature		$P_{\text{exptl}}$		$P_{\text{calc}}$		Difference* (%)
°C	K	Torr	Pa	Torr	Pa	
<b>Denuder</b>						
-9.8	263.35	$4.245 \times 10^{-5}$	$5.66 \times 10^{-3}$	$5.871 \times 10^{-5}$	$7.827 \times 10^{-3}$	-27.69
-9.8	263.35	$8.551 \times 10^{-5}$	$1.14 \times 10^{-2}$	$5.871 \times 10^{-5}$	$7.827 \times 10^{-3}$	45.64
0.0	273.15	$2.085 \times 10^{-4}$	$2.78 \times 10^{-2}$	$1.979 \times 10^{-4}$	$2.638 \times 10^{-2}$	5.36
5.0	278.15	$4.538 \times 10^{-4}$	$6.05 \times 10^{-2}$	$3.548 \times 10^{-4}$	$4.730 \times 10^{-2}$	27.90
10.0	283.15	$4.470 \times 10^{-4}$	$5.96 \times 10^{-2}$	$6.219 \times 10^{-4}$	$8.291 \times 10^{-2}$	-28.11
10.0	283.15	$5.295 \times 10^{-4}$	$7.06 \times 10^{-2}$	$6.219 \times 10^{-4}$	$8.291 \times 10^{-2}$	-14.84
10.0	283.15	$5.243 \times 10^{-4}$	$6.99 \times 10^{-2}$	$6.219 \times 10^{-4}$	$8.291 \times 10^{-2}$	-15.69
10.0	283.15	$7.351 \times 10^{-4}$	$9.80 \times 10^{-2}$	$6.219 \times 10^{-4}$	$8.291 \times 10^{-2}$	18.21
15.0	288.15	$1.058 \times 10^{-3}$	$1.41 \times 10^{-1}$	$1.067 \times 10^{-3}$	$1.423 \times 10^{-1}$	-0.88
20.0	293.15	$2.138 \times 10^{-3}$	$2.85 \times 10^{-1}$	$1.794 \times 10^{-3}$	$2.392 \times 10^{-1}$	19.15
20.0	293.15	$1.275 \times 10^{-3}$	$1.70 \times 10^{-1}$	$1.794 \times 10^{-3}$	$2.392 \times 10^{-1}$	-28.93
20.0	293.15	$1.598 \times 10^{-3}$	$2.13 \times 10^{-1}$	$1.794 \times 10^{-3}$	$2.392 \times 10^{-1}$	-10.95
20.0	293.15	$2.153 \times 10^{-3}$	$2.87 \times 10^{-1}$	$1.794 \times 10^{-3}$	$2.392 \times 10^{-1}$	19.98
25.0	298.15	$3.998 \times 10^{-3}$	$5.33 \times 10^{-1}$	$2.960 \times 10^{-3}$	$3.946 \times 10^{-1}$	35.06
30.0	303.15	$4.673 \times 10^{-3}$	$6.23 \times 10^{-1}$	$4.797 \times 10^{-3}$	$6.395 \times 10^{-1}$	-2.58
30.0	303.15	$3.833 \times 10^{-3}$	$5.11 \times 10^{-1}$	$4.797 \times 10^{-3}$	$6.395 \times 10^{-1}$	-20.10
30.0	303.15	$5.520 \times 10^{-3}$	$7.36 \times 10^{-1}$	$4.797 \times 10^{-3}$	$6.395 \times 10^{-1}$	15.09
30.0	303.15	$5.948 \times 10^{-3}$	$7.93 \times 10^{-1}$	$4.797 \times 10^{-3}$	$6.395 \times 10^{-1}$	24.00
35.0	308.15	$7.876 \times 10^{-3}$	$1.05 \times 10^0$	$7.642 \times 10^{-3}$	$1.019 \times 10^0$	3.06
40.0	313.15	$1.215 \times 10^{-2}$	$1.62 \times 10^0$	$1.198 \times 10^{-2}$	$1.597 \times 10^0$	1.44
40.0	313.15	$8.926 \times 10^{-3}$	$1.19 \times 10^0$	$1.198 \times 10^{-2}$	$1.597 \times 10^0$	-25.49
<b>DSC</b>						
112.92	386.07	$2.39 \times 10^0$	$3.18 \times 10^2$	$2.048 \times 10^0$	$2.731 \times 10^2$	16.54
132.46	405.61	$5.91 \times 10^0$	$7.88 \times 10^2$	$5.814 \times 10^0$	$7.751 \times 10^2$	1.73
143.56	416.71	$1.126 \times 10^1$	$1.501 \times 10^3$	$1.004 \times 10^1$	$1.339 \times 10^3$	12.12
163.13	436.28	$2.113 \times 10^1$	$2.817 \times 10^3$	$2.448 \times 10^1$	$3.264 \times 10^3$	-13.67
175.31	448.46	$3.927 \times 10^1$	$5.236 \times 10^3$	$4.089 \times 10^1$	$5.452 \times 10^3$	-3.97

\*( $P_{\text{exptl}} - P_{\text{calc}}$ )/ $P_{\text{calc}}$  × 100, where  $P_{\text{exptl}}$  is the experimental pressure and  $P_{\text{calc}}$  is the calculated pressure.

The denuder and DSC results were combined and fitted to a three-parameter Antoine equation<sup>18</sup> (eq 1) over the experimental temperature range by minimizing the sum of the squares of the differences of the logarithms of measured and calculated values.<sup>19</sup> The Antoine equation constants for the vapor pressure of VM are listed in Table 3.

$$\ln(P) = a - b/(c + T) \quad (1)$$

where

$a$ ,  $b$ , and  $c$  are correlation constants;

$P$  is vapor pressure (Pa); and

$T$  is temperature (K).

This equation may be converted to Torr–Celsius units using eqs 2–4.

$$A = [a - \ln(101325/760)]/\ln(10) \quad (2)$$

$$B = b/\ln(10) \quad (3)$$

$$C = c + 273.15 \quad (4)$$

Using these substitutions, eq 1 becomes eq 5:

$$\log(p) = A - B/(C + t) \quad (5)$$

where

$A$ ,  $B$ , and  $C$  are correlation constants;

$p$  is vapor pressure (Torr); and

$t$  is temperature (°C).

Table 3. Antoine Coefficients for VM Vapor Pressure

<b><math>\ln(P) = a - b/(c + T)</math></b>		
<i>a</i>	<i>b</i>	<i>c</i>
25.93748	7342.604	-24.85791
Temperature range: 263.35 to 448.46 K		
<b><math>\log(p) = A - B/(C + t)</math></b>		
<i>A</i>	<i>B</i>	<i>C</i>
9.139603	3188.853	248.2921
Temperature range: -9.8 to 175.31 °C		

Enthalpy of vaporization and saturation concentration, which is often referred to as volatility, were calculated using eqs 6 and 7, respectively. These values, along with vapor pressure, are listed at selected temperatures in Table 4.

The enthalpy of vaporization is calculated as follows:

$$\Delta H_{\text{vap}} = R \times b \times [T/(c + T)]^2 \quad (6)$$

where

$\Delta H_{\text{vap}}$  is enthalpy of vaporization (kJ/mol);  
 $R$  is gas constant (8.314 J/K mol);  
 $b$  and  $c$  are Antoine constants; and  
 $T$  is temperature (K).

The saturation concentration,  $C_{\text{sat}}$  (mg/m<sup>3</sup>), is calculated as follows:

$$C_{\text{sat}} = P \times \text{MW}/RT \quad (7)$$

where

$P$  is vapor pressure (Pa);  
 $\text{MW}$  is molecular weight (g/mol);  
 $R$  is gas constant (8.314 Pa m<sup>3</sup>/K mol); and  
 $T$  is temperature (K).

A plot of the experimental vapor pressure data and the Antoine fit for VM are shown in Figure 3, along with the Antoine curves for the nerve agents VX and RVX,<sup>20</sup> the two reduced boiling points from Coulter et al.<sup>1</sup> (0.1 Torr at 75–76 °C and 0.09 Torr at 75–77 °C), and the value reported by Samuel et al.<sup>4</sup> at 25 °C (0.0021 Torr). The two reduced boiling points reported by Coulter are closer to the values for VX than for VM in this temperature range. We have found that values generated by methods that are not specifically designed for measurement of vapor pressure are less accurate than the data measured using standard vapor pressure techniques. This is especially true for reduced boiling points below 1 Torr. Although Samuel et al. did not identify a source for their cited value, it is in good agreement with the value estimated using the method of Hass and Newton<sup>21</sup> and the VM denuder data at 25 °C.

Table 4. Calculated Properties for VM at Selected Temperatures

Temperature (°C)	Vapor Pressure		Volatility (mg/m <sup>3</sup> )	Heat of Vaporization (kJ/mol)
	Torr	Pa		
-40*	$6.762 \times 10^{-7}$	$9.015 \times 10^{-5}$	$1.113 \times 10^{-2}$	76.49
-30*	$3.399 \times 10^{-6}$	$4.532 \times 10^{-4}$	$5.365 \times 10^{-2}$	75.75
-20*	$1.484 \times 10^{-5}$	$1.978 \times 10^{-3}$	$2.249 \times 10^{-1}$	75.07
-10*	$5.721 \times 10^{-5}$	$7.628 \times 10^{-3}$	$8.343 \times 10^{-1}$	74.45
0	$1.979 \times 10^{-4}$	$2.638 \times 10^{-2}$	$2.780 \times 10^0$	73.89
10	$6.219 \times 10^{-4}$	$8.291 \times 10^{-2}$	$8.428 \times 10^0$	73.37
20	$1.794 \times 10^{-3}$	$2.392 \times 10^{-1}$	$2.349 \times 10^1$	72.89
25	$2.960 \times 10^{-3}$	$3.946 \times 10^{-1}$	$3.810 \times 10^1$	72.66
30	$4.797 \times 10^{-3}$	$6.395 \times 10^{-1}$	$6.072 \times 10^1$	72.44
35	$7.642 \times 10^{-3}$	$1.019 \times 10^0$	$9.516 \times 10^1$	72.23
40	$1.198 \times 10^{-2}$	$1.597 \times 10^0$	$1.468 \times 10^2$	72.03
45	$1.849 \times 10^{-2}$	$2.465 \times 10^0$	$2.230 \times 10^2$	71.84
50	$2.813 \times 10^{-2}$	$3.751 \times 10^0$	$3.341 \times 10^2$	71.65
55	$4.222 \times 10^{-2}$	$5.628 \times 10^0$	$4.937 \times 10^2$	71.47
60	$6.252 \times 10^{-2}$	$8.335 \times 10^0$	$7.201 \times 10^2$	71.29
70	$1.321 \times 10^{-1}$	$1.761 \times 10^1$	$1.477 \times 10^3$	70.96
80	$2.668 \times 10^{-1}$	$3.557 \times 10^1$	$2.899 \times 10^3$	70.65
90	$5.167 \times 10^{-1}$	$6.889 \times 10^1$	$5.460 \times 10^3$	70.35
100	$9.636 \times 10^{-1}$	$1.285 \times 10^2$	$9.910 \times 10^3$	70.08
120	$3.028 \times 10^0$	$4.037 \times 10^2$	$2.955 \times 10^4$	69.57
140	$8.455 \times 10^0$	$1.127 \times 10^3$	$7.853 \times 10^4$	69.12
160	$2.135 \times 10^1$	$2.846 \times 10^3$	$1.891 \times 10^5$	68.71
180 <sup>†</sup>	$4.944 \times 10^1$	$6.592 \times 10^3$	$4.187 \times 10^5$	68.34
200 <sup>†</sup>	$1.062 \times 10^2$	$1.416 \times 10^4$	$8.616 \times 10^5$	68.01
220 <sup>†</sup>	$2.138 \times 10^2$	$2.851 \times 10^4$	$1.664 \times 10^6$	67.70
240 <sup>†</sup>	$4.064 \times 10^2$	$5.419 \times 10^4$	$3.039 \times 10^6$	67.42
260 <sup>†</sup>	$7.344 \times 10^2$	$9.791 \times 10^4$	$5.286 \times 10^6$	67.17
261.2 <sup>†</sup>	$7.600 \times 10^2$	$1.013 \times 10^5$	$5.458 \times 10^6$	67.15

\*Extrapolated.

<sup>†</sup>Extrapolated, decomposes (decomposition detected by DSC above 176 °C).

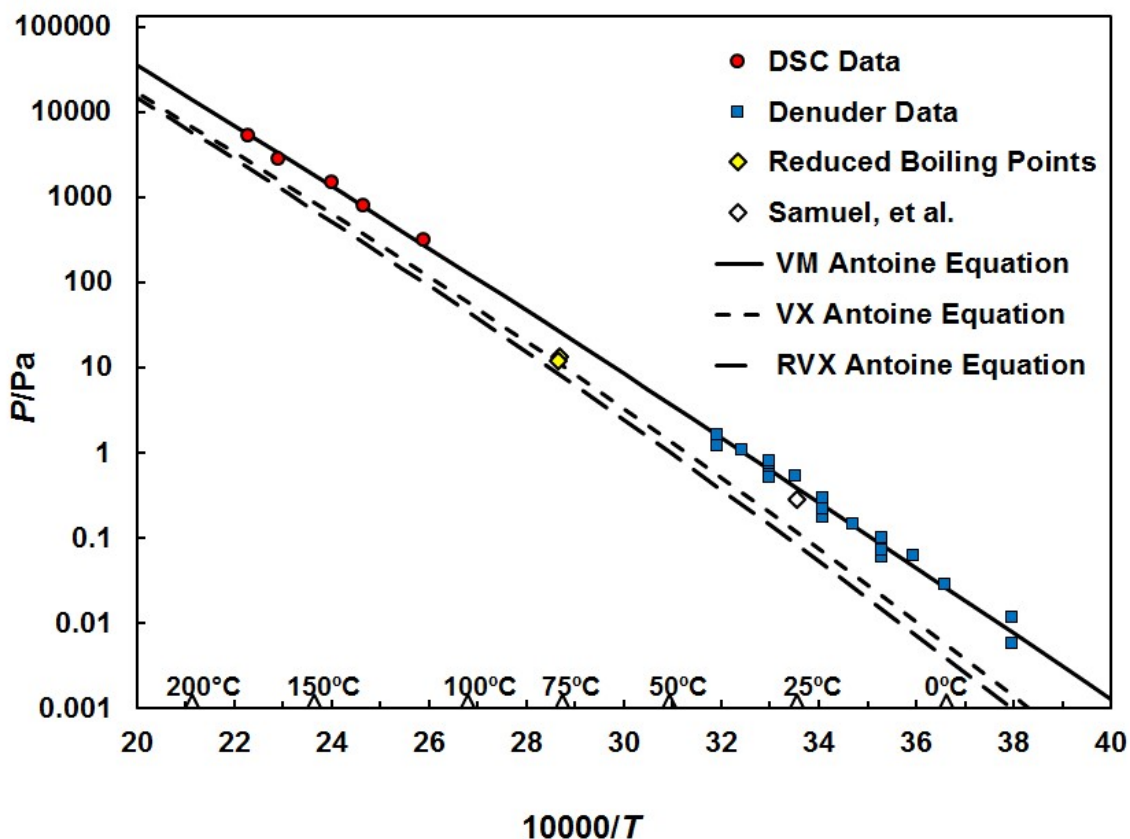


Figure 3. Experimental vapor pressure data for VM and Antoine curves for VM, VX, and RVX.

### 3.2 Density

The experimental and calculated results for VM are provided in Table 5. These calculated values were derived from eq 8 and are plotted in Figure 4 along with the correlations for VX and RVX.<sup>20</sup>

The density is calculated with the following equation:

$$\rho = \alpha + \beta \times t \quad (8)$$

where

$\rho$  is density (g/mL);  
 $\alpha$  is intercept;  
 $\beta$  is slope; and  
 $t$  is temperature (°C).

Table 5. Liquid Density of VM

Temperature (°C)	Density* (g/mL)		Difference <sup>†</sup> (%)
	Experimental	Calculated	
25.0	1.02225	1.02221	0.004
35.0	1.01349	1.01356	-0.006
50.0	1.00060	1.00057	0.003
$\rho = 1.04385 - 8.6547 \times 10^{-4} \times t$			

\*The uncertainty of each measurement is  $\leq 0.00004$  g/mL, based on instrument validation with NIST standard toluene.

<sup>†</sup> $(\rho_{\text{exptl}} - \rho_{\text{calc}})/\rho_{\text{calc}} \times 100$ , where  $\rho_{\text{exptl}}$  is experimental density and  $\rho_{\text{calc}}$  is calculated density

Coulter et al.<sup>1</sup> state that their density values for VM “are probably somewhat different from those which will be obtained with 100% pure samples”. Our results, which were obtained using a 99% pure sample, are 0.7% lower than the mean of his results.

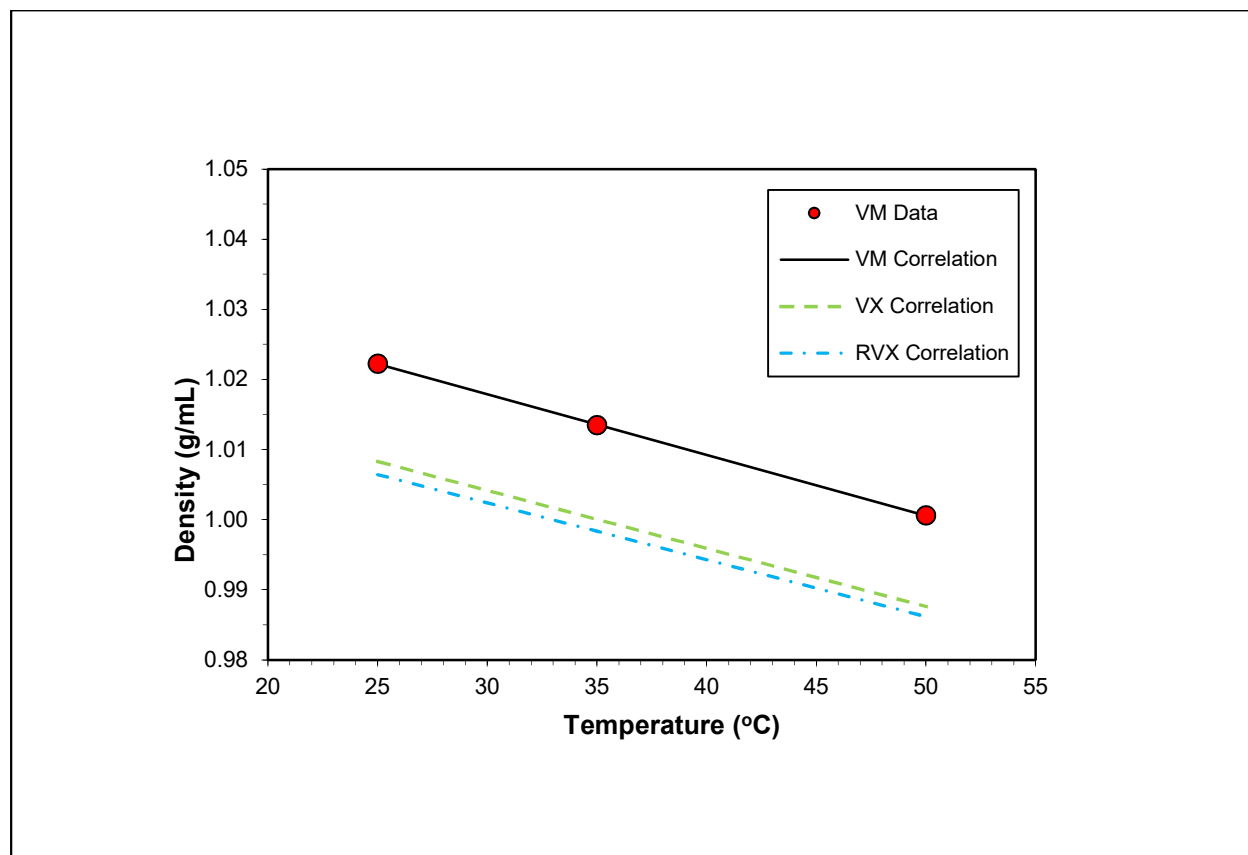


Figure 4. Liquid density of VM compared to correlations of VX and RVX.

### 3.3 Viscosity

The experimental kinematic viscosity results from this work are provided in Table 6. This data was fitted to the Antoine equation,<sup>18</sup> which is also listed in Table 6 with values calculated over the experimental temperature range. The experimental results and the Antoine correlation for VM are plotted in Figure 5 along with the viscosities of VX and RVX.<sup>20</sup> Our data are 7% lower than the VM viscosity values reported by Coulter et al.<sup>1</sup>

Table 6. Viscosity of VM

Temperature (°C)	Viscosity (cSt)			Difference <sup>†</sup> (%)
	Experimental	Experimental Mean*	Calculated	
25.0	5.4556	5.457	5.45670	-0.02
25.0	5.4602			0.06
25.0	5.4543			-0.04
35.0	4.0540	4.060	4.05960	-0.14
35.0	4.0628			0.08
35.0	4.0620			0.06
50.0	2.7942	2.791	2.79058	0.13
50.0	2.7892			-0.05
50.0	2.7883			-0.08
50.0	2.7937			0.11
50.0	2.7875			-0.11
$\log \nu = -1.14090 + 255.7525 / (111.195 + t)$ ; temperature range of 25–50 °C				

\*The uncertainty of each measurement is  $\leq 0.005$  cSt.

<sup>†</sup> $(\nu_{\text{exptl}} - \nu_{\text{calc}}) / \nu_{\text{calc}} \times 100$ , where  $\nu_{\text{exptl}}$  is experimental viscosity and  $\nu_{\text{calc}}$  is calculated viscosity.

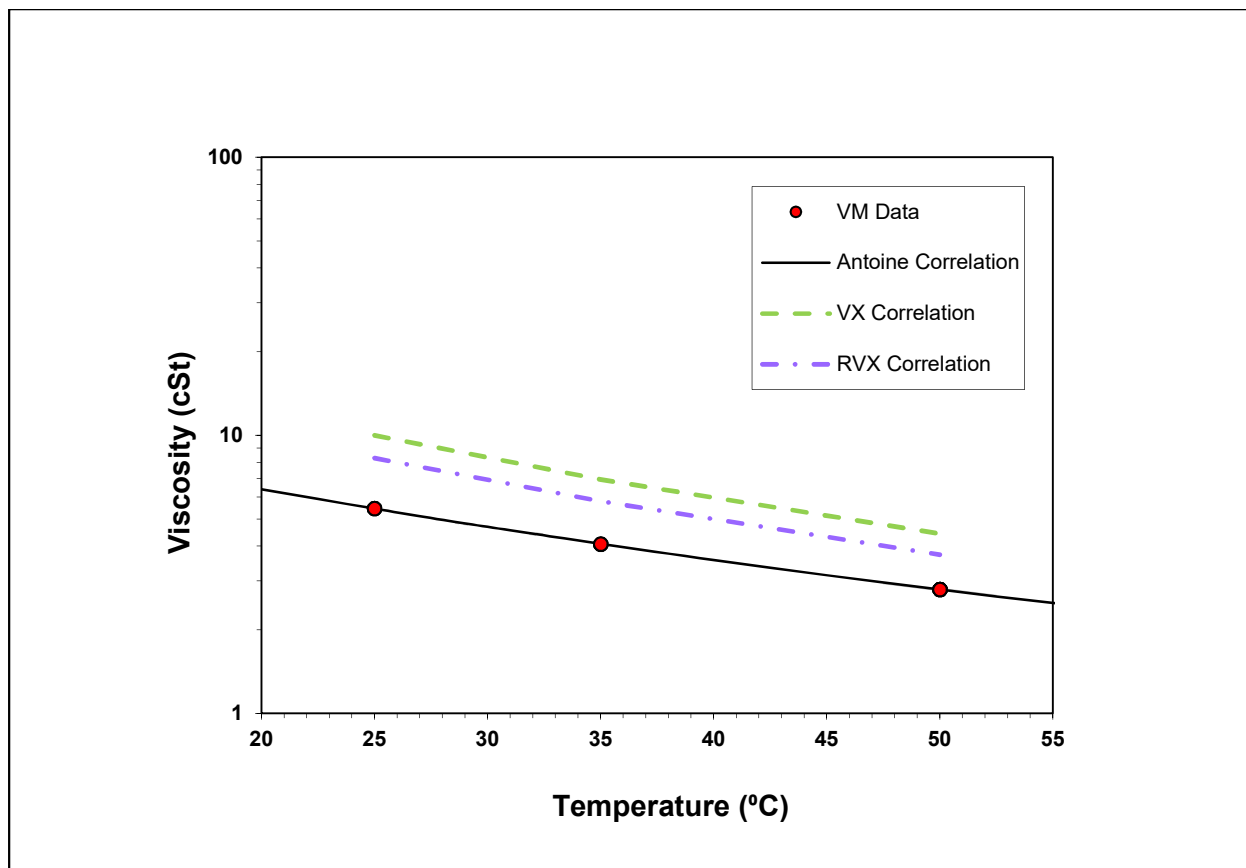


Figure 5. Viscosity of VM compared to correlations of VX and RVX.

### 3.4 Surface Tension

The experimental surface tension data for VM is provided in Table 7. This value represents the mean of 10 measurements. There is a 13% difference between our data and the mean of the values reported by Coulter et al.<sup>1</sup> at 25 °C. The latter were generated using several different methods. It is not possible to determine if the difference between our value and that of Coulter et al. is due to inherent differences in the methods or sample purity. For comparison, the surface tensions of VX and RVX at 25 °C are 30.20 and 26.89 dyn/cm, respectively.<sup>20</sup>

Table 7. Surface Tension of VM

Temperature (°C)	Surface Tension (dyn/cm)
25.0	26.97 ± 0.15

### 3.5 Flash Point

The literature flash point value of VM is 236 °C.<sup>4</sup> This measurement was conducted in the late 1950s by Link<sup>5</sup> using the open cup McCutchan and Young micro method.<sup>22</sup> There is, however, some concern with the accuracy of this value because Link states that “it was very difficult to get a value since almost the entire sample had evaporated during the heating process”.<sup>5</sup> This statement suggests that the reported value is suspect, especially in light of the tendency for VM to decompose at elevated temperatures. To address this concern, the flash point of VM was redetermined using the CCCFP method.<sup>16,17</sup>

Due to sample volume limitations, flash point measurements were conducted using three different samples of VM (Table 1). However, the reported results are only based on two of these samples. Flash points were determined in triplicate for each sample, and the results are provided in Table 8.

Table 8. Flash Point of VM Using the Miniflash Tester

Compound	Purity/Lot No.	Flash Point (°C)	Mean Flash Point (°C ± SD)
VM (Sample 1)	80% 04-0057-68 Bottle 2	93	93 ± 1
		92	
		93	
VM (Sample 2)	96% 04-0046-101.2	107	107 ± 0
		107	
		107	
VM (Sample 3)	95% 04-0046-102.1	119*	N/A <sup>†</sup>
		N/A	
		N/A	

SD, standard deviation.

\*This was not a valid test because the value resulted from a decrease in pressure rather than a pressure increase.

<sup>†</sup>None of the measurements came close to the  $\Delta p \geq 20$  kPa criterion.

The results obtained from the first two VM samples produced very stable pressure readings from 60 °C up to at least 93 °C. At this point, a sharp and well-defined pressure increase of  $\geq 17$  kPa occurred at 93 °C for sample 1 and at 107 °C for sample 2. The results for each sample were reproducible. This behavior is consistent with a typical flash using the CCCFP method. The pressure profiles of VM samples 1 and 2 are shown in Figures 6 and 7, respectively. The 14 °C temperature difference between these two results is assumed to be due to differences in the sample purities.

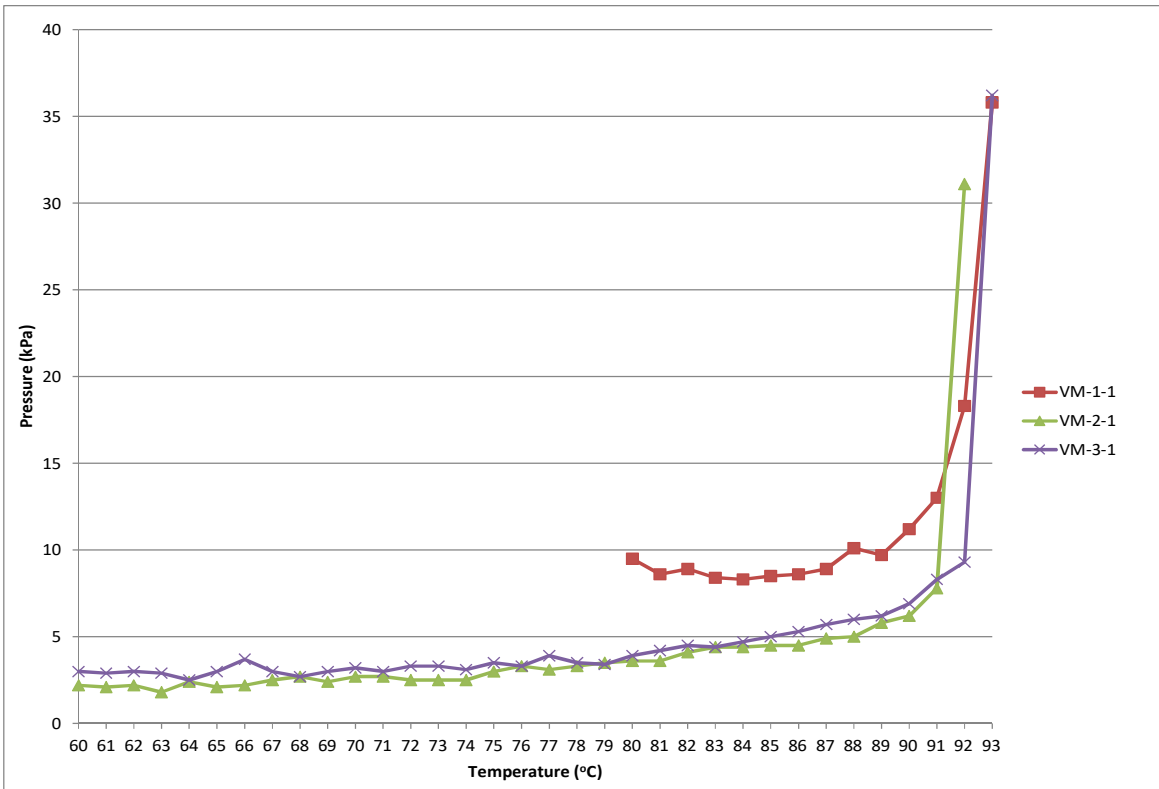


Figure 6. Pressure profile of VM (sample 1) using the Miniflash tester.

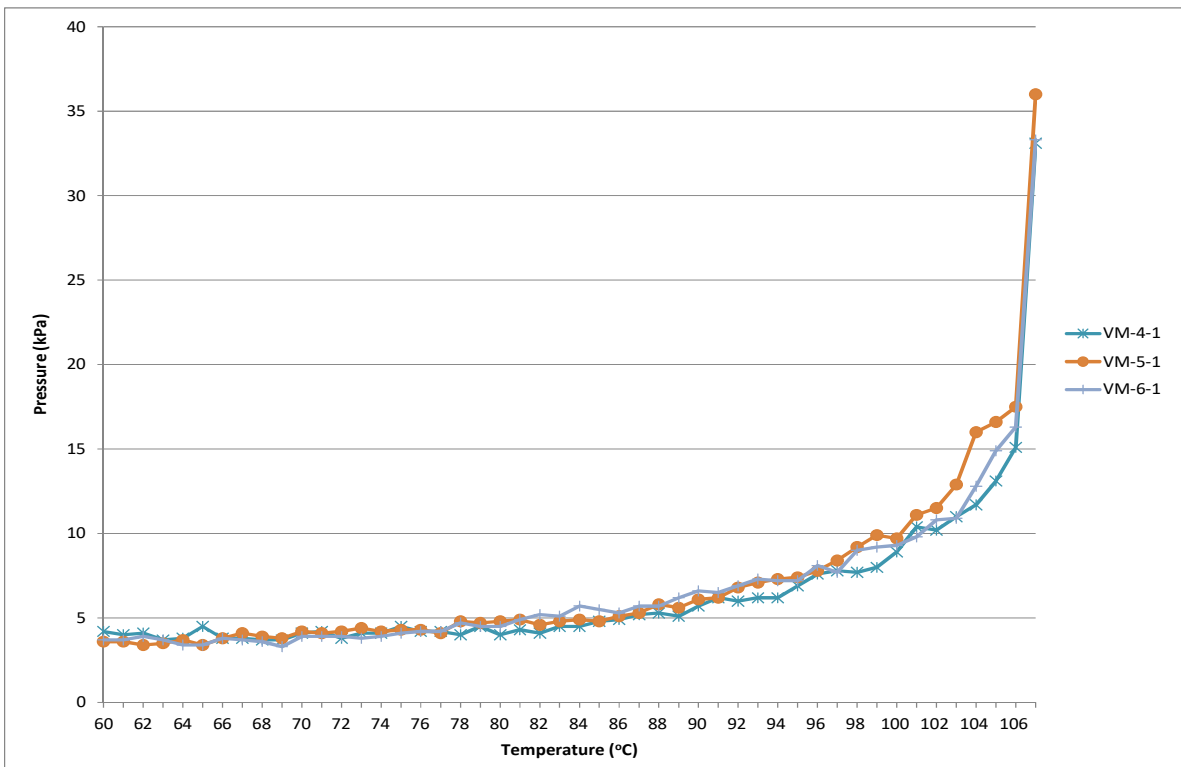


Figure 7. Pressure profile of VM (sample 2) using the Miniflash tester.

Measurements conducted using VM sample 3 are shown in Figure 8. Sample 3 produced a gradual pressure increase, followed by several pressure spikes. However, none of the pressure spikes met the ASTM International flash criterion of  $\Delta p \geq 20$  kPa. Although one of the specimens from this third sample produced a  $\Delta p$  that came close to the criterion, this change in pressure was caused by a decrease in pressure instead of an increase; therefore, none of the results from this sample are being reported. It is unclear at this time why the results from this third sample varied so much from those of the other two samples.

To understand the large difference between our flash point data and the value reported by Link,<sup>5</sup> we can examine our own vapor pressure results, which showed signs of sample degradation above 180 °C. This suggests that the flash reported by Link at 236 °C was probably due to VM degradation products rather than to VM itself. In addition, for safety considerations, we recommend that the flash point of VM be reported as the lowest value observed, 93 °C, rather than the mean value for samples 1 and 2.

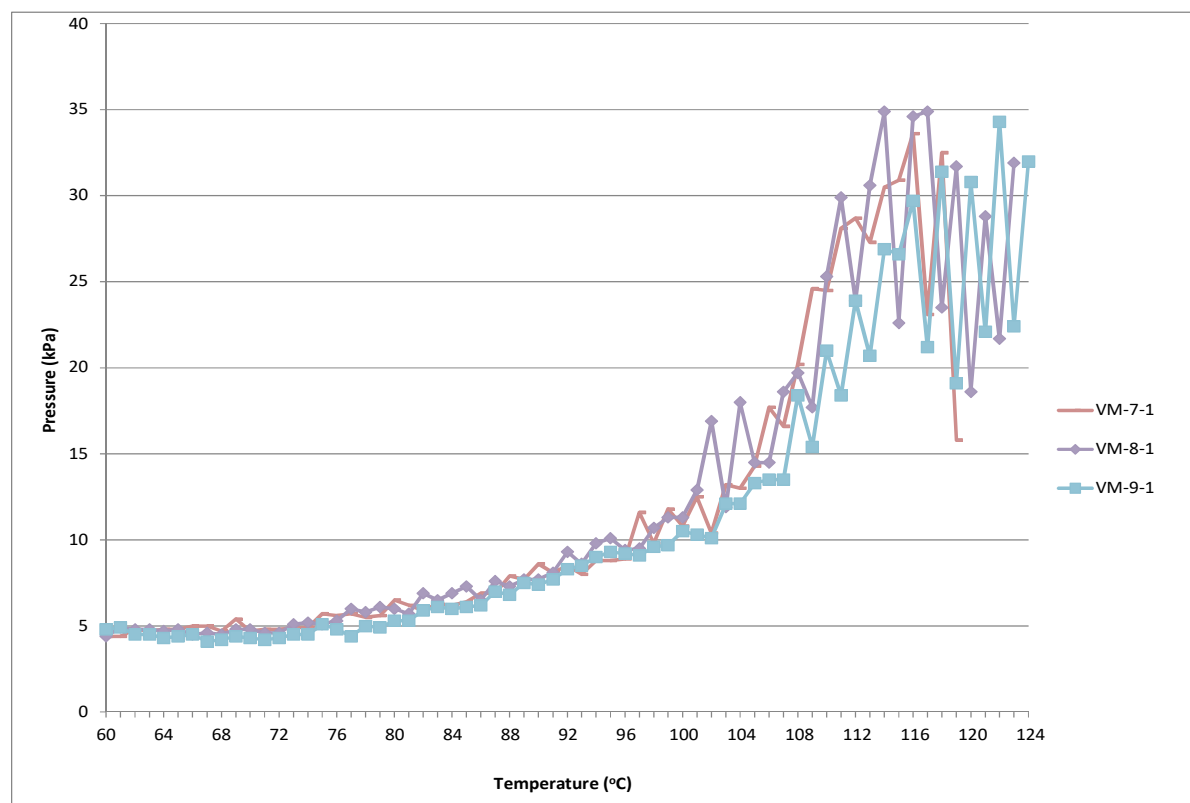


Figure 8. Pressure profile of VM (sample 3) using the Miniflash tester.

### 3.6 Selected Physical Properties of VM, VX, and RVX

Because VM has a similar chemical structure to that of VX and RVX, selected physical properties of VM, VX, and RVX are listed in Table 9 with calculated values at 25 °C.

Table 9. Selected Physical Properties of VM, VX, and RVX

Property	VM	VX <sup>20</sup>	RVX <sup>20</sup>
Vapor Pressure at 25 °C (Pa)	$3.946 \times 10^{-1}$	$1.179 \times 10^{-1}$	$8.391 \times 10^{-2}$
Vapor Pressure at 25 °C (Torr)	$2.960 \times 10^{-3}$	$8.843 \times 10^{-4}$	$6.294 \times 10^{-4}$
Volatility at 25 °C (mg/m <sup>3</sup> )	38.1	12.7	9.05
Heat of Vaporization at 25 °C (kJ/mol)	72.66	80.32	80.98
Normal Boiling Point (°C)	261.2	291.6	294.7
Density at 25 °C (g/mL)	1.02221	1.00833	1.00651
Viscosity at 25 °C (cSt)	5.457	10.02	8.290
Surface Tension at 25 °C (dyn/cm)	26.97	30.20	26.89
Flash Point (°C) (closed cup)	93 (purity 80%)	127 (purity 95.8%)	127 (purity 95.7%)
	107 (purity 96%)		

#### 4. CONCLUSIONS

The physical properties of VM, which is structurally similar to VX and RVX, were investigated using samples of known purity. These properties include vapor pressure, density, viscosity, surface tension, and flash point. This work was accomplished to address concerns regarding the reliability of the existing literature data.

Vapor pressure data measured using DSC was combined with literature data generated using the complementary denuder–LC–MS method. A three-parameter Antoine correlation was derived to describe the data. The correlation reflects measurements over a large

temperature range (-9.8 to 175 °C); however, VM degraded at temperatures above 175 °C. These results show that the vapor pressure of VM is about 3–5 times higher than that of VX or RVX, which was expected based on differences in molecular structure.

The correlations provided for density and viscosity show that VM is more dense and less viscous than VX and RVX. The new density and viscosity data for VM are 0.7% and 7% lower, respectively, than those reported for VM by Coulter et al.<sup>1</sup>

The surface tension of VM at 25 °C falls between those of VX and RVX. Our surface tension data is 13% lower than the mean value reported by Coulter et al. We assume this difference is due to variations in sample purities.

Reproducible flash points differed by 14 °C for two different lots of VM that were tested. A third lot showed a gradual pressure increase and unexpected pressure spikes that constituted an invalid test. These inconsistencies may be due to the presence of volatile, flammable impurities, but these results are still considered to be more reliable than the earlier open cup value reported by Link.<sup>5</sup> Our DSC data suggest that Link's results were based on a degraded sample.

Based on these results, a single definitive flash point for VM could not be determined; however, as a safety consideration, it is recommended that the flash point of VM be reported as  $\geq 93$  °C by the continuously closed cup method.

Using established methods to measure properties on samples of known purity allows for greater confidence in the results. The improved reliability of the data will facilitate the modeling of more accurate forecasts of potential threats.

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## ACRONYMS AND ABBREVIATIONS

$\Delta H_{\text{vap}}$	enthalpy of vaporization
$\Delta p$	pressure change
$\rho$	density
$\rho_{\text{exptl}}$	experimental density
$\rho_{\text{calc}}$	calculated density
$\nu$	viscosity
CB	chemical and biological
CCCFP	continuously closed cup flash point
$C_{\text{sat}}$	saturation concentration
denuder–LC–MS	denuder–liquid chromatography–mass spectrometry
DSC	differential scanning calorimetry
ECBC	U.S. Army Edgewood Chemical Biological Center
FLPH	flash point high temperature
MW	molecular weight
NIST	National Institute of Standards and Technology
$P$	pressure (Pa)
$P_{\text{calc}}$	calculated pressure
$P_{\text{exptl}}$	experimental pressure
$p$	pressure (Torr)
$R$	gas constant
RVX	<i>O</i> -isobutyl <i>S</i> -[(2-diethylamino) ethyl] methylphosphonothiolate
SD	standard deviation
$t$	temperature (Celsius)
$T$	temperature (kelvin)
VM	<i>O</i> -ethyl <i>S</i> -[(2-diethylamino) ethyl] methylphosphonothiolate
VX	<i>O</i> -ethyl <i>S</i> -[(2-diisopropylamino) ethyl] methylphosphonothiolate

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