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Sublimation Rates of Explosive Materials – Method Development and Initial Results

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Sublimation Rates of Explosive Materials – Method Development and Initial Results

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Abstract

Vapor detection of explosives continues to be a technological basis for security applications. This study began experimental work to measure the chemical emanation rates of pure explosive materials as a basis for determining emanation rates of security threats containing explosives. Sublimation rates for TNT were determined with thermo gravimetric analysis using two different techniques. Data were compared with other literature values to provide sublimation rates from 25 to 70°C. The enthalpy of sublimation for the combined data was found to be 115 kJ/mol, which corresponds well with previously reported data from vapor pressure determinations. A simple Gaussian atmospheric dispersion model was used to estimate downrange concentrations based on continuous, steady-state conditions at 20, 45 and 62°C for a nominal exposed block of TNT under low wind conditions. Recommendations are made for extension of the experimental vapor emanation rate determinations and development of turbulent flow computational fluid dynamics based atmospheric dispersion estimates of standoff vapor concentrations.

Acknowledgements

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

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1.0 Introduction

Vapor detection of explosives continues to be a goal for security in various types of applications. The basis for this goal is that the target explosives are principally organic chemicals that have the potential to escape and be detected. The explosive signature is directly related to the threat and is not inferred from other properties that may also be found in other materials (e.g. x-ray). However, the explosive signature is small, indeed very small for certain explosives under normal conditions. But, chemical detection technology is evolving with greater sensitivity and specificity and with smaller dimensions and lower cost.

The objective of this effort is to better define the emanation rates of explosives and the atmospheric dispersion of the molecules, which will provide better estimates of the standoff concentrations available for detection. We have begun this effort by measuring the single component emanation rate of TNT as a function of temperature followed by Gaussian atmospheric dispersion to estimate downrange vapor concentrations. This is far from realistic, but it provides a strong basis for the quantitative magnitude of explosive emanations and the average downrange concentration.

This initial effort will be extended to include multi-component mixtures (e.g. CompB and C4) and packaged explosives that might be found emanating from suicide bombers or military artillery configured as an improvised explosive device. Advanced computational tools will be employed that will give us more insight into the non-Gaussian atmospheric dispersion, where turbulent flows can cause small scale eddies that have localized concentrations that may be much larger than the average in larger volumes. These tendrils of vapor are the targets for small volume detection technology that is emerging via micro-technology. With greater understanding of the nature of explosive vapor emanations from target objects and the molecular dispersion through the near-field atmosphere, we can be better prepared to design and field new generations of explosive detection technology.

2.0 Background

The volatilization of a solid chemical can be described by Fick's law of diffusion

$$\frac{dm}{A \cdot dt} = D \cdot \left(\frac{C_s - C_b}{L} \right) \quad [1]$$

where, m is mass, A is the surface area of the solid, t is time, D is the diffusion coefficient for the vapor in air, C_s and C_b are the concentrations of the vapor at the solid surface and in air, respectively, and L is the diffusion layer thickness. This equation describes the net transport of molecules via intermolecular collisions enhanced by concentration gradients. This process is more commonly known as sublimation.

Estimates of the sublimation rate through Fick's law will help define quantitative measurement requirements in laboratory tests. In Eq. [1], the diffusion coefficient can be estimated from molecular properties and was calculated for TNT to be 5530 cm²/day (Webb et al., 1999) via the FSG method (Tucker and Nelken, 1990). Since C_b is \ll than C_s , $C_s - C_b$ can be reduced to the concentration gradient of a saturated vapor at the solid surface over the boundary layer thickness, L . The boundary layer thickness for chemical diffusion depends on air flow, thermal gradients and the lateral dimensions of the vapor emanations. For simplicity, the boundary layer thickness will be estimated to be on the order of 0.5 cm as suggested by Jury et al., 1983.

For TNT, vapor density values were determined from the vapor pressure data of Pella, 1977. Sublimation rate estimates were then calculated to be 2.5 ng/cm²-sec at 70°C and 0.2 ng/cm²-sec at 45°C.

3.0 Methods and Materials

3.1 Thermo Gravimetric Analysis

Thermo gravimetric analysis used a TA Instruments AutoTGA 2950HR with V6.1A data acquisition software to determine the mass loss as a function of time. A low profile platinum cup (10 μL capacity) was filled with about 10 mg of TNT to completely cover the entire base of the cup. The TNT filled cups were preheated to 90°C then cooled to create a uniform crystalline mass. The TGA cup was placed onto the balance and the oven moves into position around the sample. This equipment uses Argon gas to flush the oven (54 cc/min) and the balance (6 cc/min). The run begins at room temperature and the ramp-up rate was set for $\sim 10^\circ\text{C}/\text{min}$ with a steady state hold time set for 4 to 12 hours. The balance sensitivity is reported to be 0.1 μg . The inside diameter of the cup was measured with a micrometer and found to be circular with a diameter of 9.35 mm. The temperature set points were chosen to provide four data sets from just below the melting point of TNT (82°C) and as low as could be determined in a nominal time of ~ 12 hours. These values were 70, 62, 55 and 45°C. The TNT used was triple recrystallized TNT provided by Pantex.

3.2 Dimple Slide Analysis

The dimple slides were 75 mm by 25 mm microscope slides (VWR P/N 48324-001) with an 11 mm dia by 0.8 mm deep depression located in the center (Figure 1 and 2). The same TNT used in the thermo gravimetric analysis was used for the dimple slide work. About 100 mg was placed onto the slide and then heated at 90°C for 10 minutes to melt the TNT into a somewhat circular pattern, then cooled to recrystallize. Four dimple slides were created as shown in Figure 2.

A Lindburg/Blue (model BF51800 Series 1100°C Box Furnace with UP150 Control) oven was adapted to contain two syringe trays connected with copper tubing for use in tests with air velocity (Figure 3). Two slides were placed side by side in the center of each tray. A variable area rotometer was connected in line to vary the flow from 1 to 7 scfm, which can provide the target linear velocity of 0.5 m/s (1 mi/hr) at 2.2 scfm over a cross sectional area of 23 cm^2 on each of the two trays.

The experimental procedure involved stabilizing the oven at the target temperature and placement of the dimple slides into the syringe trays in the oven. The dimple slides were kept at the target temperature for a specified time period then removed and placed into a desiccator for 5 minutes. All dimple slide movements were by metal tongs to ensure mass loss accuracy to the sensitivity of the

balance (0.00001 g). One thermocouple was placed under each syringe tray and the temperature was recorded once per minute with a Campbell Scientific 21X data logger.



Figure 1. Dimple Slide Containing TNT

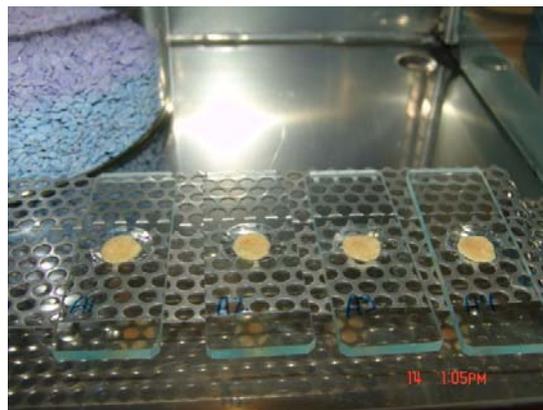


Figure 2. Four Dimple Slides in Desiccator



Figure 3. Interior of Oven with Air Velocity Chambers

4.0 Results and Discussion

4.1 TNT

4.1.1 Thermo Gravimetric Analysis

Figure 4 shows the temperature stabilization profile of the TNT TGA runs. The target temperatures were all achieved in about 20 minutes and remained stable until test completion.

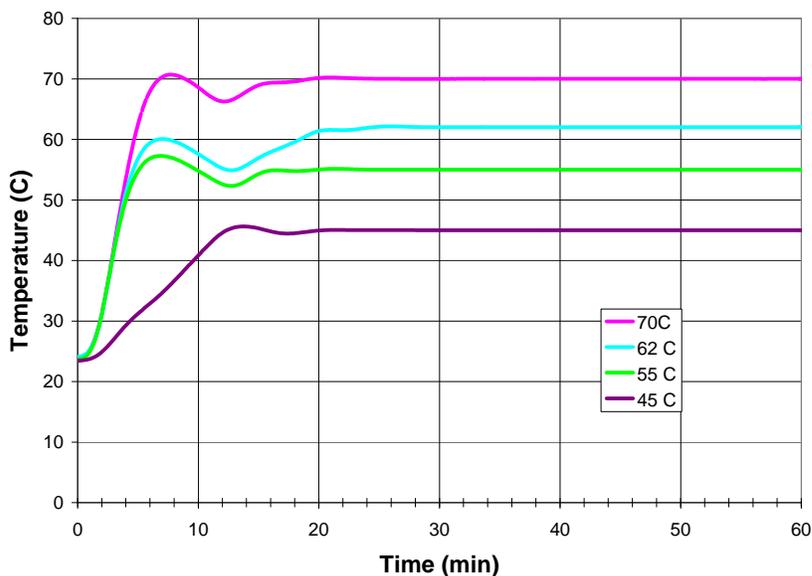


Figure 4. Temperature Stabilization Profile

Figure 5 shows the total mass change as a function of time. Figure 6 shows the mass loss for selected intervals from each test: 20 to 110 minutes for the 70°C run, 50 minutes to 200 minutes at 62°C, 100 to 300 minutes at 55°C, and from 100 to 400 minutes for the 45 °C run. The 45°C run showed some variation in mass loss not seen in the higher temperature runs. This is likely due to the low mass loss rate. Only one run was performed at each temperature.

Table 1 shows the summary results of the TGA runs. The calculated sublimation rate uses the measured diameter of the platinum cup (9.35 mm). This table was structured to provide the data for plotting the inverse of the absolute temperature versus the natural logarithm of the sublimation rate – also known as an Arrhenius plot (Figure 7). If the data falls on a line, then the slope of the line is an estimate of the enthalpy of sublimation and the intercept is an estimate of the entropy of the measurement system. Table 1 and Figure 7 show very good correlation for the four data points ($r^2 = 0.9925$) and a calculated enthalpy of sublimation of 111 kJ/mol.

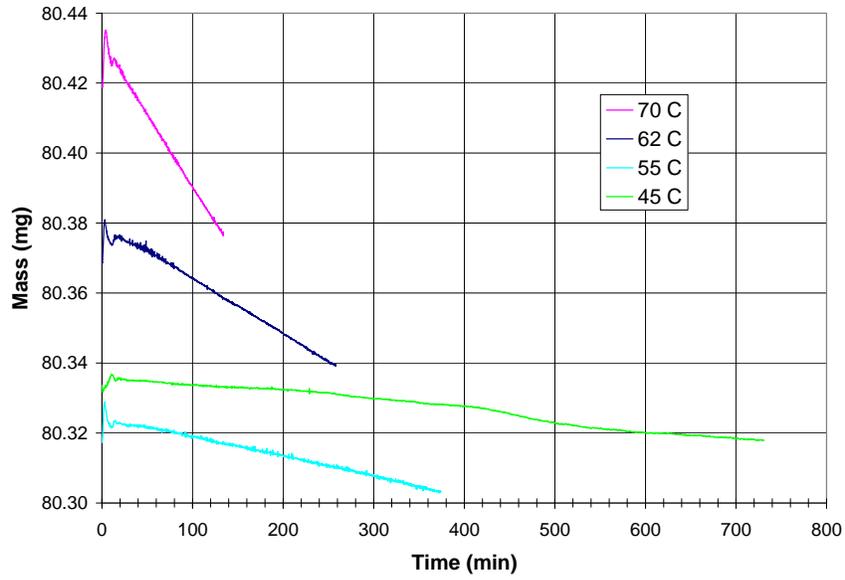


Figure 5. Total Mass Change Over Entire Test Duration

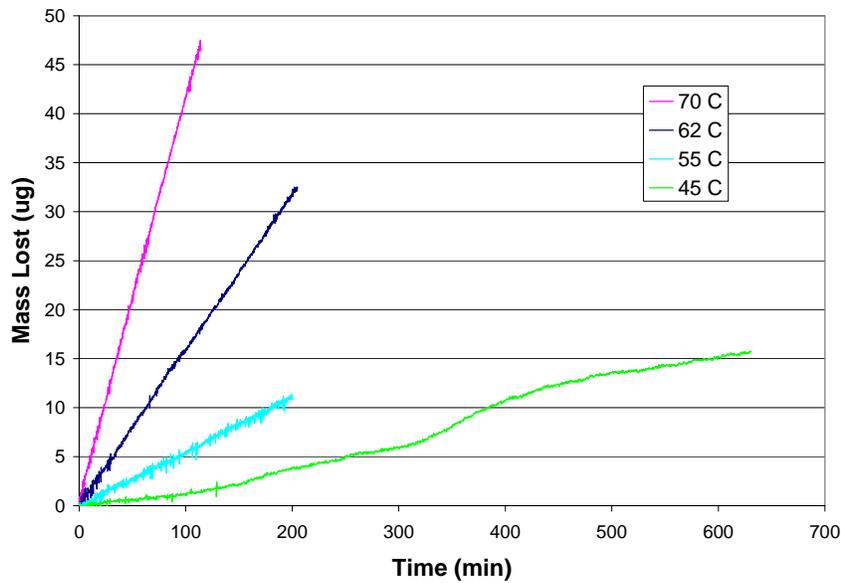


Figure 6. Mass Loss Over Selected Time Interval

Table 1. TNT TGA Data Summary

| T (°C) | T (°K) | 1/T (°K ⁻¹) | Sub Rate (ng/cm ² -sec) | Ln Sub Rate |
|--------|--------|-------------------------|------------------------------------|-------------|
| 70 | 343 | 0.002915 | 10.082 | 2.310785 |
| 62 | 335 | 0.002985 | 3.8389 | 1.345198 |
| 55 | 328 | 0.003049 | 1.3592 | 0.306959 |
| 45 | 318 | 0.003144 | 0.4853 | -0.7229 |
| | | | slope (E _a /R) | -13389 |
| | | | E _a | -111 kJ/mol |
| | | | intercept | 41.29 |
| | | | r ² | 0.9925 |

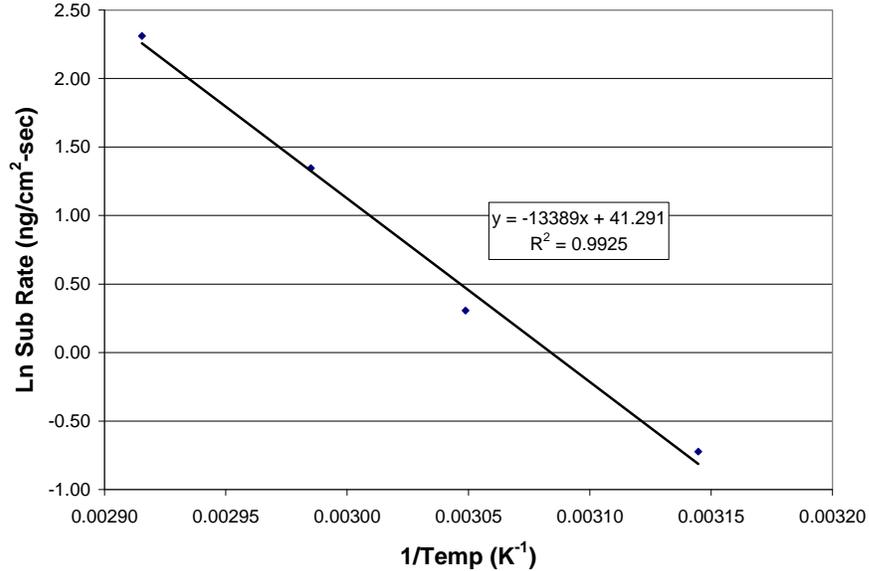


Figure 7. TNT TGA Arrhenius Plot

4.1.2 Dimple Slide Analysis

The surface area of the dimple slide TNT was determined by photographing each slide with a reference scale (Figure 1). The photographs were printed twice and the area of the dimple was cut and weighed from one and the irregular area of the TNT crystal was cut and weighed from the other. The actual magnification was determined by measurement of the reference scale. Table 2 shows the results of the determination of the surface area of the TNT crystal.

Table 2. Dimple Slide TNT Area Estimates

| Sample | Photo circle mass (g) | Photo TNT mass (g) | photo circle dia (mm) | photo circle ref scale | actual circle dia (mm) | actual circle area (mm ²) | photo area calibration factor (mm ² /g) | TNT area (mm ²) | TNT area (cm ²) |
|--------|-----------------------|--------------------|-----------------------|------------------------|------------------------|---------------------------------------|--|-----------------------------|-----------------------------|
| A1 | 5.216 | 2.613 | 165 | 0.105 | 17.368 | 236.925 | 45.423 | 118.690 | 1.187 |
| A2 | 5.124 | 2.374 | 164 | 0.105 | 17.263 | 234.062 | 45.679 | 108.443 | 1.084 |
| A3 | 4.96 | 2.394 | 162 | 0.105 | 17.053 | 228.388 | 46.046 | 110.234 | 1.102 |
| A4 | 5.774 | 2.281 | 171 | 0.105 | 18.000 | 254.469 | 44.072 | 100.527 | 1.005 |

Figure 8 shows the temperature history from each thermocouple measurement during the 70°C runs. The oven set point was set for 70°C, however, the proportional temperature control uses the central oven air as the control point and hence the actual steady state temperature was ~67.5°C. Figure 8 shows that the temperature is stable shortly after placement of the samples in the oven. The oven is rated for very high temperatures and contains large heating elements, so the overshoot in temperature after placement of the samples could not be avoided. The auto tune function on the proportional controller was

used to optimize the heating rate for the contents and target temperature. Figure 9 shows the details of the temperature excursion during a sample removal, weighing and sample replacement series that required opening the oven door twice. The temperature ranged from 75 to 65°C over a 140-minute period.

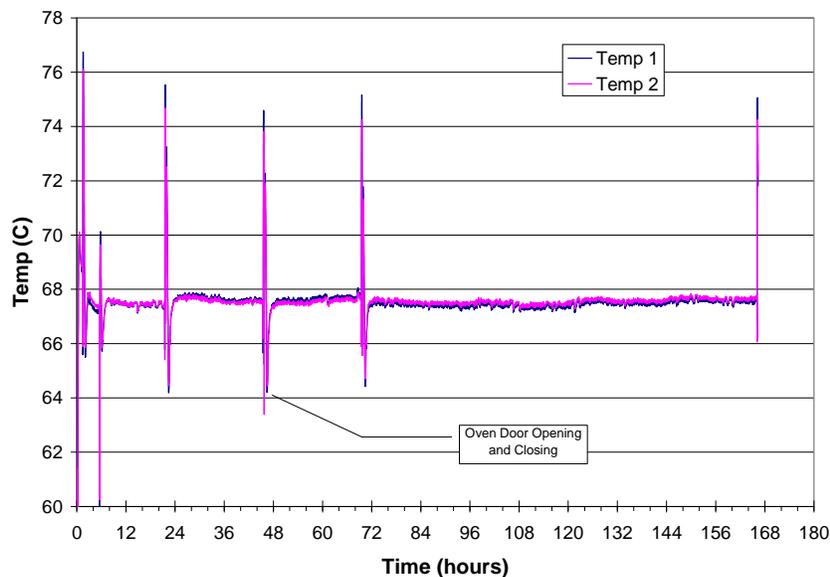


Figure 8. Temperature Stability

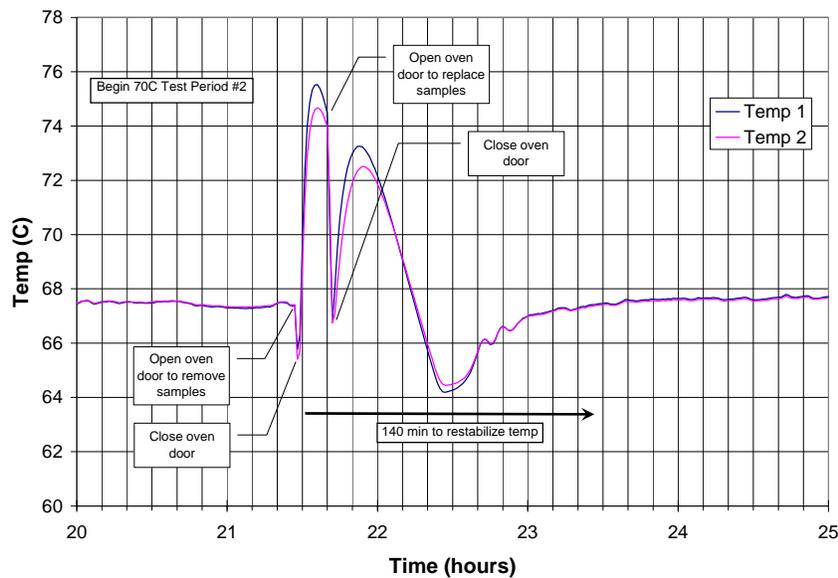


Figure 9. Detail Showing Oven Temperature Stabilization

The results for the four replicate dimple slides at three temperatures are shown in Figure 10. The 45°C tests were not attempted because the estimated time for adequate gravimetric resolution was too long - approximately 7 days. Four replicates were used at each temperature because of the expected larger variance compared to the well-controlled TGA tests. The average temperature was determined by an average of each minute interval over the entire time period that the samples were in the oven, including

the stabilization period. The test durations varied (Table 3), but were targeted for a mass loss of ~ 300 µg. The actual mass loss for each test ranged from 140 µg to 880 µg.

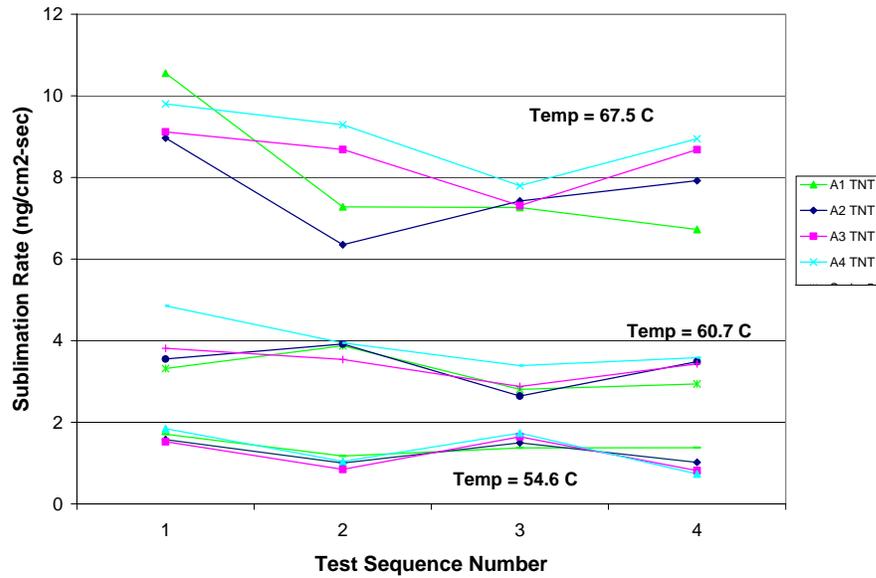


Figure 10. TNT Dimple Slide Sublimation Flux Data by Test Sequence Number

Table 3. Elapsed Time for Each Test Sequence (hours)

| Sequence | 67.5°C | 60.7°C | 54.6°C |
|----------|--------|--------|--------|
| 1 | 16 | 32 | 96 |
| 2 | 24 | 40 | 72 |
| 3 | 24 | 72 | 118 |
| 4 | 96 | 48 | 53 |

The summary statistics for each temperature are shown in Tables 4 and 5. Table 4 shows the average, standard deviation and percent relative standard deviation ($RSD = STDEV/AVG$) for each dimple slide by test temperature. The variation within a single dimple slide through the four sequences (Table 4) is 10 to 40%, where the greater variation was observed at 54.6°C. Figure 10 shows greater absolute variation for the 67.5°C test series, however, when referenced to the average with the RSD, the 54.6°C test series has a greater relative variation. Table 5 shows the variation among the sequences. There does not appear to be any trend with sequence number and the variation appears slightly less in a sequence (among slides A1 to A4) than for a single slide (among sequence 1 to 4).

Table 4. TNT Dimple Slide Summary Statistics – Dimple Slide by Temperature

| Slide | n = | Temp = 67.5°C | | | Temp = 60.7°C | | | Temp = 54.6°C | | |
|-------|-----|---------------|-------|------|---------------|-------|------|---------------|-------|------|
| | | AVG | STDEV | RSD | AVG | STDEV | RSD | AVG | STDEV | RSD |
| A1 | 4 | 7.95 | 1.75 | 22.0 | 3.23 | 0.48 | 14.8 | 1.41 | 0.22 | 15.7 |
| A2 | 4 | 7.66 | 1.09 | 14.2 | 3.40 | 0.54 | 15.9 | 1.27 | 0.31 | 24.0 |
| A3 | 4 | 8.45 | 0.78 | 9.3 | 3.41 | 0.39 | 11.5 | 1.21 | 0.44 | 36.5 |
| A4 | 4 | 8.96 | 0.85 | 9.5 | 3.94 | 0.65 | 16.5 | 1.34 | 0.54 | 40.2 |
| All | 16 | 8.26 | 1.17 | 14.2 | 3.50 | 0.54 | 15.5 | 1.31 | 0.39 | 30.2 |
| Temp | 16 | 67.5 | 0.09 | 0.1 | 60.7 | 0.08 | 0.1 | 54.6 | 0.10 | 0.2 |

Table 5. TNT Dimple Slide Summary Statistics – Sequence by Temperature

| Sequence | n = | 67.5 | | | 60.7 | | | 54.6 | | |
|----------|-----|------|-------|------|------|-------|------|------|-------|-------|
| | | avg | stdev | rsd | avg | stdev | rsd | avg | stdev | rsd |
| 1 | 4 | 9.61 | 0.73 | 7.6 | 3.88 | 0.68 | 17.5 | 1.66 | 0.14 | 8.6 |
| 2 | 4 | 7.90 | 1.33 | 16.9 | 3.82 | 0.19 | 5.0 | 1.01 | 0.14 | 13.45 |
| 3 | 4 | 7.45 | 0.32 | 3.2 | 2.93 | 0.32 | 11.0 | 1.56 | 0.16 | 10.30 |
| 4 | 4 | 8.07 | 0.99 | 12.3 | 3.36 | 0.29 | 8.6 | 0.99 | 0.29 | 29.12 |

The tests were performed with variation in elapsed time (Table 3) to evaluate whether elapsed time influences sublimation rate variability. Figure 11 shows the relationship between elapsed time and RSD for each temperature series sequence and no significant pattern emerges with this limited data set.

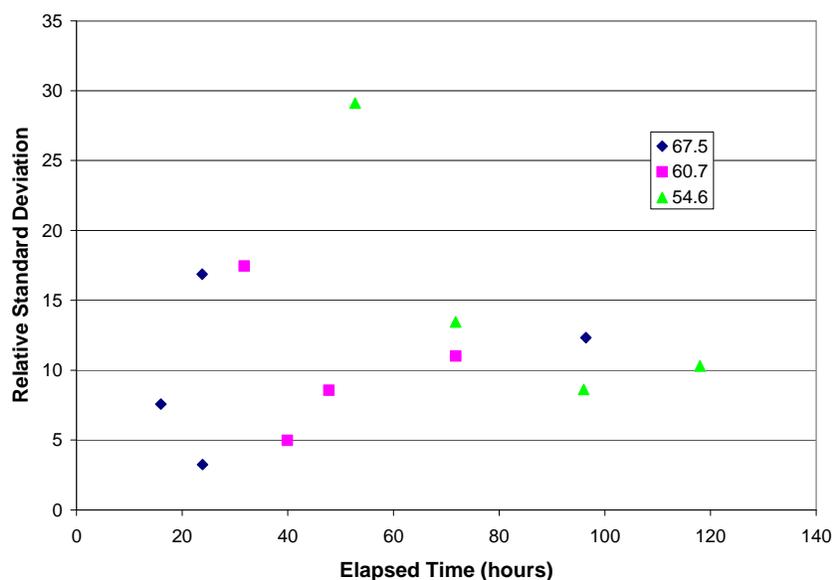


Figure 11. Effect of Test Elapsed Time on the Relative Standard Deviation

Table 6 shows the sublimation rate summary data for the dimple slide test. The average of all 16 tests (all 4 slides, all 4 sequences) was selected to represent the data. The data in Table 6 are presented to show the Arrhenius relationship as shown in Figure 12. For the dimple slide, the enthalpy of sublimation was calculated to be 132 kJ/mol, ~20% higher than for the TGA method described above. The correlation is still very strong ($r^2 = 0.996$) even though only three points were available.

Table 6. Dimple Slide Data Summary

| T (°C) | T (°K) | 1/T (°K ⁻¹) | Sub Rate (ng/cm ² -sec) | Ln Sub Rate |
|--------|--------|---------------------------|------------------------------------|-------------|
| 67.5 | 340.5 | 0.00294 | 8.26 | 2.11 |
| 60.7 | 333.7 | 0.00300 | 3.50 | 1.25 |
| 54.6 | 327.6 | 0.00305 | 1.31 | 0.27 |
| | | slope (E _a /R) | -15864 | |
| | | E _a | -132 | kJ/mol |
| | | intercept | 48.73 | |
| | | r ² | 0.996 | |

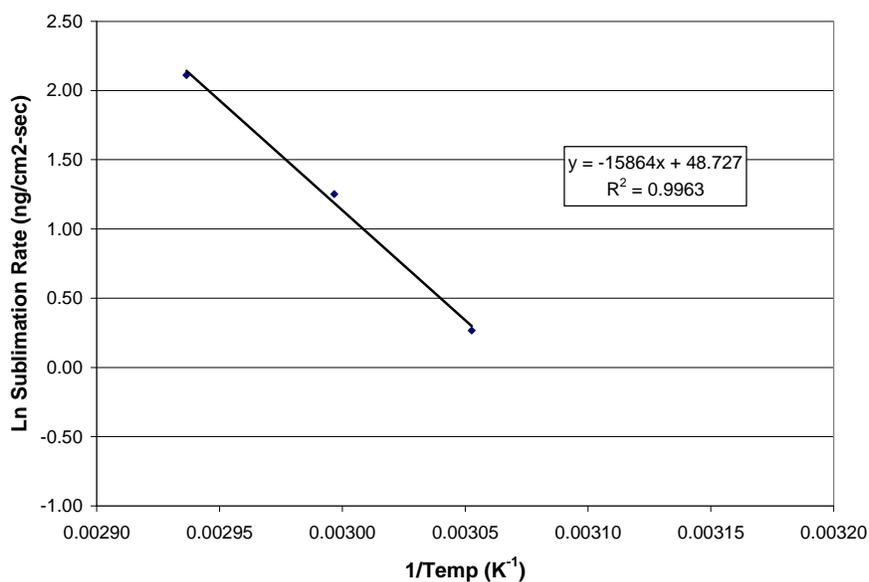


Figure 12. TNT Dimple Slide Arrhenius Plot

4.1.3 Combined Sublimation Data

The data determined with the TGA and the Dimple Slide tests were combined with data from the literature for TNT sublimation measurements using quartz crystal microbalance (QCM) methods (Mu et al., 2003). The QCM method provides a very sensitive determination of mass loss and the reported results included temperatures below the limits of our method. Table 7 shows the combined data for all three experimental methods. The enthalpy of sublimation for all three data sets was found to be 115 kJ/mol with a strong correlation of $r^2 = 0.999$ and is shown in Figure 13.

Table 7. Combined Data Summary

| Method | T (°C) | T(°K) | 1/T (K ⁻¹) | Sub Rate (ng/cm ² -sec) | Ln Sub Rate |
|--------------|--------|-------|---------------------------|------------------------------------|-------------|
| TGA -Pt | 70 | 343 | 0.002915 | 10.0823 | 2.310785 |
| | 62 | 335 | 0.002985 | 3.8389 | 1.345198 |
| | 45 | 318 | 0.003145 | 0.4853 | -0.7229 |
| | 55 | 328 | 0.003049 | 1.3593 | 0.306959 |
| Mu/QCM | 25 | 298 | 0.003356 | 0.0248 | -3.69651 |
| | 30 | 303 | 0.0033 | 0.0496 | -3.00336 |
| | 35 | 308 | 0.003247 | 0.0992 | -2.31021 |
| | 40 | 313 | 0.003195 | 0.2233 | -1.49928 |
| Dimple Slide | 68 | 341 | 0.002937 | 8.2555 | 2.110878 |
| | 61 | 334 | 0.002997 | 3.4968 | 1.251836 |
| | 55 | 328 | 0.003049 | 1.6613 | 0.507624 |
| | | | slope (E _a /R) | -13782 | |
| | | | E _a | -115 | kJ/mol |
| | | | intercept | 42.51 | |
| | | | r ² | 0.999 | |

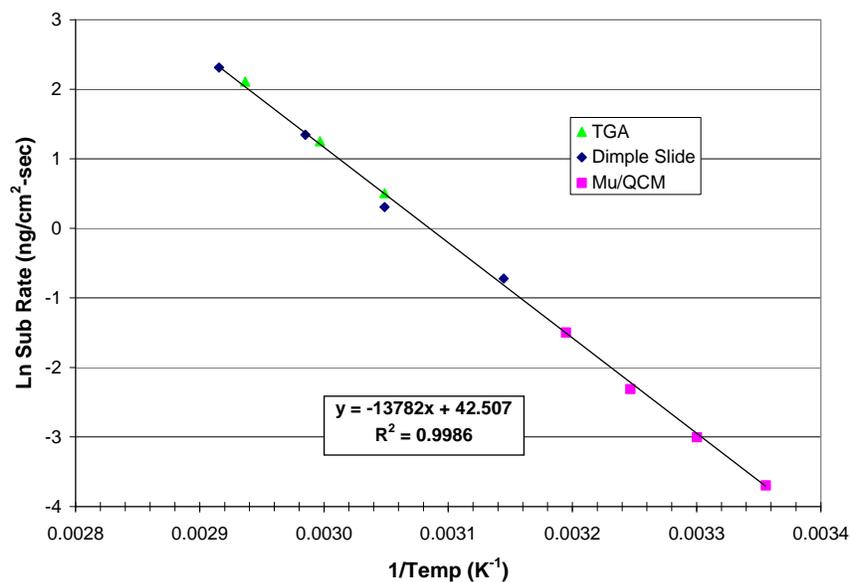


Figure 13. Combined Data Sets Arrhenius Plot

Figure 14 shows a more convenient view of the sublimation rate as a function of temperature. This shows that TNT sublimation increases by a factor of four for each 10°C change in temperature. Table 8 shows the enthalpy of sublimation for TNT based on this work and other approaches found in the literature. Vapor pressure determinations also typically report sublimation enthalpies. Variations in sublimation enthalpies are attributable to changes in technique and source material.

Using the combined data, the measured sublimation rate at 70°C is 10 ng/cm²-sec compared to a value of 2.5 ng/cm²-sec estimated from Fick's Law (Section 2.0). At 45°C, the measured sublimation rate is 0.4 ng/cm²-sec compared to 0.2 ng/cm²-sec from Fick's Law. The differences are a factor of 2 to 4, which is quite good given the uncertainties in boundary layer thickness and saturated vapor pressure values used in the Fick's Law estimates.

Table 8. TNT Enthalpy of Vaporization from Various Methods

| Source | Enthalpy of Sublimation, E _a (kJ/mol) | Temperature Range (°C) | Method |
|--------------------------|--|------------------------|---|
| This work - TGA | 111 | 45 - 70 | Sublimation - Gravimetric |
| This work - Dimple Slide | 132 | 55 - 68 | Sublimation - Gravimetric |
| Mu et al | 113 | 25 - 40 | Sublimation - Quartz Crystal Microbalance |
| Lenchitz & Velicky | 103 | 55 - 76 | Vapor Pressure - Knudsen Diffusion Cell |
| Pella | 99 | 14 - 57 | Vapor Pressure - Mass Transfer |
| Dionne et al | 105 | 13 - 144 | Vapor Pressure - Data Summary |

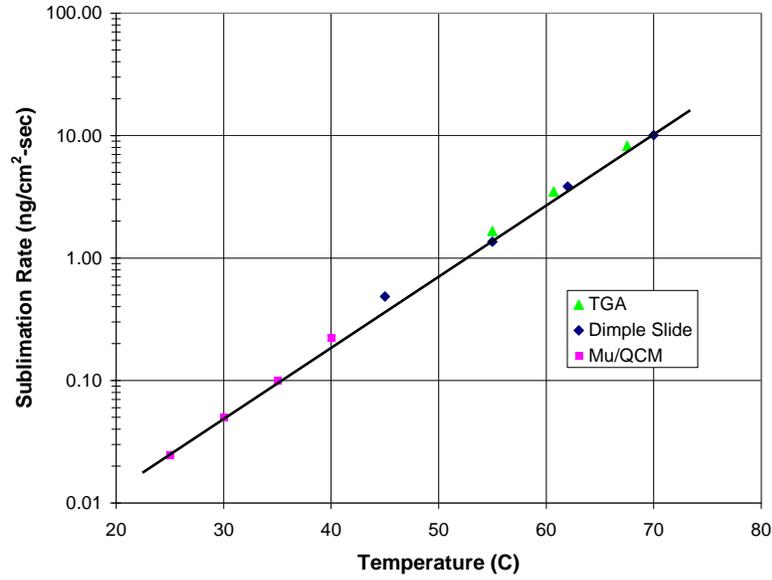


Figure 14. TNT Sublimation Rate as a Function of Temperature (25 to 70°C)

4.2 Atmospheric Dispersion

The principal purpose for the experimental determination of the sublimation rate of TNT was to use the data for an emission rate in estimation of standoff vapor concentrations with distance. A simple Gaussian steady state atmospheric dispersion model was selected for initial estimates. The assumptions in Gaussian modeling include (Turner, 1994):

- Continuous Emissions – the chemical emissions are continuously emitted and do not vary over time.
- Conservation of Mass – during atmospheric transport, the mass remains in the atmosphere.
- Steady-State Conditions – the meteorological conditions do not change over the travel time from emission to destination.
- Crosswind and Vertical Concentration Distributions – the time averaged (~ one hour) concentration profiles are represented by a Gaussian distribution.

The concentration of a chemical in the atmosphere located at x downwind, y crosswind and a height z above the ground from an emission that occurs from an effective height of H is estimated by

$$\chi(x, y, z; H) = \frac{Q}{2 \cdot \pi \cdot u \cdot \sigma_y \cdot \sigma_z} \cdot \exp\left[-\frac{y^2}{2 \cdot \sigma_y^2}\right] \left\{ \exp\left[-\frac{(H-z)^2}{2 \cdot \sigma_z^2}\right] + \exp\left[-\frac{(H+z)^2}{2 \cdot \sigma_z^2}\right] \right\} \quad [2]$$

where, χ is the chemical concentration in air (g/m^3), Q is the emission rate (g/s), u is the wind velocity at the point of release (m/s), σ_y is the standard deviation of the concentration distribution in the crosswind direction at the downwind distance x, σ_z is the standard deviation of the concentration distribution in the

vertical direction at the downwind distance x , and H is the effective height of the centerline of the emitted vapor.

To calculate concentrations at the plume centerline, $y = 0$, $z = H$, equation [2] simplifies to

$$\chi(x,0,H;H) = \frac{Q}{2 \cdot \pi \cdot u \cdot \sigma_y \cdot \sigma_z} \left\{ 1 + \exp \left[-\frac{H^2}{2 \cdot \sigma_z^2} \right] \right\} \quad [3]$$

The horizontal and vertical dispersion parameters (σ_y and σ_z) are estimated for each atmospheric stability class (A through F) by Pasquill-Gifford dispersion parameters. Strongly unstable conditions (class A), which occur with strong incoming solar radiation (midday sun), produce the greatest dispersion and were chosen for the initial atmospheric dispersion estimates. Table 9 summarizes the Gaussian dispersion model input parameters selected for this initial evaluation. The combined sublimation data (Figure 13) were used to estimate the TNT emission rate at three different temperatures (62, 45 and 20°C) from a very small area of 100 cm².

Table 9. Gaussian Dispersion Model Parameters

| Parameter | Value | Units |
|-----------------|-------|-------|
| Q (20°C) | 1 | ng/s |
| Q (45°C) | 44 | ng/s |
| Q (62°C) | 390 | ng/s |
| Stability Class | A | |
| H | 0.5 | m |
| u | 0.5 | m/s |

Equation [3] was then used to estimate the TNT concentrations from 1 m to 100 m. The results from these calculations are shown in Figure 15. One must be cautioned that these estimates are an extrapolation of the typical application of Gaussian plume dispersion over much greater distances (>100 m). The time averaging assumption of Gaussian models implies that at short distances there may be insufficient mixing to produce Gaussian conditions. Tables in Turner (1994) describing the atmospheric dispersion parameters show the lowest distance range of 100 m, and here we have extended that down to 1 m, which implies that extreme caution should be exercised when interpreting these values.

Under these conditions, at a nominal distance of 10 m and at 20°C, the estimated vapor concentrations at 0.5 m above the ground directly downrange with a 0.5 m/s wind is about 0.01 ppt – a value that is below current real-time explosive vapor sensing technology. However, at greater temperatures, the estimated vapor concentrations are much more and if time is available, preconcentration approaches can improve detection of these very low vapor concentrations.

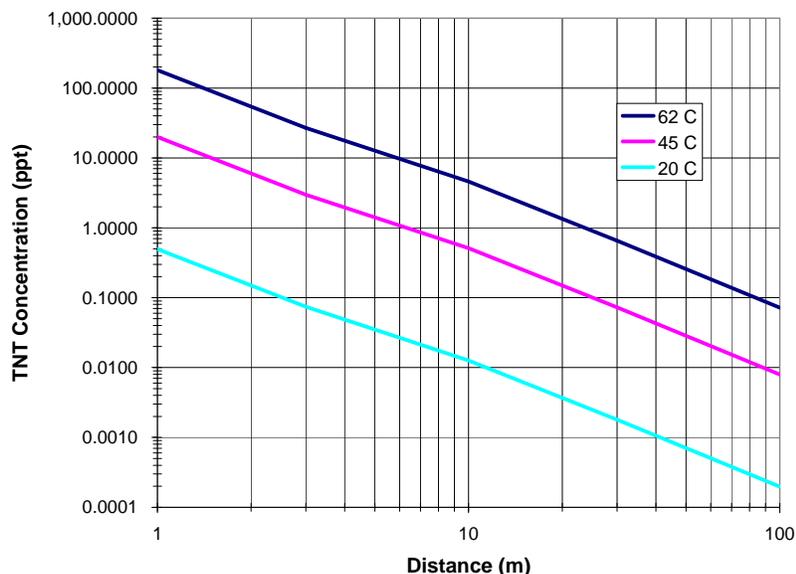


Figure 15. TNT Gaussian Dispersion Results

4.3 Future Plans

This interim report describes the methods and initial results for emanations of explosive vapors with applications to developing performance requirements for vapor sensing at standoff distances. This work was begun using single component, multi-temperature, steady-state methods to develop maximum emission rates. In the real world, the explosives are often in mixtures (e.g. CompB and C4), the explosives may be enclosed in packaging materials, and the temperatures are not steady.

We have developed plans to continue the TGA and dimple slide work for pure-RDX, albeit these will necessarily have to be at temperatures of 100 to 140°C. The dimple slide apparatus we have is designed to evaluate the influence of wind on explosive emission rates. Literature suggests that increasing velocity could increase the emission rates by a factor of ~ 5 (Tinsley, 1979). We have developed experimental tests that would extend the TGA method with evolved gas measurements to determine the emanation rates of explosive constituents in a mixture. The TGA instrument can be programmed for a thermal cycle that will give us the data to compare extrapolated steady-state temperature sublimation rates applied to the thermal cycle to gravimetric loss during the programmed thermal cycle. This will help understand lag times in the emanation rates as a function of heating and cooling rates.

These well controlled experiments will provide the scientific understanding before proceeding to more real world materials such as improvised explosive devices (e.g. artillery projectiles and mortars) or emissions from fingerprints or contaminated objects and clothing. The experimental apparatus for these types of tests are conceived to be a volumetric chamber with air inlet and exhaust where vapors can be collected or directly measured.

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