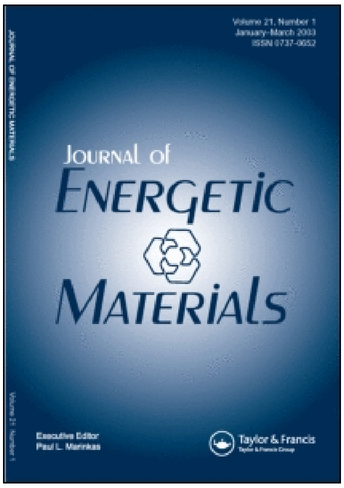

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VAPOR PRESSURE OF EXPLOSIVES

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Abstract

New vapor pressure data is presented for RDX, PETN, TNT, nitroglycerin, and ammonium nitrate. By comparison with the data of previous workers, it has been possible to calculate global vapor pressure expressions which are valid over a wide range of temperatures.

INTRODUCTION

Literature reports on the vapor pressure of many explosives vary by several orders of magnitude. In the case of PETN, for example, published values differ by

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values are reasonably consistent; we report new confirmatory determinations at room temperature only.

For ammonium nitrate, we report determinations over a wide temperature range and a limited range of carrier gas humidity . Volatilization of ammonium nitrate is an occurence well known to atmospheric scientists who have studied its presence in atmospheric aerosols. Losses of 50% of the amount of ammonium nitrate loaded onto Teflon and glass fiber filters have been observed [10]. Forrest et al.[11] reported that the greatest NH_4NO_3 losses occured at relative humidities below 60%; at 100% relative humidity, no NH_4NO_3 was lost. The mechanism by which these losses occur was not clear. Smith et al. [12] reported that ammonium nitrate losses produced equimolar amounts of ammonium and nitrate ions, which tends to support molecular sublimation of ammonium nitrate. However, dissociation of the salt to ammonia and nitric acid has also been proposed [10, 13, 14] to account for the ammonium nitrate losses and the effect of humidity. This paper is concerned with the vapor pressure of ammonium nitrate for explosives detection purposes, and does not address volatilization mechanisms.

Accurate knowledge of the vapor pressure of explosives is essential in planning whether bomb three orders of magnitude at room temperature [1-4]. At very low vapor pressures, measurements based on mass depletion or direct pressure measurement tend to be high due to trace amounts of more volatile impurities. Isotope dilution mass spectrometry has been employed in an effort to enhance selectivity. However, this technique yields results that are sometimes anomolously higher than non-selective determinations.

Using a new vapor pressure generator coupled with selective detection of the explosive, we report new determinations for the vapor pressure of a variety of explosives, and discuss the results vis-a-vis previously published determinations. The generating system consists of a small amount of the explosive in equilibrium with a carrier gas. To characterize the generator, the effluent was collected quantitatively in a cold trap, and the output then analysed both quantitatively and qualitatively using a gas chromatograph (GC) in conjunction with a Thermedics TEA Analyzer. The GC-TEA technique [5-8] has been shown to be selective for nitro-based compounds and has been used to identify and quantitate explosives in post-blast residues and hand-swab experiments [9].

For RDX and PETN, we report measurements over a wide temperature range. For TNT and NG, published detection is best achieved by vapor detection or by remote sensing.

MATERIALS

Military grade RDX, C-4, and PETN were obtained from the FBI. C-4, which contains about 90% RDX [15], was used in the vapor generator, and RDX solutions were used as standards in GC-TEA analysis. The PETN sample was used for both the generator and the standard solutions. TNT was obtained from Sandia Laboratories and was used in the generator and for the standard solutions. Nitroglycerine, NG, at a mole fraction of 0.96 dissolved in an uncured liquid polymer polymer solution (ICI America, Inc., Wilmington, DE, USA) was used for the generator. The NG used for preparation of standard solutions was obtained by methanol extraction of a dispersion of NG in lactose (ICI America, Inc.) and separation of the lactose by centrifugation. Ammonium nitrate, NH_4NO_3, used for both the generator and standard solutions, was Baker Analyzed Reagent grade prills. All explosives were used as received without further purification.

Acetone used for solubilization of RDX, PETN, NG, and TNT was Burdick and Jackson Reagent grade. Water used in NH_4NO_3 experiments was Baker Reagent grade. Nitrogen used as the carrier gas in the vapor generator was of a commercial grade supplied by Suburban Welders.

APPARATUS AND PROCEDURES

Vapor Generator Apparatus

A constant stream of explosive vapors in a carrier gas was generated in the apparatus illustrated in Figure 1. The nitrogen carrier gas passed, in order, through a Drierite/molecular sieve filter, a Tylan Mass Flow controller, and into Teflon tubing to a modified glass Midget Impinger (Kontes Glassware, Inc.) which contained the explosive sample. The generator glassware was immersed in a heated sand bath which allowed the temperature to be regulated to within 0.1°C. The gas containing the explosive vapor exited from the impinger through a glass transfer line which was temperature-controlled independently of the sand bath. The temperature of the transfer line was always kept above the temperature of the sand bath to prevent condensation of the explosive vapor onto the walls of the transfer line. Ball and socket joints on the transfer line were used to attach traps for collection of explosives vapors. The far end of the transfer line

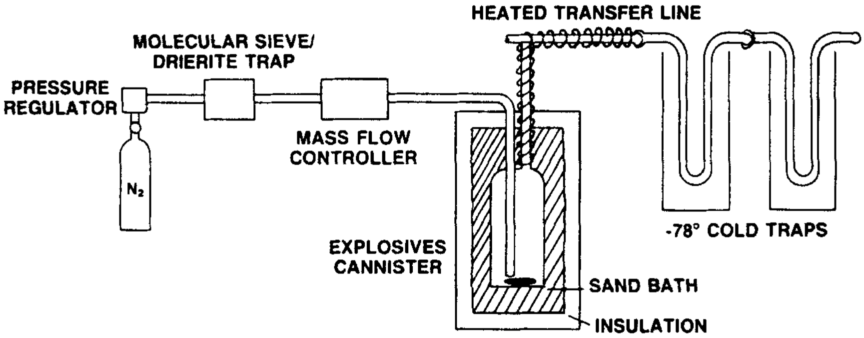


FIGURE 1
Explosives Vapor Generator Apparatus

could be capped with a Teflon plug, or it could be joined to a nitrogen line for dilution of the vapor stream. The temperature of the generator system was monitored by the use of 5 thermocouples: 3 were attached to the impinger which was submerged in the sand bath, and 2 were placed on the transfer line.

For the ammonium nitrate experiments, a vapor stream was generated at different humidity levels. This was accomplished by using two streams of nitrogen, with each flow being regulated by a Tylan mass flow controller, and passing one of the N_2 lines through a water-bubbler. Different humidity levels were achieved by varying the proportion of N_2 which passed through the water.

Separate generator systems were assembled for each explosive. For C-4 and NH_4NO_3, approximately one gram was placed directly into the generators. PETN and TNT were added by dissolving about 200 mg in acetone, and wetting the walls of the glassware so that the sides were coated, and then evaporating the solvent. In the NG generator, approximately 5 ml of the polymer solution was used. Before the apparatus was used, it was operated with carrier gas flowing, for a minimum of one week to allow equilibration.

Vapor Collection

Vapor collection experiments were initiated by attaching traps to the transfer line of the generator via the ball and socket joints. For RDX, PETN, NG, and TNT, the traps consisted of dimpled U-tubes immersed in dry ice/acetone baths (-78°C). The presence of H_2O in NH_4NO_3 vapor collection experiments necessitated a different trapping system. Here midget impingers connected by ball and socket joints, immersed in ice water, were used.

In order to establish the trapping efficiency, two identical traps were placed in series. The concentration of explosives emerging from the generator, C_0, could be calcuated from the following equations:

Where a = the trapping efficiency,

C_1 = the amount of explosive in the first trap,

C_2 = the amount of explosive in the second trap, and

C_0 = the actual amount of explosive emerging from the generator.

$$C_1 = a\ C_0$$

$$C_2 = a\ (C_0 - C_1)$$

Thus $a = 1 - C_2/C_1$, and $C_0 = C_1/a$.

The trapping efficiency, a, was found to be in the range 95-99% in all cases.

Following collection for a measured time duration, the traps were removed and then quantitatively rinsed with solvent(acetone for RDX, PETN, NG, and TNT, and H_2O for NH_4NO_3). The washings were analyzed to determine the total amount, C_0, of explosive that emerged from the generator.

Since the mass flow rate of carrier gas through the generator and the time duration of the trapping experiments were determined experimentally, the total number of moles of gas which passed through the generator could be calculated, and hence the concentration of explosives vapor in the carrier gas.

The RDX measurements were conducted over the temperature range of 37°C to 102°C. Three separate sets of apparatus were used, one for each temperature. The temperature of the glass transfer line was kept at 155°C, since decomposition was shown to occur above 175°C. The collection time from 30 minutes for high temperature to 5500 minutes for low temperature experiments. The flow rate of the N_2 carrier in the generator was 200 cc/minute during the 102°C collection. For the other experiments, the flow rate was maintained at 400 cc/minute.

The PETN experiments were similar to those for

RDX. The transfer line temperature was 50°C, and the vapor pressure was measured over the range of 18°C to 38°C. The nitrogen flow rate through the generator was held at 470 cc/minute, and the collection periods ranged from 500 to 900 minutes.

The vapor pressure of TNT was measured at 25°C, with a transfer line temperature of 55°C. The carrier flow rate was maintained at 400 cc/minute, and the trapping times varied from 500 to 1400 minutes.

NG vapor was generated at 26°C. The N_2 flow rate was 105 cc/minute, and the trapping times were 600 to 900 minutes.

NH_4NO_3 vapors were collected over the temperature range 40°C to 80°C for three humidity levels: dry nitrogen, and with 30% and 80% of the nitrogen passing through a water bubbler. Actual water contents of 0.19% and 0.57% H_2O by weight, respectively, were determined from the weight of water collected in the trap. The transfer line was held at 105°C. Nitrogen flowed through the generator at a rate of 400 cc/minute. The collection time for NH_4NO_3 vapors varied from 300 to 1000 minutes.

Analysis of RDX, PETN, NG, and TNT

The washings obtained from the traps was analyzed by GC-TEA. A Hewlett-Packard 5840A gas chromatograph was used equipped with 30 meter DB5 Megabore column. Argon was used as the carrier gas. The TEA (Thermedics Inc. Model 502) was operated in the nitrogen mode. The pyrolyzer was kept at 900°C, and the interface region between the GC and the pyrolyzer was set at 280°C. This system was used to compare sample solutions to gravimetrically prepared standard solutions. Detection limits were about 30-50 pg for these explosives. Reported values represent the average of at least three separate GC-TEA determinations.

Analysis of Ammonium Nitrate

The method used to detect ammonium nitrate was similar to high performance liquid chromatography (HPLC)-TEA [8, 9, 16] without the column. The mobile phase, H_2O, was pumped by an HPLC pump (Varian Model 8500) at a flow rate of 70 ml/hour. Ammonium nitrate sample solutions were introduced through an injector (Rheodyne Model 7125) equipped with a 20 ul sample loop. The stream then entered the TEA furnace, operated in the nitrogen mode at 840°C. Oxygen was introduced into the furnace at a flow rate of 7 cc/minute. Under the pyrolysis conditions used for NH_4NO_3, the TEA produced a signal response for the nitrate ion, and not for the ammonium ion. This was established by injecting solutions of known concentrations of NH_4Cl and KNO_3 into the detection system; Equimolar responses were obtained for KNO_3 and NH_4NO_3. The detection limit for NK_4NO_3 was 3 ng.

The same H_2O was used to humidify the nitrogen in the generator system, to rinse the traps, for the standard solutions, and as a carrier in the detector. To ensure that the system was free from contamination, a vapor collection experiment was performed with the explosives source removed but with the system plumbing otherwise unchanged. After flowing N_2 through the apparatus at 400 cc/min., with 30% of the N_2 passing through the H_2O-bubbler, for a period of 6 hrs., the H_2O in the trap was analyzed. No signal was observed for this experiment, which had an ammonium nitrate detection limit of 1 ppb. This limit is 2% of the vapor pressure at the lowest temperature studied; therefore any source of detectable signal other than explosive was negligible.

RESULTS AND DISCUSSION

RDX

The measured RDX vapor pressures, expressed in parts per trillion (v/v) are plotted against the reciprocal of the absolute temperature, in Figure 2, in accordance with the Clausius- Clapeyron equation:

$$\text{Log } P = H_{sub}/(2.303\ RT) + H_{sub}/(2.303RT_0)$$

where T is the temperature expressed in Kelvin, and H_{sub} is the heat of sublimation.

RDX vapor pressure data from three other sources, utilizing three different experimental methods, are also plotted in Figure 2. The data of Edwards [1] was based on weight loss due to diffusion of the explosive through a small orifice. Rosen and Dickinson [17] employed the Langmuir method, which is based upon the weight loss of the sample heated in vacuum. The data of St. John et. al.[2] were obtained by isotope dilution analysis. The graph shows excellent consistency between the new data and the data of Edwards, and Rosen and Dickinson. The results of St. John et. al. appear to be anomolous, particularly because the weight loss techniques used by Edwards and by Rosen and Dickinson would, if anything, have yielded elevated results from traces of more volatile impurities.

A least squares analysis incorporating the data in Figure 2 (except the 60°C point of St. John et al.) gives a global expression over the entire temperature range:

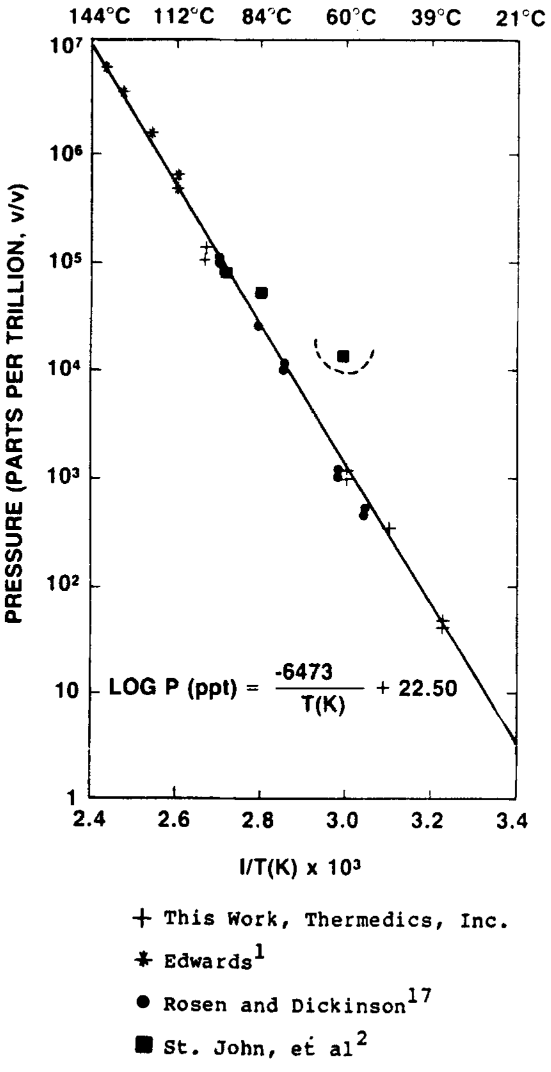


FIGURE 2
Vapor Pressure of RDX

$$\text{Log } P \text{ (ppt)} = -6473/T(K) + 22.50$$

From this equation, the vapor pressure of RDX at room temperature (25°C) is 6.0 parts per trillion (v/v).

PETN

The PETN data are displayed in Figure 3 together with other published values. The data of Edwards (as with RDX) was based upon the rate of diffusion of PETN through a small orifice [1]. Ng et al.[3] directly measured the pressure change resulting from heating the sample in an high vacuum system. Using Knudsen diffusion techniques similar to those of Edwards, Crimmins [4] obtained vapor pressures higher than those of Edwards, Ng et. al., and this work. Crimmins did, however, detect traces of two impurities in his PETN sample by thin layer chromatography.

The PETN vapor pressure measurement of St. John et al. [2] relies upon a technique which is in principle chemically selective: isotope dilution analysis. However, their data for PETN were obtained by monitoring NO_2 ions, since the parent PETN ion was not sufficiently stable in the mass spectrometer. Their greatly elevated vapor pressure results are apparently due to contamination by other species that can produce NO_2 ions in the mass spectrometer.

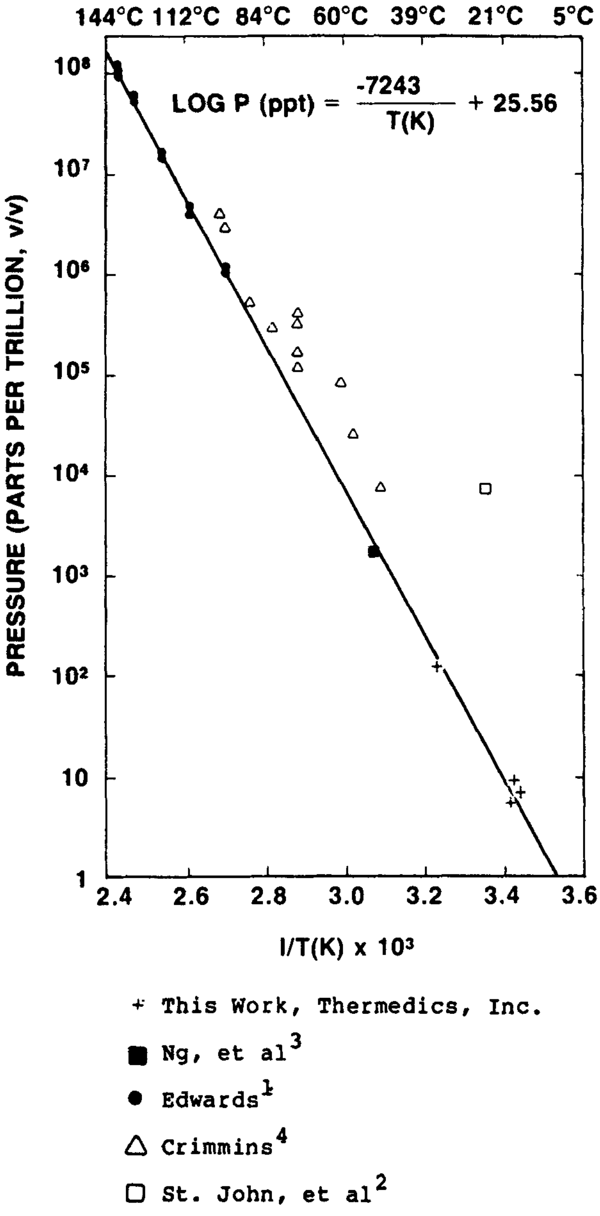


FIGURE 3
Vapor Pressure of PETN

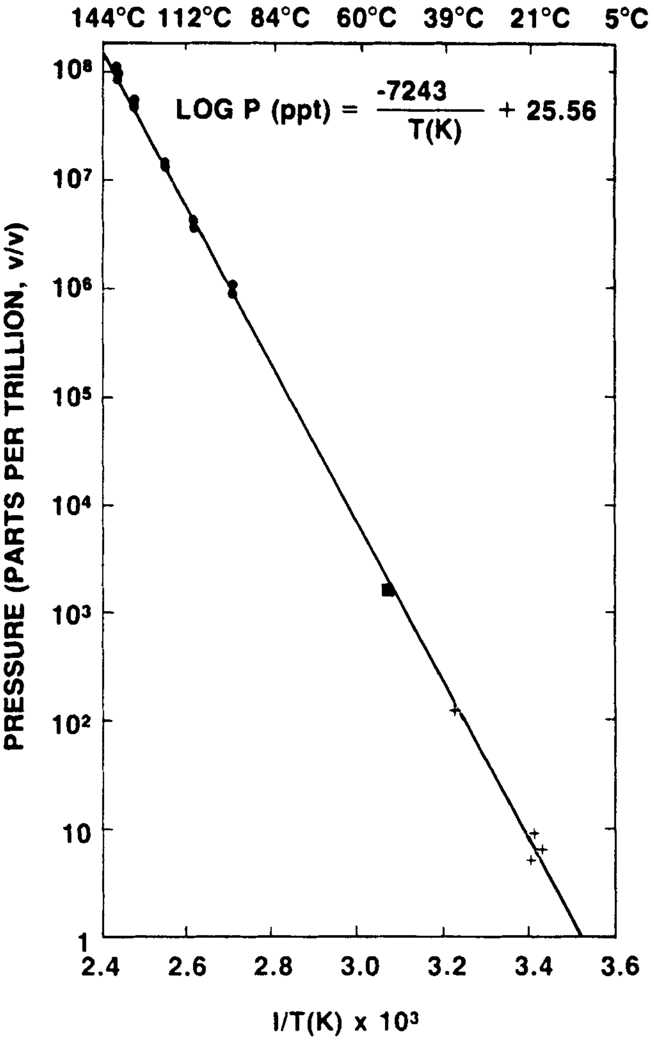
The excellent agreement between the data of Edwards, Ng, et al., and the present work is apparent from Figure 4. The current data extend the range of measured data to lower temperatures and vapor pressures. The least squares analysis on the three data sets gives the global equation:

$$\text{Log } P \text{ (ppt)} = -7243/T(K) + 25.56$$

Evaluation of this equation leads to a vapor pressure of 18 ppt v/v for PETN at 25°C.

TNT

Three separate determinations for TNT at 25°C gave an average vapor pressure of 7.7 ± 0.4 ppb v/v. This value is plotted along with other published values in Figure 5. All of the data from Edwards[18] and Pella[19] was used in our calculations, but for convenience only a limited number of data points from these references are reproduced in the figure. Reasonable agreement is observed between all sources, with the exception of Menzies[20] who measured pressure changes over an intentionally unpurified sample using a McLeod gauge. Presumably, the impurities are responsible for his elevated vapor pressure values. Leggett et al.[21] utilized a gas chromatographic headspace technique. The overall agreement between different sets of workers is



+ This Work, Thermedics, Inc.

■ Ng, et al[3]

● Edwards[1]

FIGURE 4
Vapor Pressure of PETN

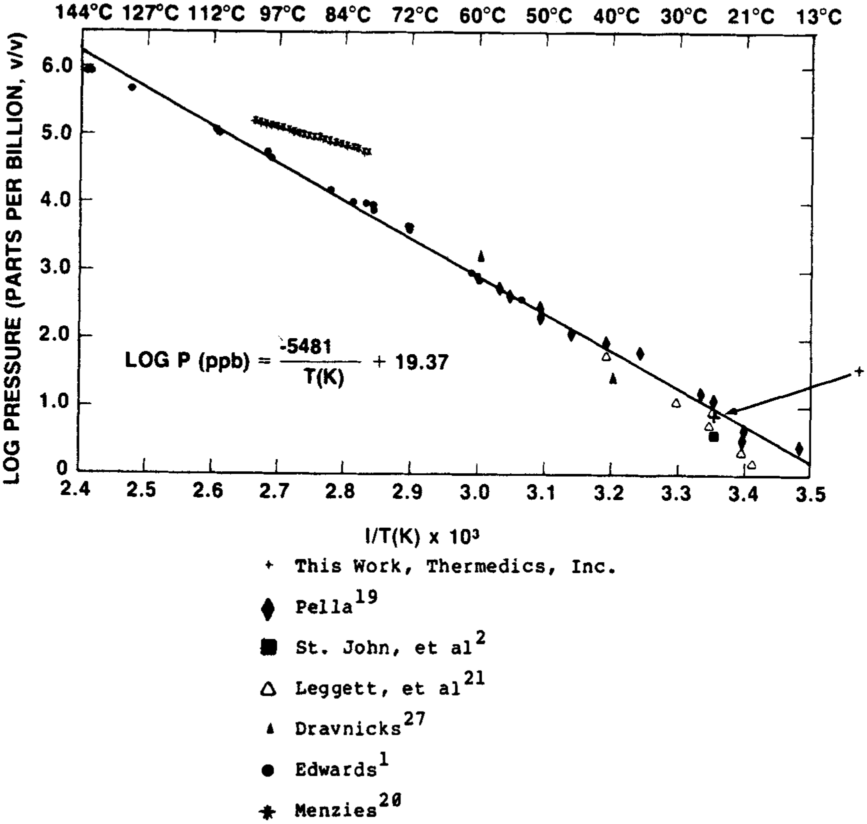


FIGURE 5
Vapor Pressure of TNT

better than that observed for PETN and RDX. This is understandable, since the vapor pressure of TNT is nearly three orders of magnitude higher than that of PETN and RDX. The least squares analysis includes all of the literature data, except for Menzies:

$$\text{Log } P = -5481/T(K) + 19.37$$

From this equation the vapor pressure of TNT at 25°C is 9.4 ppb v/v, which is very close to our measured value of 7.7 ppb.

NG

Two NG vapor trapping experiments yielded an average vapor pressure of 409 $^{+}/_{-}$ 11 ppb at 26°C (including a small correction for the mole fraction (0.96) of the source NG material in the generator). This average has been plotted in Figure 6 along with values obtained from previously published data [2, 22, 23, 24, 25]. The present data is in reasonable agreement with earlier work. The values reported by Rinkenbach [22] and by Naoum and Meyer [23] are higher than the rest of the data; the presence of impurities is suspected. St. John et al. using isotope dilution analysis data [7], quote an NG vapor pressure which is 19 times lower than the value given by the slope of the line in Figure 6. The reason for this difference is not

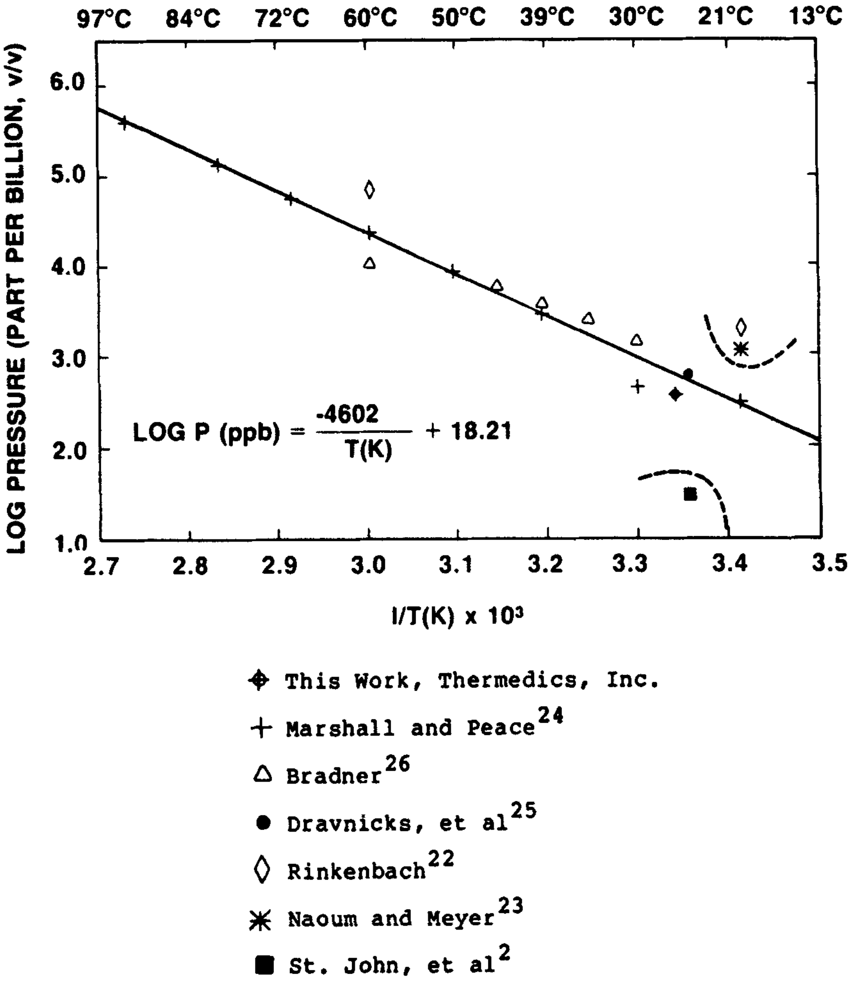


FIGURE 6
Vapor Pressure of Nitroglycerine

understood. The data of St. John, et al., and Naoum and Meyer, and the low temperature data point of Rinkenbach have been excluded from the least squares analysis:

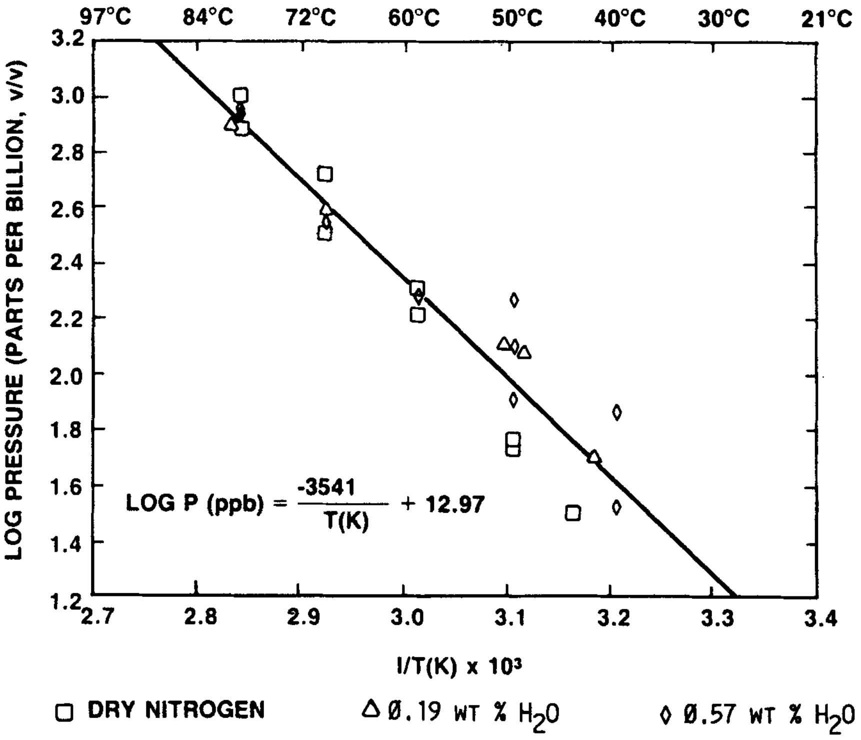
$$\text{Log } P \text{ (ppb)} = -4602/T(K) + 18.21$$

NH_4NO_3

Our results for the vapor pressure of ammonium nitrate are shown in Figure 7. Ammonium nitrate has a rather high apparent vapor pressure of 12 ppb v/v at 25°C, on the order of the vapor pressure of TNT. In our experiments, the water content of the carrier gas was varied from 0 to 0.56 weight percent; therefore, the maximum relative humidity varied from 27% at 40°C to 4% at 80°C. Over the temperature and humidity range studied, no clear dependence of vapor pressure on humidity was observed. Despite the experimental scatter, the Clausius-Clapeyron plot appears to be linear. Least squares analysis of the data yields the following equation:

$$\text{Log } P \text{ (ppb)} = -3541.77/T(K) + 12.97$$

The data of Appel et al. [10] suggest a lower limit of 4-5 ppb for the vapor pressure at 21°C. This is consistent with the value of 8.4 ppb for this temperature calculated from our least squares equation.


97°C
84°C
72°C
60°C
50°C
40°C
30°C
21°C
LOG PRESSURE (PARTS PER BILLION, v/v)
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
$\text{LOG P (ppb)} = \frac{-3541}{T(K)} + 12.97$
2.7
2.8
2.9
3.0
3.1
3.2
3.3
3.4
$I/T(K) \times 10^3$
□ DRY NITROGEN
△ 0.19 WT % H_2O
◊ 0.57 WT % H_2O

CONCLUSIONS

A new, chemically selective method for determination of explosives vapor pressures has been used to measure the vapor pressure of five common explosives. Data from this study and other published sources were critically compiled. A clear picture of the vapor pressure of these explosives emerges from the extremely close agreement between our new data and much of the earlier work. Most of the conflicting data can be explained on the basis that non-selective techniques will overestimate the vapor pressure if traces of volatile impurities are present.

The compiled data was used to generate global least squares Clausius-Clapeyron equations over wide temperature ranges. From these equations, the vapor pressures of RDX, PETN, TNT, NG, and NH_4NO_3 at 25°C were determined to be 0.006, 0.018, 9.4, 580, and 12 ppb v/v, respectively.

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