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Safe Deactivation of Energetic Materials and Use of By-products as Epoxy Curing Agents

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Safe Deactivation of Energetic Materials and Use of By-products as Epoxy Curing Agents

Final Report – SERDP Project CP-1079

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Abstract

Sandia National Laboratories is developing innovative alternative technology to replace open burn/open detonation (OB/OD) operations for the destruction and disposal of obsolete, excess, and off-spec energetic materials. Alternatives to OB/OD are necessary to comply with increasingly stringent regulations. This program is developing an alternative technology to destruct energetic materials using organic amines with minimal discharge of toxic chemicals to the environment and defining the application of the by-products for the manufacture of structural materials.

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Safe Deactivation of Energetic Materials and Use of By-products as Epoxy Curing Agents

Introduction

The DoD has a significant number of weapons components which need destroying. The Department of Defense (DoD) faces many environmental and legal issues in the demilitarization of these obsolete and excess energetic materials and assembled munitions. The current DoD stockpile of energetic materials that needs to be destroyed is about 700,000 tons. This total increases at a rate of approximately 60,000 tons per year.

Organic amines were found to react with TNT, RDX and Comp B at moderate temperatures, leading to a safe breakdown of the explosive materials without detonation, deflagration, or uncontrolled cook-off. The reaction of the explosive materials with the amines resulted in evolution of gaseous products, which were collected and analyzed. The resulting liquid by-products were found to be effective curing agents for conventional epoxy resins. Epoxies produced by this method were found to be safe and non-detonable. Mechanical properties of these epoxies were measured and can be tailored to the final requirements of any epoxy use. Commercial uses for this epoxy could complete the recycle of explosives.

Excerpts from the Joint Ordnance Commanders Group FY95 report¹ to Congress, summarizes the overview of munitions demilitarization. (A more current version will be published September 2001. This is the most recent report available at this time.) Looking to the future, the Army Science Board emphasizes including the life-cycle of the energetics in the early stages of designing and acquiring weapons. Table 1 lists the current stockpiles as of 31 March 1999. The generation of energetics forecasted for the period of FY2000 – 2009 is found in Table 2. Tables 1 and 2 list the amounts TNT and RDX found in the MIDAS¹ (www.dac.army.mil/TD/Midas) database.

Table 1. Estimation of Current and Forecasted Conventional Ammunition Inventories (31 March 1999)

(31 March 1999)

Type of Explosive	Current (lbs)	Forecasted (lbs)	Total (lbs)
Composition A, 91% TNT	7,319,586	14,806,530	22,126,116
Composition B, 60% TNT/40%RDX	6,176,766	12,859,588	19,036,354
Composition C, 12% TNT/88%RDX	571,069	4,678,031	5,249,100
H-6	449,835	585,756	1,035,591
HBX	5,553,120	2,950,125	8,503,245
PBX	63,767	17,670	81,437
RDX	56,927	404,440	461,367
TNT	7,530,996	12,912,769	20,443,765
Tritonal	57,351,405	16,874,385	74,225,790

Table 2. Estimation of Current and Forecasted Tactical Missile Resource Recovery and Disposition Account Inventories (31 March 1999)

Type of Explosive	Current (lbs)	Forecasted (lbs)	Total (lbs)
COMP A-5, 99% TNT	0	1,148,960	1,148,960
COMP B	200,860	1,718,238	1,919,098
COMP B-4,	0	325,593	325,593
CYCLOTOL	24,850	160,448	185,298
DESTEX	131,795	1,014,800	1,146,595
H-6	225,200	706,230	931,430
HTA-3	16,487	106,646	123,133
OCTOL	285,365	3,238,926	3,524,291
PBX	3,750	22,500	26,250
PBXN-107	4,136	25,427	29,563
PBXN-109	142,416	870,228	1,012,644

In the current and forecasted munitions for demilitarization operations, there are 93 million and 40 million pounds of TNT and RDX, respectively, that are available for resource recovery, recycle, or disposition. This represents less than one percent of the total 538,436 tons of stockpile.

1.0 Laboratory-Scale Process

Preliminary work investigating the reactions between explosives and amines was done for Sandia National Laboratories by the IIT Research Institute, as reported in Appendix A. Several amines were reacted with the explosives TNT, RDX, and Comp B to find the optimum amine to decompose the explosives. Monoethanolamine, diethanolamine, diethylenetriamine (DETA), n-

tributylamine, and ethylenediamine were all candidates. DETA is particularly interesting because it is the major constituent of DoD's decontamination solution for chemical agents, known as DS2. Thousands of tons of DS2 stockpile need destroying because it corrodes the containers in which it is stored. The potential application of DETA in DS2 for demilitarization of energetic materials, as well as chemical agents, is attractive and could substantially reduce the cost of the demilitarization. One requirement in selecting an amine was that the handling safety was well documented. The commercial product "Jeffamine" T-403 (polyoxypropylenetriamine, Huntsman Corp.), an amine curing agent used in 2-part epoxies, was chosen because of its commercial availability in large quantities, it has a low viscosity, and it has a well-documented safety record.

There are many considerations in choosing the optimum ratio of "Jeffamine" to be mixed with the explosive. One is a desire to consume as much explosive per unit of reacting agent as possible to destroy large quantities of surplus explosives. However, this produces a high-viscosity curing agent product, which is unworkable in the follow-on epoxy mixture. The ratio also affects the chemistry of the reaction and the production of N₂O (greenhouse) versus NO₂ (noxious) gases.

Several laboratory techniques were used to characterize the reaction between "Jeffamine" and the explosives. Laboratory-scale experiments were carried out on small quantities, 20 g or less of explosive. Running the reaction at temperatures lower than 120°C resulted in very low reaction rates for TNT and Comp B, and no apparent reaction with RDX. Temperatures between 120°C and 130°C also resulted in long reaction times. It was found that reaction temperatures between 130°C and 140°C were ideal and resulted in manageable reaction rates without concerns of uncontrolled reactions taking place at higher temperatures due to explosive cook-off. Batch reactions were done in a 500 milliliter beaker on a stir/heat plate. "Jeffamine" was heated to 130°C, then approximately 20 grams of explosive were added incrementally. After the chemical reaction, the modified "Jeffamine", crosslinks with an epoxy resin, such as Epon 828, and forms a mechanically useful epoxy.

1.1 Liquid By-Products

Epoxies produced by this method were found to be non-energetic as evident by thermal analysis, liquid chromatography, and burn tests. Mechanical properties of these epoxies were measured and found to be comparable to control samples of epoxy formed from conventional resins and curing agents.

Thermogravimetry (TGA) was used to determine the optimum temperature at which these reactions should take place. A typical TGA curve is shown in Figure 1. In this example, TGA was used to measure the weight loss of RDX, "Jeffamine", and a mixture of the two as they were dynamically heated at 10°C/minute. A TA Instruments Simultaneous DTA/TGA was used for all runs. The sample size of the mixture was a nominal 12 milligrams (e.g., 2 milligrams RDX +10 milligrams "Jeffamine").

Figure 1 shows that the weight loss of RDX alone due to decomposition begins at approximately 210°C. "Jeffamine" shows a gradual weight loss starting at 160°C. When RDX is mixed with "Jeffamine," the decomposition reaction begins at a much lower temperature, 120 - 130°C.

Therefore, it was determined that 130°C was the optimum temperature to be used for all laboratory and scale-up reactions. A 1:4 ratio of RDX:“Jeffamine” was chosen for future experiments. The resulting modified amine curing agent has sufficiently low viscosity to allow processing an epoxy with good mechanical properties. The density of the virgin “Jeffamine” is 0.98 gram/cm³, and the density of the liquid “Jeffamine” after reaction with the explosive is 1.03. With this ratio, there is approximately a 13% weight loss due to the gaseous decomposition of RDX.

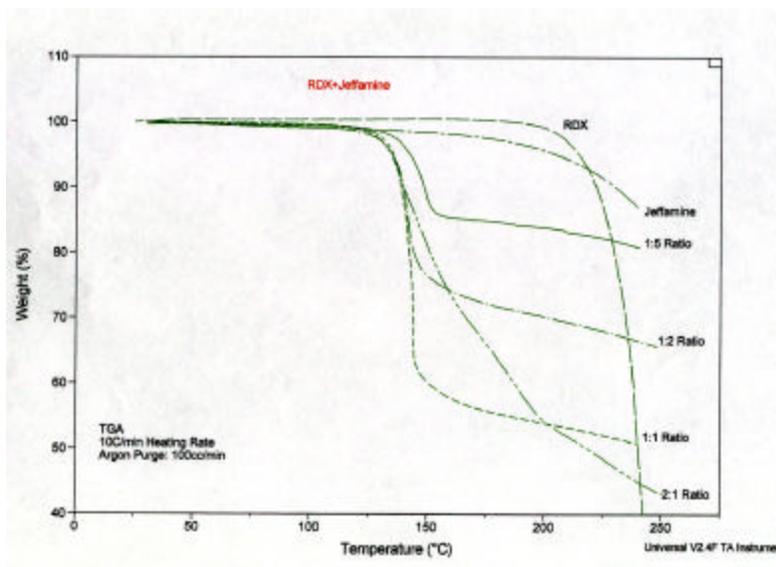


Figure 1. Weight Loss of RDX Added to “Jeffamine”

Using similar TGA experiments, the approximate ratios chosen for mixing “Jeffamine” with TNT and Comp B (60% RDX, 39% TNT, 1% wax) are 9:1 and 4:1, respectively.

As explosive is added to the hot “Jeffamine,” it begins to foam due to the formation of decomposition gases in the viscous liquid. Surfactants were examined to determine their effectiveness in controlling this foaming. A few drops of surfactants, such as “X-Air”, “Super Air-Out”, or “Air Out” were added to the reaction vessel, to evaluate their ability to minimize this excessive foaming. “Air Out” worked the best and could be used to minimize foaming in future operations.

Figure 2 shows a typical differential scanning calorimetry trace with any exotherm, such as the RDX in Comp B decomposing at approximately 230°C, as a positive peak. Endothermic transitions, such as the TNT in the Comp B melting at 80°, are negative peaks. When Comp B is added to the hot amine, as in the second trace, there is a reaction exotherm of 468 calories per gram of explosive, peaking at approximately 145°C. This value of the heat evolved during this reaction was used to determine the cooling capacity necessary in the scaled-up reactor (section 2.1).

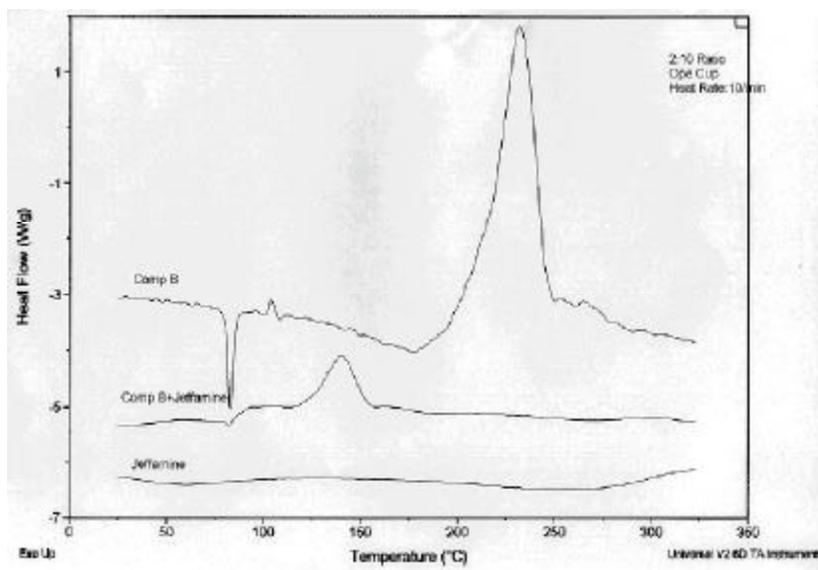


Figure 2. DSC Curve of Comp B and "Jeffamine"

Heat capacity measurements of the virgin "Jeffamine" were made using modulated differential scanning calorimetry. A 2910 model DSC made by TA instruments with a refrigerated cooling system was used. Argon was purged at 50 cc/min to displace the air in the DSC cell. The material was tested in a hermetically-sealed aluminum pan. Both the sample pan and the reference pan used in the DSC were within a weight variance of 0.5 mg. The unit was first calibrated for the heat capacity constant using a sapphire standard. The sample was heated from ambient to 200°C, ramping at 5°C/min, modulating +/- 1.00°C every 60 seconds. It was assumed that the heat capacity of the resulting reacted Comp B/Jeffamine solutions were similar to the heat capacity of virgin Jeffamine. These heat capacity values (Table 3) were used as input data to the computer modeling that was done on the scale-up calculations (section 2.2).

Progress was made towards the characterization of the colored reaction products of Jeffamine with TNT and RDX. Infrared analysis suggests that an amide is being formed as a result of the amine/RDX reaction. NMR analyses showed that in the case of RDX/amine interactions, the product contains amide groups formed as a result of charge transfer interactions between the amine and nitro group. In the case of the TNT/amine reactions, nucleophilic aromatic substitution takes place leading to the formation of Meisenheimer complexes and subsequent rearrangement to form C-N bonds².

Table 3. Heat Capacity Values for Virgin “Jeffamine”

Temp (C)	Heat Capacity
	J/g/deg C
50	1.583
60	1.626
70	1.674
80	1.724
90	1.782
100	1.848
110	1.880
120	1.988
130	2.030
140	2.039
150	2.011
160	1.962
170	1.924
180	1.878
190	1.814

1.2 Gas Analyses

Gas chromatography was used to further define the optimum ratio of “Jeffamine” to be reacted with explosive. The goal was to determine a ratio of the two starting products, which would favor formation of N₂O (a greenhouse gas), rather than NO₂, which is a noxious gas regulated by the EPA.

Gaseous products formed during the reactions were analyzed by gas chromatography. A sealed stainless-steel chemical reaction tube (CRT) was used to react explosive with “Jeffamine”. The reaction system was attached to a Hewlett-Packard gas chromatograph equipped with an internal gas-sampling valve and a combination thermal conductivity/flame ionization detector. Liquid nitrogen cooled the GC temperature to –50°C before the 20 C/minute heating ramp began. After reaction for the pre-determined time period, the CRT was opened, the pressure recorded, and the gas-sampling valve injected into the gas chromatograph for analysis of the evolved reaction product gases.

Figure 3 shows how varying the ratio of “Jeffamine”-to-explosive can vary the amount of N₂O formed. When this ratio is approximately 2 moles “Jeffamine”:1 mole explosive, N₂O formation is enhanced (figure 2).

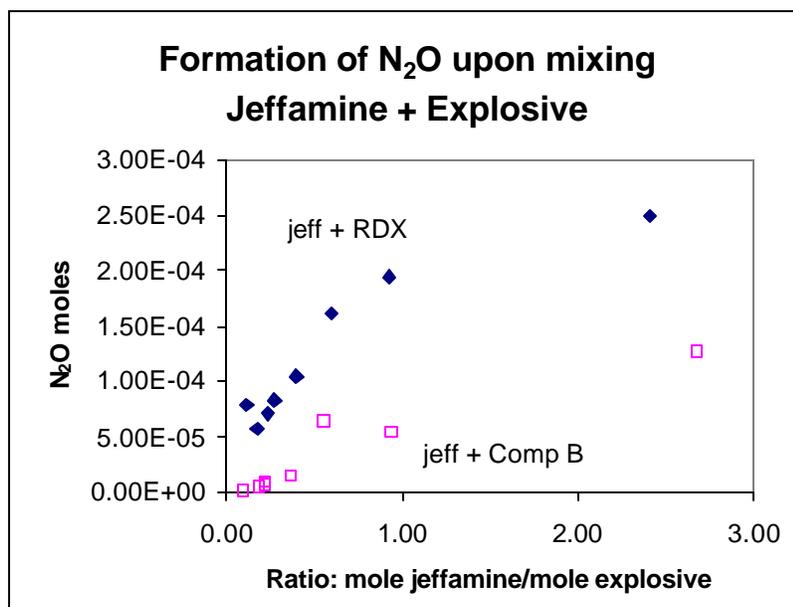


Figure 3. Ratio of Jeffamine:Explosive to Achieve Maximum N₂O formation

To look at the contributions of the individual components of Comp B to the total gas evolved, RDX and TNT were reacted with “Jeffamine” separately. Figure 4 shows a typical gas chromatogram for the reaction between RDX and “Jeffamine.” Notice the large nitrous oxide (N₂O) peak, which forms when RDX is the explosive.

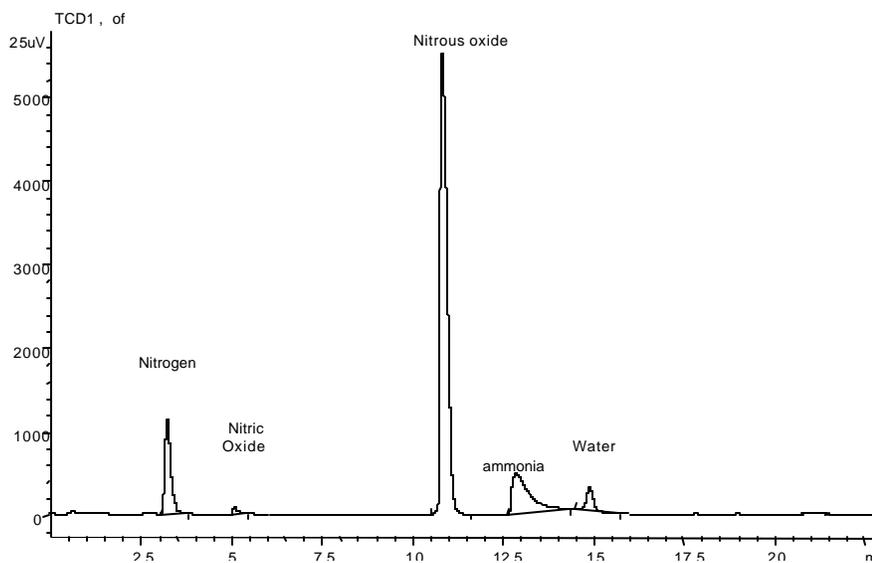


Figure 4. Gas chromatogram of RDX mixed with “Jeffamine” 130°C/1hr

Contrast this to the next figure to see the difference in the reaction stoichiometry when TNT is the explosive.

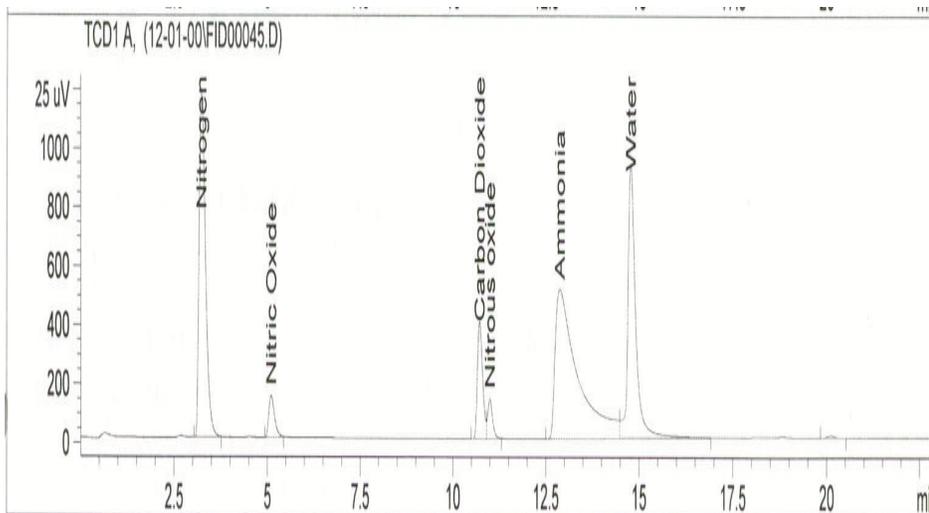


Figure 5. Gas chromatogram of TNT mixed with "Jeffamine" 130°C/1 hr

The fraction of N₂O (nitrous oxide) in the evolved gases is minimal when TNT is the explosive. Based on visual observations of tests mixing TNT and "Jeffamine", there is a considerable amount of brown gas formed, which would be NO₂. This gas is not detected by gas chromatography and, therefore, was not quantitated. Using "Jeffamine" to destroy TNT does not accomplish the goal of producing non-toxic gaseous by-products.

The amounts of six different gases formed during the reaction of "Jeffamine" with Comp B are plotted in Figure 6.

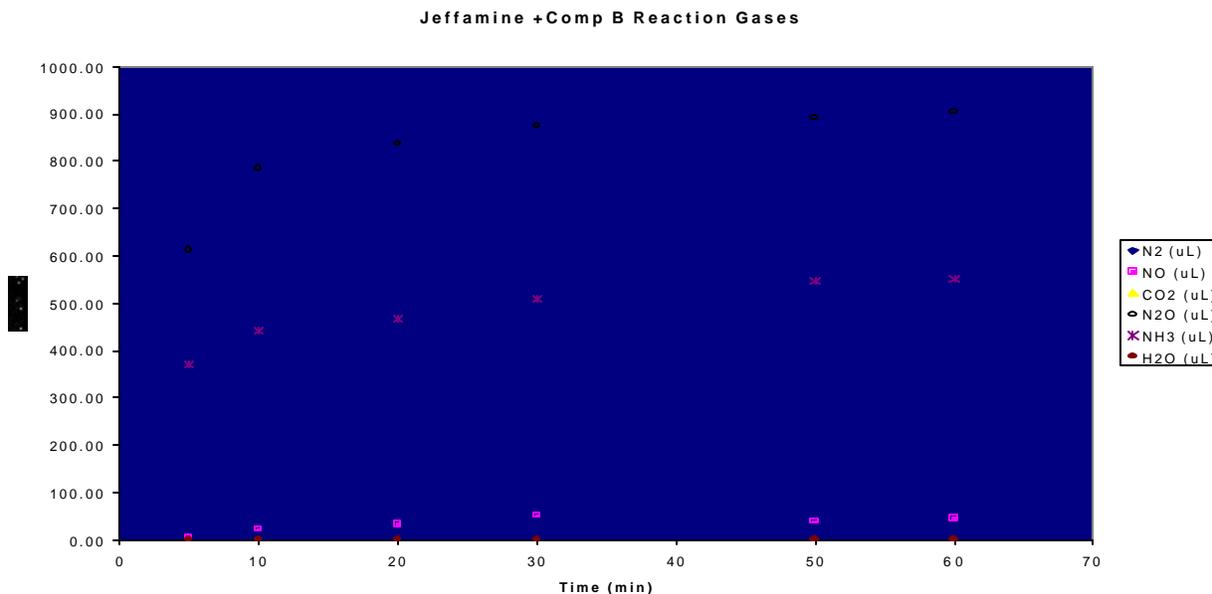


Figure 6. Gases formed during the Reaction of "Jeffamine" and Comp B at 130C.

The amount of gas formed during the reaction of TNT with “Jeffamine” is shown in Figure 7. Notice the y-scale is different than that in Figure 6 and indicates that the amount of gas generated in this reaction is less than that in Figure 6. Although Comp B is 40% TNT, the majority of gases formed by the degradation is due to the RDX. Ammonia is a major component of the gases formed when TNT is the explosive, and it contributes 21% to the total ammonia formed when Comp B is reacted.

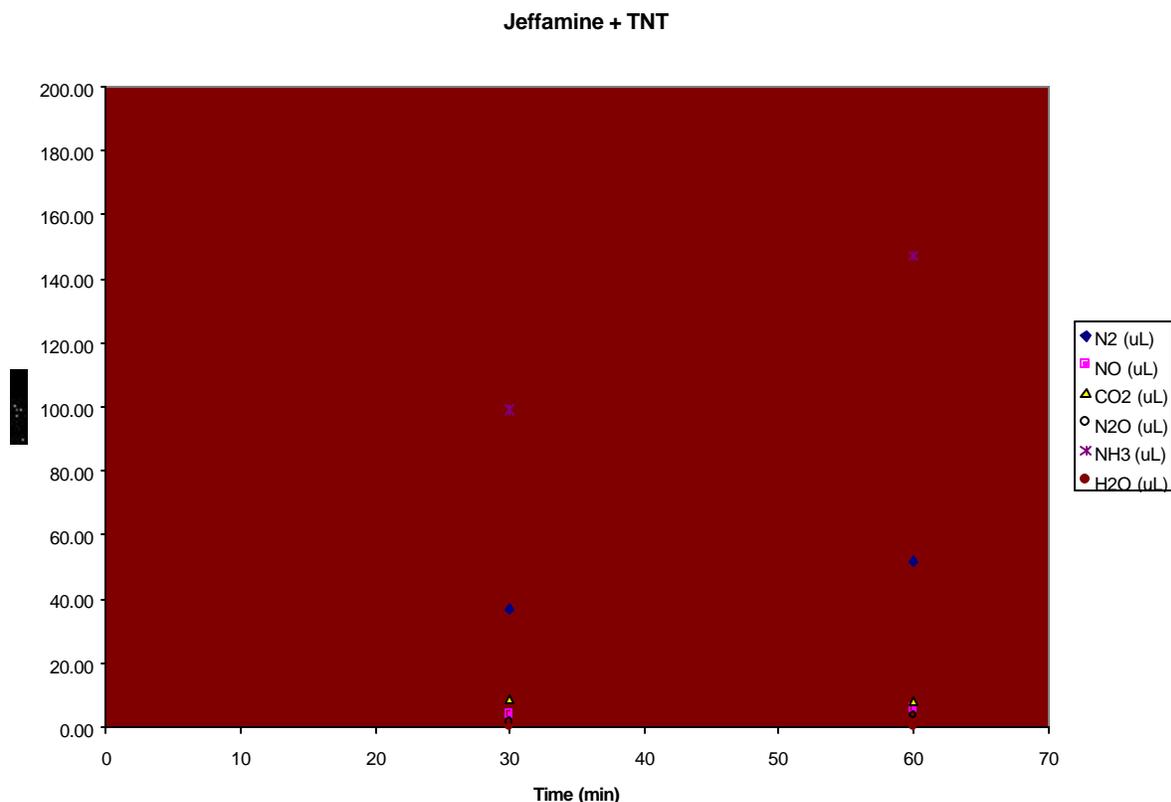


Figure 7. Gases formed during the Reaction of TNT and “Jeffamine”

Based on gas quantities formed during the reactions, chemical reactions are presented which represent these degradation reactions:

- 1 mole Comp B \rightarrow 0.5 N₂ + 0.09 NO + 1.8 N₂O + 1.1 NH₃ + .0001 H₂O + x₁NO₂
- 1 mole TNT \rightarrow
 $0.26 \text{ N}_2 + 0.03 \text{ NO} + 0.02 \text{ N}_2\text{O} + 0.73 \text{ NH}_3 + .0002 \text{ H}_2\text{O} + 0.04 \text{ CO}_2 + x_2 \text{ NO}_2$

The values of x₁ and x₂ are unknown as the GC analyses could neither detect nor quantitate NO₂.

Gases evolved during the reaction of RDX with the amine in an open beaker were carefully analyzed for escaping RDX vapor. A solid phase microextraction (SPME) fiber (polydimethylsiloxane/divinylbenzene, PDMS/DVB, Supelco, Inc. part no. 5710-U) designed to collect traces of explosives from air, was used. The fiber was held at various distances above the solution for a period of 10 seconds. After the collection period, the fiber was introduced into a PCP model 111 Ion Mobility Spectrometer and quickly heated to 165°C. The intensity of any resulting signal would be proportional to the concentration of RDX being released from the solution. A sample of “Jeffamine” alone did not produce a signal in the IMS. The concentration of RDX in the gases above the reaction mixture was measured at various positions. The concentration in all cases was less than that obtained from a sample of RDX when heated to that temperature.

1.3 Epoxy

Epoxies were made from the by-products of mixing “Jeffamine” T-403 and the three explosives, TNT, RDX, and Comp B (Figure 8). Epon 828 resin was heated at 71°C for 30 minutes. Silicone molds were coated with MS122 dry release agent and also heated at 71°C. The ratio of resin to modified-Jeffamine was varied, resulting in varied mechanical properties. The mixture was cured overnight at room temperature, followed by four hours at 71°C.

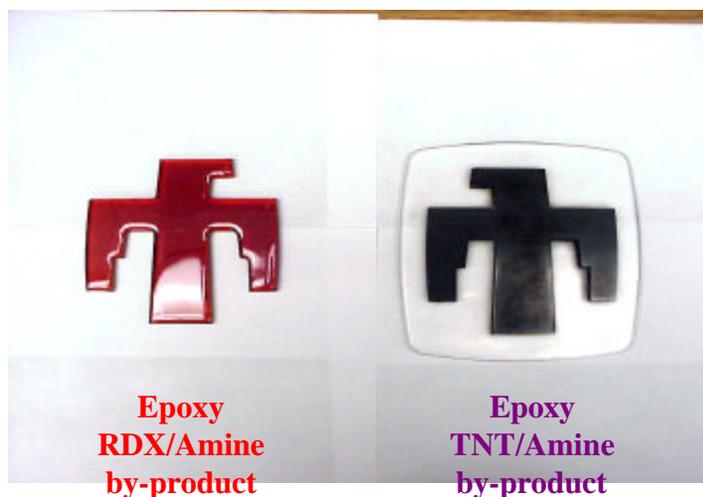


Figure 8. Epoxies made from Modified Amine Curing Agents

These modified epoxies were compared to standard batches of baseline epoxy which require 100 grams of preheated Epon 828 added to 41 grams of preheated curing agent. Testing was done to characterize both the baseline and modified epoxies.

Mechanical properties (shear modulus) and glass transition temperatures (T_g , when epoxies soften) for epoxy produced using the by-products were compared to those of epoxy produced with virgin “Jeffamine” curing agent. These tests were performed with a Rheometrics ARES Dynamic Mechanical analyzer using a torsion rectangular fixture at a frequency of 1 Hz and a temperature ramp rate of 3°C/min. The samples had nominal dimensions of length = 45 mm,

width = 12.5mm and thickness = 1.3mm. A typical curve and scheme for selecting T_g of these samples is shown in Figure 9.

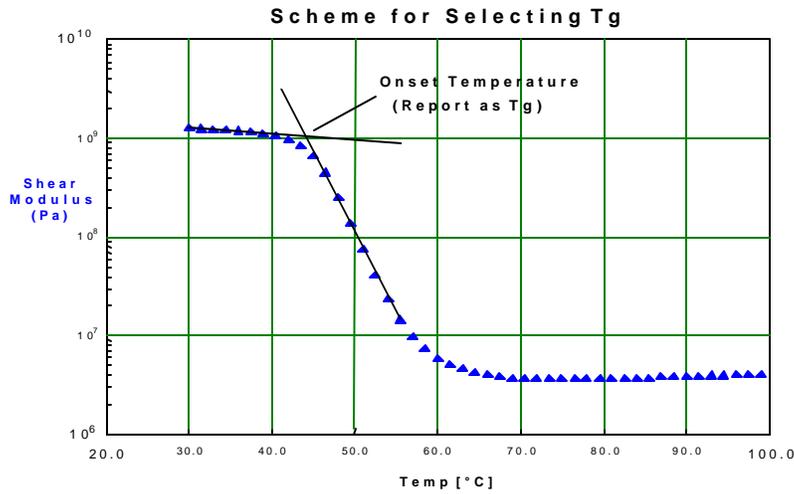


Figure 9. Typical curve for determining Glass Transition Temperature

Figure 10 shows the T_g 's of epoxies made with varying concentrations of Epon 828 epoxy resin and "Jeffamine" T-403/RDX by-product. The right-most curve gives the T_g of baseline Epon 828 virgin/"Jeffamine" T-403 epoxy. This epoxy, made with 100g Epon resin and 41g "Jeffamine" T-403, softens at 71.4°C. When RDX is reacted with the curing agent, the T_g decreases. The left-most curve shows epoxy made with 100g 828 and 80g T403+RDX has a T_g at 27°C and is flexible at temperatures slightly above room temperature. Varying the concentration of the 2-parts of the epoxy can tailor the T_g for future epoxy applications.

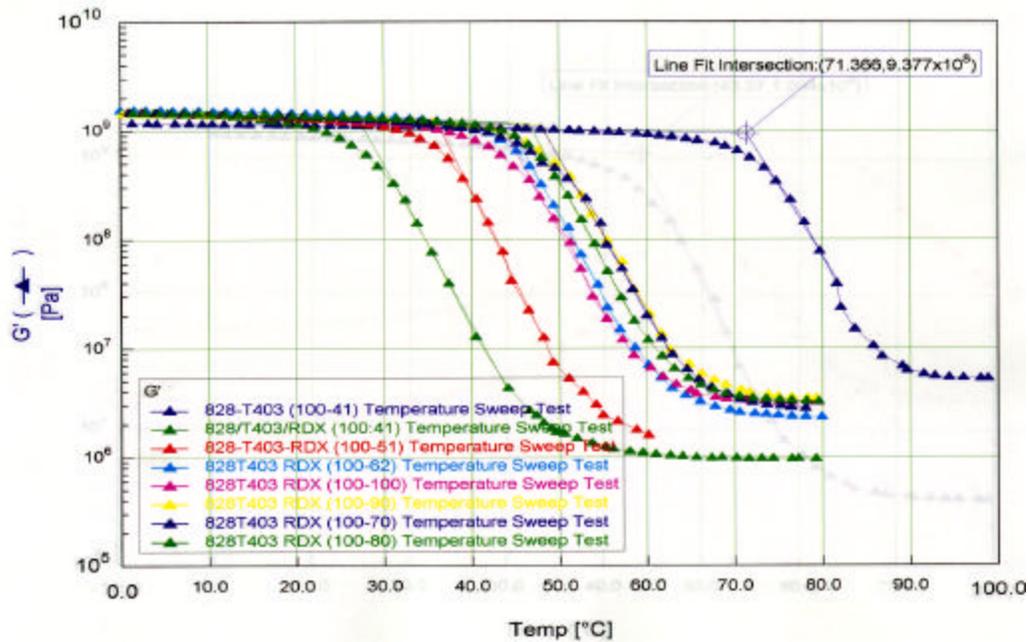


Figure 10. T_g of Epon 828 epoxies made with “Jeffamine”/RDX by-product

Figure 11 shows the T_g of Epon 828 epoxies made with “Jeffamine” curing agent modified with Comp B added at 15, 20, or 25%. The best ratio to mix Epon 828 and modified “Jeffamine” must be determined by the mechanical properties required for the final use of the epoxy.

Sample ID	T_g (C)
828/15% Comp B (25/25)	51
828/20% Comp B (25/25)	49
828/25% Comp B (25/25)	55
828/20% RDX (50/50)	44

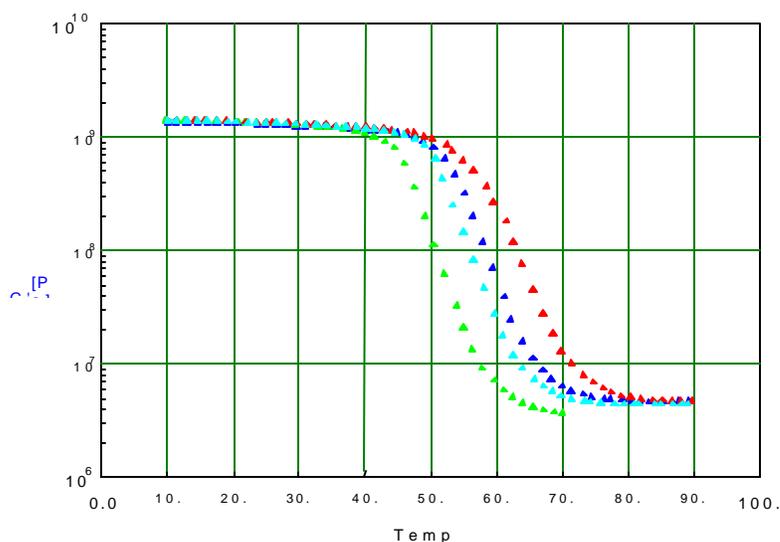


Figure 11. T_g of Epon 828 epoxy made with "Jeffamine"/Comp B by-product

These modified epoxies are intended for future commercial products and must be safe for persons handling the material. Therefore, the toxicity of these modified epoxies was investigated. The commercial, biosensor-based Microtox Toxicity system was used to test powders of epoxy samples prepared from a curing agent ("Jeffamine"), which was first reacted with RDX and with TNT. The Microtox test is based upon the use of luminescent bacteria, which produce light as a by-product of their cellular respiration³. Any inhibition of cellular activity due to toxicity results in a decreased rate of respiration and a corresponding decrease in the rate of luminescence. The more toxic the sample, the greater the percent light loss from the test suspension of luminescent bacteria. Bacterial bioluminescence has proved to be a convenient measure of cellular metabolism and consequently, a reliable sensor for measuring the presence of toxic chemicals in aquatic samples.

The baseline and modified epoxy powders were each mixed with water (2% NaCl) in glass centrifuge tubes to make 50% solutions. The mixture was shaken for 24 hours on a wrist-action shaker, then centrifuged for 15 minutes to extract water-soluble toxins. These solutions were then diluted down several times to a final concentration of 3% epoxy in water. The bioluminescence was measured at 5, 15, and 30 minutes after the bacteria were introduced.

The baseline epoxy powder solution was colorless, slightly cloudy, with a visible powdery gray film on the surface. The RDX/"Jeffamine" epoxy solution was colorless with a few very small orange crystals in the surface film. The TNT/"Jeffamine" epoxy solution was colorless without surface film. The concentration (in percent) of the epoxy solutions at which 50 percent of the illumination was quenched (EC_{50}) was determined to be as follows:

Table 4. Toxicity of Epoxies in Water

Sample	5 minute EC₅₀	15 min EC₅₀	30 minute EC₅₀
baseline epoxy	13.5%	7.5%	4.9%
RDX epoxy	34.9%	16.4%	16.2%
TNT epoxy	35.3%	29.4%	23.7%

Baseline epoxy is toxic at a concentration of 13.5%. As the water extracts more chemicals from the epoxy over time, the solution is more toxic at 30 minutes, with a concentration of just 4.9% causing 50% of the bacteria to die. The RDX and TNT epoxies are actually less toxic than the baseline epoxy. Environmental criteria were established for TNT and RDX effluents with the allowable limits in aqueous discharge of 60 ppb and 200 ppb for TNT and RDX, respectively⁴. The “Jeffamine” epoxy toxicity results in Table II indicate that they less toxic by orders of magnitude, because these solutions do not become toxic until they are at the percent (%) level, rather than at the ppb level.

Flammability and shock testing of epoxy produced using the by-products indicated no explosive or flammability hazards. Velocity Interferometer System for Any Reflector (VISAR) tests were done to determine if the epoxies could be detonated. The VISAR has become the accepted standard for measuring particle velocities of shock loaded materials. Diffused light from the target containing Doppler-shift information is collected by a lens, split in half, with half of the signal being sent through a reference leg and half sent through a delay leg. A delay is caused between the two legs, and the beams are then recombined at the main beam-splitter where interference is developed. The target velocity information is contained in the motion of the interference fringes in each of the beams.

Epoxies made from modified “Jeffamine” were tested by shocking them with a PETN-boosted detonator to provide sufficient power to achieve a detonation in the epoxy, should sufficient explosive material still exist.

Three epoxies were tested:

- Virgin “Jeffamine” T403 only and 838 epoxy (control)
- 20% by weight TNT in the “Jeffamine” T403 and 828 epoxy mix
- 20% by weight RDX in the “Jeffamine” T403 and 828 epoxy mix.

Table 5. VISAR Data for Cured Epoxies

Test Type	Unit Length (cm)	Function time (microsec)	Initial peak velocity (m/sec)
Baseline epoxy	70	32	22
Baseline epoxy	70	28	35
Baseline epoxy	70	30	30
20% by wt TNT	80	47	<10
20% by wt TNT	83	38	<10
20% by wt TNT	88	40	<20
20% by wt RDX	74	35	10
20% by wt RDX	80	40	15
20% by wt RDX	72	33	10

A detonation is determined by an initial peak velocity of 1000 m/sec or greater. The peak velocity and signature of the velocity data conclusively prove that none of the epoxy/explosive material detonated.

2.0 Process Scale-Up

A small scale-up operation was completed at Sandia National Laboratories to consume one kilogram of explosive. The waste explosive chosen for the scale-up operation was from the McAlester Army Ammunition Plant meltdown facility. The Comp B explosive is from shells such as 8-inch World War II battleship rounds and 105mm artillery projectiles. The shells are inverted and placed in heated and pressurized vats that melt the explosive⁵. The beige-colored liquid flows onto a chilled conveyor belt where it cools, hardens, then drops into cardboard boxes placed at the end of the belt. The explosive is now ready for reuse, recycle, or disposal. Fifty pounds each of melt-out TNT and Comp B were received from McAlester AAP for use in this study. These chunks are an appropriate size for a direct feedstock into the scale-up reactor.

The engineering parameters critical for scale up were evaluated. The gases evolved when the “Jeffamine” reacts with the explosive were characterized (section 1.2) to consider scrubbing these emissions in the final design. Gas chromatography analyses done on these gases show ammonia to be a relatively large component (10 – 20%), as is NO₂ when TNT is reacted, and both would be an air emissions concern in a large operation. Due to the small quantities involved in our studies, local Environmental Protection Agency requirements waived any scrubbing. However, upon future scale-up processes, the local requirements in that area would have to be consulted to ensure compliance.

2.1 Hardware

The reaction rate kinetics were determined to size the reactor. Thermogravimetric analyses were used to determine the weight loss due to gas formation. Samples of “Jeffamine” mixed with Comp B were heated at four different heating ramps (2.5, 5, 10, and 20 °C/min). The kinetics software on the TA Instruments TGA determined the activation energy, and preexponential

factor, and a reaction time of 5 minutes. As decomposing the explosive in hot “Jeffamine” is quite fast, a vessel to accomplish this can be small. A 13 gallon aluminum vessel was fabricated and delivered to contain the reacting solution and foaming.

The scale-up process is a continuous operation, rather than a batch process. A conveyor belt carries the dry, chunk Comp B explosive up to the reaction vessel. This conveyor belt was chosen so that it could be added to the final step of an existing demil operation, such as that at McAlester Army Ammunition Plant. The conveyor is 9 feet long and 18 inches wide and has an anti-static polymeric belt, variable-speed drive, explosion-proof motor, and height adjustments. The control unit was mounted for remote operation. The conveyor belt delivered 1000g of Comp B explosive in 5 minutes (Table 6).

The ambient-pressure reaction vessel was designed and sized to meet two constraints. One is the net explosive weight limit of the building, 1000 grams in the test chamber. The reaction must proceed at a rate, which allows slow introduction of the explosive to ensure complete reaction. This influences the second constraint, which is the rapid removal of the heat generated by the reaction. A worst case was assumed to determine the temperature increase during a typical run, assuming 468 calories/gram of explosive. As our scaled-up reactions were limited due to building capacity, a 4 kW water chiller amply maintained constant temperature in the baffled water jacket surrounding the reactor during reaction.

Examples of processing times and feedstock rates to consume 1000 grams of explosive are shown in Table 6.

Table 6. Examples of Scale-Up Processing Parameters

Processing Time:	10 min	5 min	3 min
Comp B (g/min)	98	200	334
“Jeffamine” (g/min)	490	1,000	1,668
total volume (liters)	17.1	35.0	58.3
calculated heat generated (cal/hr) @ 468 cal/g explosive	2,752,941	5,616,000	9,360,000
kilowatts generated	3.20	6.53	10.88

The reactor was fabricated from aluminum because the thermal conductivity is higher than that of stainless steel, and allows better temperature control during the reaction. Calculations were done to design the side-wall baffles, impeller size, shape, and position. An air-driven motor stirs the vessel. The specifications for the custom reaction vessel (figure 12) were:

- Tank height: 27 inches
- stirrer: 3-bladed mixing propeller
- stirrer diameter: 5.5 inches
- stirrer offset from bottom: 2.75 inches (allowing for variable placement later)
- side baffles: 1 inch wide
- side baffles offset from bottom: 2.7 inches

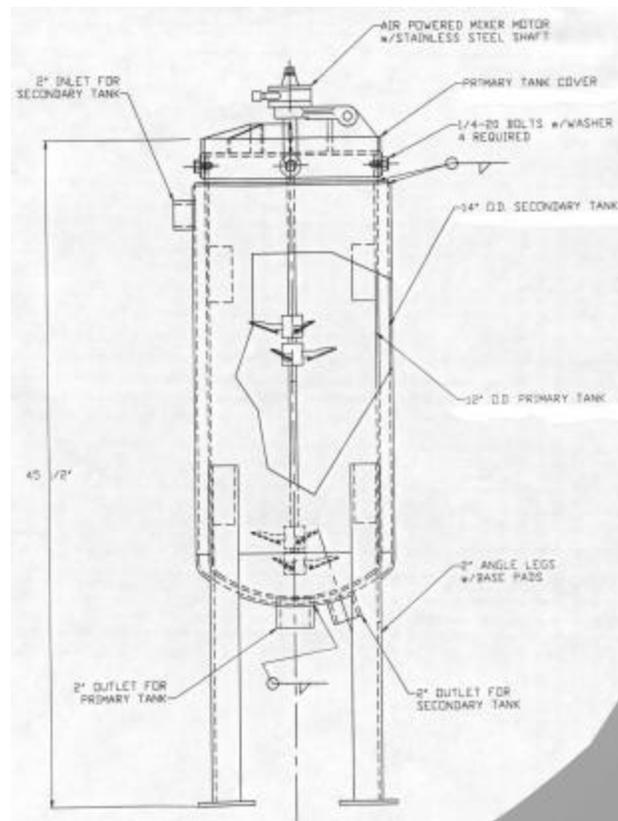


Figure 12. Drawing of Scale-up Reaction Vessel

Three small-scale safety tests were run to assure that during development of the scale-up process, a detonation would not occur during the addition of explosive to “Jeffamine.” Assuming a worst-case scenario, each safety test had 100 grams of “Jeffamine” heated in a one-liter pyrex beaker at the operation temperature of 130°C in a chamber room rated to contain a 1 Kg explosion. Then, one 20 gram chunk of Comp B from the munitions melt-out facility at McAlester Army Ammunition Plant was added all at once using remote control.

The exotherm of the reaction ramped the temperature of the solution up to approximately 170°C, the solution foamed violently, but there was no detonation or fire. The temperature trace was tracked with an Omega Super MCJ Thermocouple-to-analog connector. This output was routed to a Tektronix TDS 784A Digitizing Oscilloscope where it was recorded. The experiment was also videotaped. Figure 13 shows the experimental set up, which was done using an empty steel tank as secondary containment.

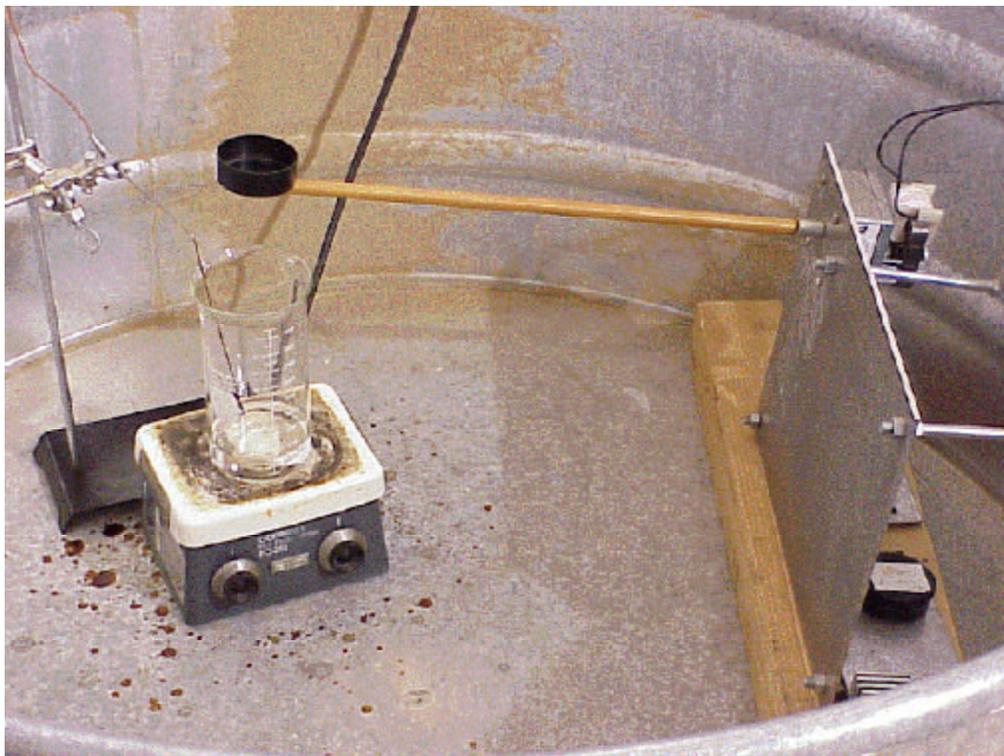


Figure 13. Equipment set-up for run-away reaction

In another experiment, a thermocouple was placed in the middle of a cylindrical cup and molten Comp B was added. Once cooled, this rod was removed from the mold, placed in another beaker of 130° C “Jeffamine”, and the temperature was monitored during the reaction. Figure 14 shows the temperature traces of both the thermocouple embedded inside the Comp B rod and the thermocouple in the hot jeffamine solution when the chunk was added at 8.9 minutes.

(The anomaly in this experiment (lower line of plot) occurred because once the Comp B rod melted, the thermocouple fell out of the beaker at 11.5 minutes and began to cool, as seen at approximately 12.5 minutes.)

Comp B + Jeffamine

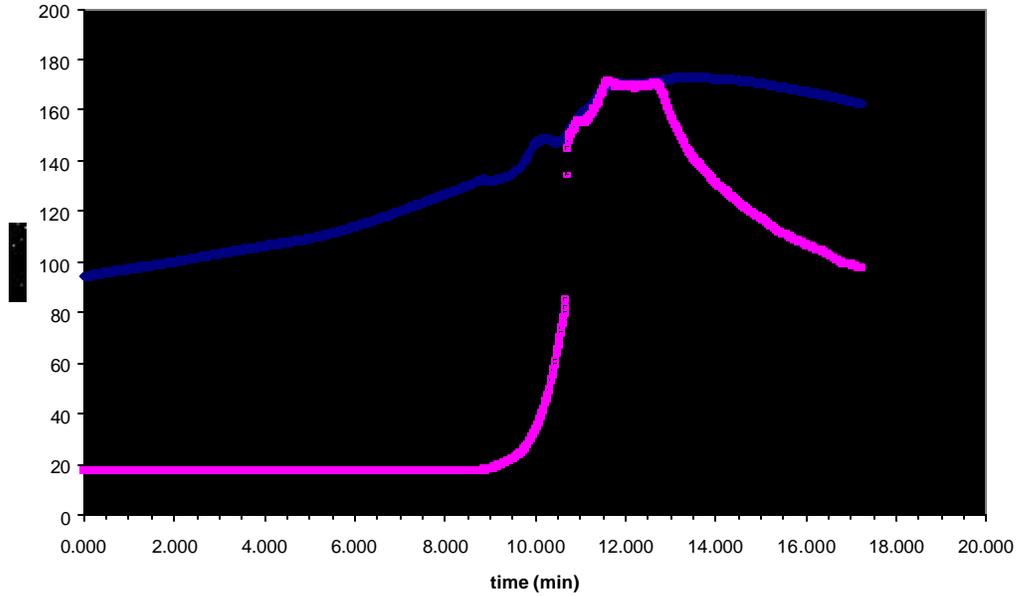


Figure 14. Typical Temperature profile of Safety test.

The viscosity of the liquid by-product was determined to provide measurements for the pumping requirements for scale-up. The viscosity measurements were made from ambient temperature up to 150° C. Typical data are shown in Figure 15.

Viscosity Tests of Liquid By-Products

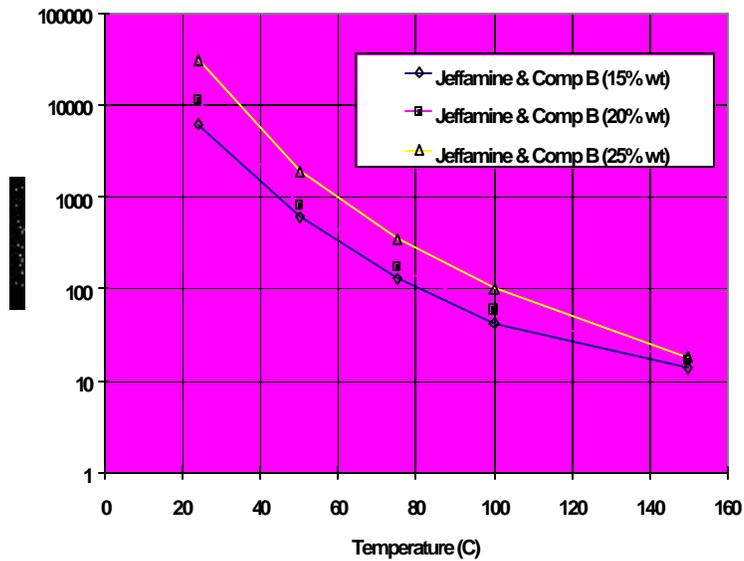


Figure 15. Typical Viscosity Data for By-Products

The sequence of the scale-up operation starts with heating of the “Jeffamine” in its supply drum. An “Electro-Flex” band heater is wrapped around the metal drum and heated to 130° C. During that time, the explosive is measured onto the conveyor belt. Because the chamber limit at Sandia National Laboratories is 1000 grams of explosive, approximately 59 grams of explosive were weighed out and put in each of 17 pockets on the conveyor belt. The pumping rate of the “Jeffamine” supply drum pump (Teel Air-Driven, ½ HP) is 1 liter/minute. The reaction vessel exit pump (Teel Centrifugal, ¼ HP) was previously set to a flow rate that prevents accumulation of liquid reaction products during the continuous operation. The data logger is started, with four channels monitoring the temperatures of the cooling jacket inlet and outlet, “Jeffamine” supply drum, and reaction temperature. The blast door to the chamber is closed and the stirrer started at 300 rpm. At time zero, the “Jeffamine” pump is started, then the conveyor belt; both run for five minutes. The reaction vessel exit pump is started to pump out the reacted liquid. The gases evolved are drawn out of the room with an exhaust fan. Samples were taken from the reaction vessel and analyzed for residual explosives by high performance liquid chromatography. None was found, indicating that the scale-up process can be done satisfactorily.

2.2 Computer Modeling of Process

The chemistry and heat production within the scale-up vessel was computer modeled to ensure complete reaction and safety during processing. A consulting contract with CFD Research Corp., Huntsville, Alabama provided computation of the flow, heat generation, heat transfer, and mass transport in the system. This model may be easily adapted for other complex geometries and process parameters. The final report from CFDRC is found in Appendix C.

The approach to modeling the Sandia reactor will be to couple the one-phase and chemistry modules in the multi-physics code, “CFD-ACE”. The code computes the flow, heat generation, heat transfer and mass transport in the system as part of the solution. The reaction mechanisms were supplied by Sandia. The developed model may be easily adapted for complex geometries and process parameters. It will allow the process engineer to evaluate the potential of over heating and reaction efficiency for a given reactor design and set of operating conditions.

The foundation for the model is the general purpose, commercial computational fluid dynamics code, CFD-ACE, which is a transient, three-dimensional, Navier-Stokes code capable of simulating multi-species transport, heat transfer (including thermal radiation, fully coupled gas-phase and surface chemistry for conventional chemical vapor deposition (CVD) reactors. The CFD-ACE package is a very flexible code, that is coupled with preprocessing and post processing software (CFD-GEOM and CFD-VIEW) that make it relatively straight-forward to set up models for complex geometries and analyze the results. The complete report can be found in Appendix C.

3.0 Technology Transfer

3.1 Economics of Degrading Bulk Explosives

Transferring this technology to another government or commercial organization was investigated. An advertisement seeking a partner to use the by-product-”Jeffamine” or to further develop the process was published in the Commerce Business Daily (see Appendix B). No responses were received.

The price of degrading explosives by this method is rather high, however, at a cost of \$21,000 per ton of explosive. This is estimated based on buying “Jeffamine” at \$2.19 per pound from the Huntsman Petrochemical Corporation, Houston, TX., USA., assuming no cost for the explosive, and loading it with 20 percent waste explosive. There would be some payback if commercial uses for the liquid or gaseous by-products could be found.

A minimal payback of this process could recover nitrous oxide for later sale. N_2O is a valuable chemical in some oxidation reactions of benzene and its derivatives to phenols, and it has use in the medical and dental fields⁶. There are zeolite molecular sieves which are available to adsorb N_2O , for later desorption. The water (steam) venting from the process would be passed through a $\gamma-Al_2O_3$ bed to be absorbed before traveling to the molecular sieves. Barium-exchanged ZSM-5 zeolites trap the nitrous oxide^{7,8} from 25 – 80°C, then desorb the gas at 150 – 220°C. These zeolites could be reused after desorbing the N_2O . On a large scale of processing tons of explosives, the reusable N_2O -stripping bed would require 26,300 lbs of zeolites, a one-time cost at the current price of \$55/lb. The economic payback of reclaiming the N_2O would only be approximately 2.4% of the cost of processing the explosives.

There are other resource recovery technologies¹ that can recover the TNT and RDX for resale. While private industry is paying \$6 - \$7/lb. for virgin RDX Class I, ANFO boosted with RDX sells for \$1/lb^{9,10}. TPL, Inc. has demonstrated 150lb/day plant at Ft. Wingate, N.M., for recovery of RDX from CompA-3. AMCOM proposed to qualify reclaimed RDX for reformulation and casting into recycled rocket motor hardware. Mechanical property, ballistic and static motor firings will be performed for the reference and reclaimed propellant formulations. Eglin AFB has developed a method for the recovery of TNT and RDX from melt/cast explosives such as Comp B and Octol. ARDEC is developing processes to rework downloaded explosives to meet specification requirements for military as well as reformulate into products for potential commercial market applications. Lawrence Livermore National Laboratory has developed a lab-scale synthesis to convert TNT to higher value products such as TATB.

3.2 Firing Range Clean-Up

Due to this high cost of processing bulk explosives, this technique was considered for environmental clean up for firing ranges and range sustainment. Low-order-detonation shrapnel from 105 mm shells fired on Sandia’s remote range was picked up and placed in a beaker of hot “Jeffamine”. A seven-minute soak cleaned sub-gram amounts of explosive from the metal parts (Figure 16), leaving just nanogram-level traces of explosive on the metal surface. Agitation of the solution or a high-pressure spray would shorten the cleaning time. Firing ranges could be

cleaned with a portable tank of hot “Jeffamine” mounted on a truck with shrapnel placed in a basket immersed in the liquid. An example of fragments to be cleaned can be found on Hawaii’s Kaho’olawe Island, which was a firing range until 1995 (Figure 17).



Figure 16. 105 mm shrapnel before and after soaking in “Jeffamine”. White material on the two left pieces is the explosive before cleaning; the right pictures are after cleaning.



Figure 17. Kaho'olawe Island, Hawaii

4.0 Conclusions

This process completely degrades RDX, TNT, and Comp B by reacting them with an amine, “Jeffamine”, a commercial product. The purity of the explosives required to accomplish this degradation was not established. However, melted-out explosive material from old munitions was used as-received from McAlester Army Ammunition Plant. The goal was to determine the best stoichiometry and reaction conditions to accomplish degrading as much explosive as possible, using the least amount of “Jeffamine”. The results show that “Jeffamine” can be loaded with approximately 25% explosive to accomplish the complete destruction of the explosive. The composition of the gaseous products can be varied by the stoichiometry to influence the amount of noxious gases. The chemistry of reacting “Jeffamine” with RDX produces more nitrous oxide (N_2O) than reacting it with TNT. Comp B (60% RDX, 40% TNT) is also consumed by this process, but the presence of TNT increases the amount of NO_2 formed during the chemical reaction. Safety tests were performed to ensure that the reactions, which are very exothermic, were safe and that no detonations or run-away reactions took place. The liquid by-product of these reactions can be used as a curing agent with an epoxy, such as Epon 828. The mechanical properties of epoxies made from the liquid by-products can be tailored for future applications.

The reaction was scaled up to process 1000 grams using Comp B and TNT from the McAlester Army Ammunition Plant meltout facility. Computer modeling computed heat flow, generation, and transfer, and mass transport to predict scale-up parameters for even larger scale-up operations.

The economics of this process indicate that the cost of degrading one ton of explosive is approximately \$21,000. Minimal payback could be realized with the recovery of the nitrous oxide produced during the reaction, and any sale of the liquid by-product for use in epoxies, if a customer could be identified.

Due to this high cost of processing bulk explosives, the process could be used instead for firing range clean up and sustainment and processing of smaller quantities of explosive materials when other disposal means are not feasible or economical. A portable vat of hot “Jeffamine” could be transported around a contaminated field, with a basket of shrapnel immersed in it to clean off residual explosives.

Acknowledgments

We would like to acknowledge the work done by other Sandia employees:

Epoxies made and T_g measurements were done by Ernie Corea.

Viscosity measurements done by Mark Stavig.

VISAR analyses were done by Theresa Broyles

Gas chromatography by Lori Montano-Martinez.

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6.0 Appendix A – IITRI Report

“Hypergolic Non-Detonative Neutralization of Energetics in Production and Demilitarization”

(The electronic version of this master document has a separate file attached that contains this IITRI Report. The hardcopy has the text included)

HYPERGOLIC NON-DETONATIVE NEUTRALIZATION OF ENERGETICS IN PRODUCTION AND DEMILITARIZATION

INTERIM TECHNICAL REPORT

IITRI Project No. C06831

in Response to

Sandia National Laboratory Document No. BC-0414

Prepared for:

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ATTENTION:

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February 1999

PREFACE

IIT Research Institute is pleased to submit this Interim Technical Report entitled "Hypergolic Non-Detonative Neutralization of Energetics in Production and Demilitarization," IITRI Project No. C06831, in response to Sandia National Laboratory Document No. BC-0414. The program was initiated on 1/29/98 for a period of eleven months. Due to difficulties with respect to renewal of the IITRI Chicago Laboratory explosive storage license, active work on the program was not initiated until May 16, 1998.

Data related to Tasks 1 and 3 are presented in this report. These data are recorded in IITRI logbook numbers C31138, C31153, C31164, C31177, C31202, C31203, C31204, C31207, C31213, C31216, C31218 and C31226. These data along with associated chromatograms, integration results and IR Spectra will be stored in IITRI archives. This report has not been audited by the IITRI Quality Assurance Unit.

Respectfully submitted,

IIT RESEARCH INSTITUTE



Alan Snelson
Science Advisor
Chemical Technology Division

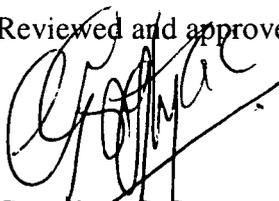
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SUMMARY

It has been known for at least twenty years that organic amines when added to explosives at ambient temperature may react hypergolically. A few grams of the amine have been shown to be capable of initiating the autocatalytic self-destruction up to 7-kg of TNT and Composition B in field tests. Amines are currently being investigated for use in the non-detonative destruction of explosives in land mines. If larger quantities of the amines are used in the initiating reaction, the reaction is not hypergolic, but results in the formation of tarry-residue, which has been shown in limited tests¹ to be non-detonable.

At the present time, the chemistries of the amine-explosive reactions are poorly understood, as are the factors responsible for the transitioning from mildly exothermic non self-propagating to self-propagating hypergolic reactions.

In this study (Task I of the work statement), the reactions of monoethanolamine (MEA), diethylenetriamine (DETA) and n-tributylamine (TBA) with TNT, RDX and TNT + RDX have been investigated under non self-propagating reaction conditions, i.e., an excess of amine. Characterization of the gaseous products formed and partial reaction stoichiometries have been identified.

In addition, preliminary tests have been made to identify conditions under which solid TNT can be burned in a "cigarette" mode in preparation for studies to characterize the gaseous products formed in the hypergolic amine-TNT reaction (Task 3 of the work statement).

Results for Task 1- Amine-Explosive Reactions Run in the Low Temperature Non-Self Propagating Mode.

The reaction of MEA, DETA and TBA with TNT, RDX and TNT + RDX were studied in the non self-propagating mode. The reactions were performed by adding \approx 10-20 g of explosive to \approx 100g of amine in a 500-mL spherical flask fitted with a condenser, thermocouple and gas collection system. The reaction flask contents were stirred (magnetic stirrer bar) and heated as required on a hot plate. Reactions were performed under helium and the temperature monitored during the process. Gases generated in the reaction were collected in polyvinylfluoride gas bags and analyzed by infrared spectroscopy (IR). After completion of the reaction, the mass of reaction product was determined and its unreacted amine content determined by gas chromatography with flame ionisation detection (GC/FID).

Based on IR analyses, NH_3 and N_2O were the only gaseous products formed in the TNT and RDX reaction with MEA and DETA. Gas samples from each of the reactions of TNT + MEA and RDX + MEA were analyzed for H_2 , N_2 and O_2 , but no significant amounts were detected. In the TNT and RDX reactions with TBA, N_2O , NO_2 and CO_2 were detected in the gas phase by IR.

Using the above data approximate, stoichiometries for the amine explosive reactions were obtained:

No. of Expts.	REACTION					
4 ⁽¹⁾	REACTION CALCULATED MOLES	TNT + MEA → Liquid Product + NH ₃ + N ₂ O				
		1	8.1±2.0 ⁽²⁾	-----	0.9±0.4	(trace)
6	REACTION CALCULATED MOLES	RDX + MEA → Liquid Product + NH ₃ + N ₂ O				
		1	5.7±1.6	-----	0.7±0.2	1.8±0.2
2	REACTION CALCULATED MOLES	TNT + RDX + MEA → Liquid Product + NH ₃ + N ₂ O				
		0.5	0.5	5.9±0.5	-----	1.0±0.2 0.8±0.0
2	REACTION CALCULATED MOLES	TNT + DETA → Liquid Product + NH ₃ + N ₂ O				
		1	7.5±1.9	-----	1.8±0.1	(trace)
3	REACTION CALCULATED MOLES	RDX + DETA → Liquid Product + NH ₃ + N ₂ O				
		1	5.2±0.6	-----	0.7±0.4	1.3±0.6
1	REACTION CALCULATED MOLES	TNT + RDX + DETA → Liquid Product + NH ₃ + N ₂ O				
		0.5	0.5	5.0	-----	1.94 0.9
2 ⁽³⁾	REACTION CALCULATED MOLES	TNT + TBA → Liquid Product ⁽⁴⁾ + N ₂ O + NO ₂ + CO ₂				
		1	-0.3±0.3	-----	0.007	0.18 0.09
3 ⁽³⁾	REACTION CALCULATED MOLES	RDX + TBA → Liquid Product ⁽⁵⁾ + N ₂ O + NO ₂ + CO ₂				
		1	0.4±0.3	-----	1.0	0.14 0.08

(1) Number of experiments used in generating data.

(2) Mean ± standard deviation.

(3) Number of experiments used to generate data for number of moles of TBA used per mole of TNT or RDX reacted. The data for moles of gaseous product formed are from single experiments.

(4) This liquid sample contained a solid pitch-like material. The liquid phase constituted ≈ 73 weight % of the reaction product.

(5) This liquid sample contained two immiscible liquid phases in the mass ratio ≈ 11:1.

Analyses of the major liquid product from selected amine explosive reactions by HPLC indicated TNT and RDX levels ≤ 5 ppm in all cases. The pitch-like material from the TBA + TNT reaction, and the minor liquid phase from the TBA + RDX reactions have not been analyzed by HPLC at this time. A qualitative IR analysis of these phases indicated that a low concentration of the explosives may be present. These phases will be analyzed by HPLC to establish precise levels.

The explosive amine reaction described above were made with a large excess of amine relative to explosive, molar ratios were in the range 18-37:1. The stoichiometry deduced above for the MEA + TNT reaction suggests a mole ratio of ~ 7:1. A reaction was run using this ratio. To control the temperature, the TNT was added in 1-5 g increments. At the end of the reaction, after

elemental analysis. The TNT content of the final reaction product was determined by HPLC at ≤ 5 ppm and the MEA content by GC/FID at $< 3\%$. Based on the above findings the stoichiometry of the reaction was determined to be:



The empirical formula of the reaction product, a black pitch-like material, was calculated at $\text{C}_{21.1}\text{H}_{31.1}\text{N}_{6.5}\text{O}_{6.0}$, an extremely oxygen deficient compound from a combustion stand point.

At the present time attempts to analyze the liquid reaction products formed in these reactions in terms of the chemical species present have not been successful. GC/MS analyses have been tried with and with out derivatization of the matrices with BSTFA to form trimethylsilyl derivatives of reactive OH, N-H and COOH groups possibly present in the product. IR analyses also have been attempted. Some preliminary analyses using NMR have shown some promise but further work is needed.

Results for Task 3 - TNT-Amine Reaction Run in the High Temperature Self-Propagating Mode

Attempts were made at the laboratory level to initiate a self-propagating reaction in a pellet of TNT in the form of a cylinder ≈ 0.5 " inch diameter and 0.5 " long (mean ≈ 2 g). The pellet was formed in a pellet press from either flake or finely ground TNT and wrapped in a few layers of aluminum foil with one end open. Attempts to ignite the "open end" of the pellet with a heat source (gas-oxygen torch) and sustain the ignition after removal of the heat source failed. Attempts to initiate ignition by placing ≈ 0.1 g of finely powdered TNT on the "open end" of the TNT pellet followed by addition of one or two drops of DETA on the powder also failed. The powder ignited but did not initiate sustained combustion in the TNT pellet.

Some success in obtaining sustained ignition in TNT pellets was obtained by activating the TNT powder prior to pelletizing. Approximately 2 g of powdered TNT was added to ≈ 15 mL of 1 weight % DETA in hexane. The powder was washed well with hexane and dried under vacuum. Pellets so prepared were initiated with ≈ 0.1 g powdered TNT and a few drops of DETA. Sustained reaction in pellets prepared this way was generally obtained. If an "activated" pellet was placed on top of "non-activated" pellet, initiation of the activated pellet sometimes resulted in sustained reaction in the second pellet.

Although the above approach holds promise for obtaining the "cigarette mode" of sustained reaction in TNT pellets, the technique at the present time is not sufficiently reliable. It is possible that a substantial effort may be required to obtain sustained reaction for TNT when reacting in the cigarette mode configuration.

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SECTION 1

RESULTS TO DATE ON TASK I

1.1 INTRODUCTION.

The primary purpose in this task is to determine the stoichiometries and chemical reaction mechanisms of amine-explosive reactions when run in the non-self propagating mode. Prior work at IITRI¹ has shown that exotherms generated in amine-explosive reactions are quite sensitive to the reaction stoichiometry. Data shown in Figure 1 demonstrate such behavior in the TNT-pyrrolidine reaction. These reactions were performed by adding 1 mL of pyrrolidine to the indicated masses of TNT (0.5, 0.25 and 0.12g) placed in a 1 mL diameter test tube and monitoring the temperature of the reaction mix with a thermocouple. As the molar ratio of amine to TNT decreased, the reaction exothermicity increased. At MEA:TNT ratios < 5.5:1, the reactants inflamed (self-propagating) with evolution of copious quantities of gas(es).

At the present time the chemistries of both the non-propagating and self-propagating reactions are poorly understood, as are the factors responsible for the transition from non- to self-induced reaction propagation. Previous work at IITRI has also shown that the reactivities of different amines with a given explosive at ambient temperature are quite variable, reaction induction times at ambient temperature spanning a range of seconds to non-occurring over a period of days.

In this task, an attempt is made to characterize the stoichiometries and the chemical species generated in reactions between the following amines and explosives:

TNT with monoethanolamine, diethylenetriamine and tributylamine,

RDX with monoethanolamine, diethylenetriamine and tributylamine, and

TNT + RDX with monoethanolamine and diethylenetriamine.

Reactions were run in the non-self propagating mode and time-temperature profiles obtained.

1.2 EXPERIMENTAL.

1.2.1 Reactor Operation.

A schematic diagram of the all glass/Teflon/stainless steel reactor and gas collection system used in the study is shown in Figure 2. The reactions took place in a 500 mL three-necked glass flask. All reactions, with one exception, were performed with approximately 100 g of amine and 8 to 25g of explosive. The following procedures, with minor variations as required, were used:

- 1) Weigh the 500-mL reaction flask with stirrer bar.
- 2) Add the required amine, = 100g, and determine weight of flask with stirrer bar and amine.

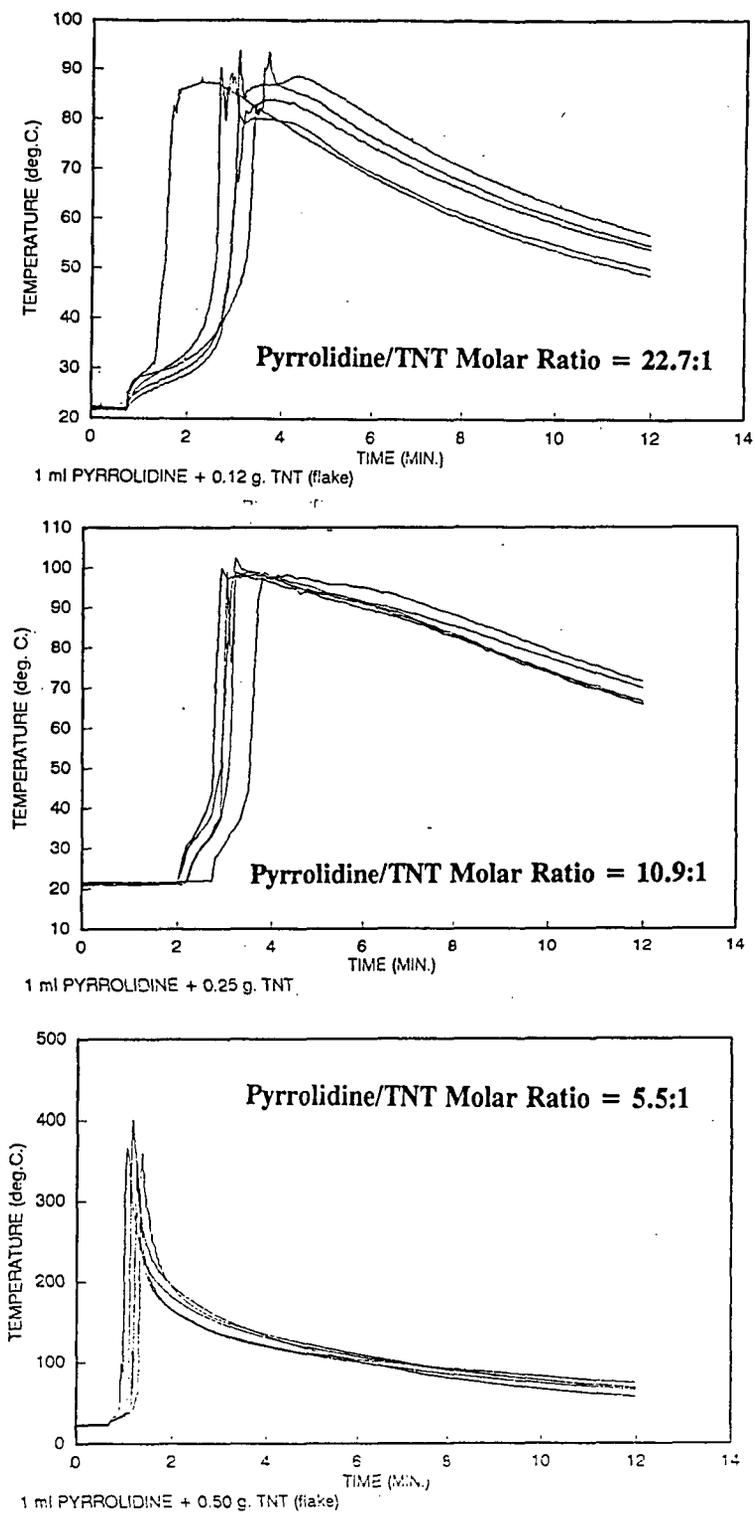


Figure 1. Data on exotherms generated in reactions of pyrrolidine with TNT at various stoichiometries. Reactions initiated at ambient temperature.

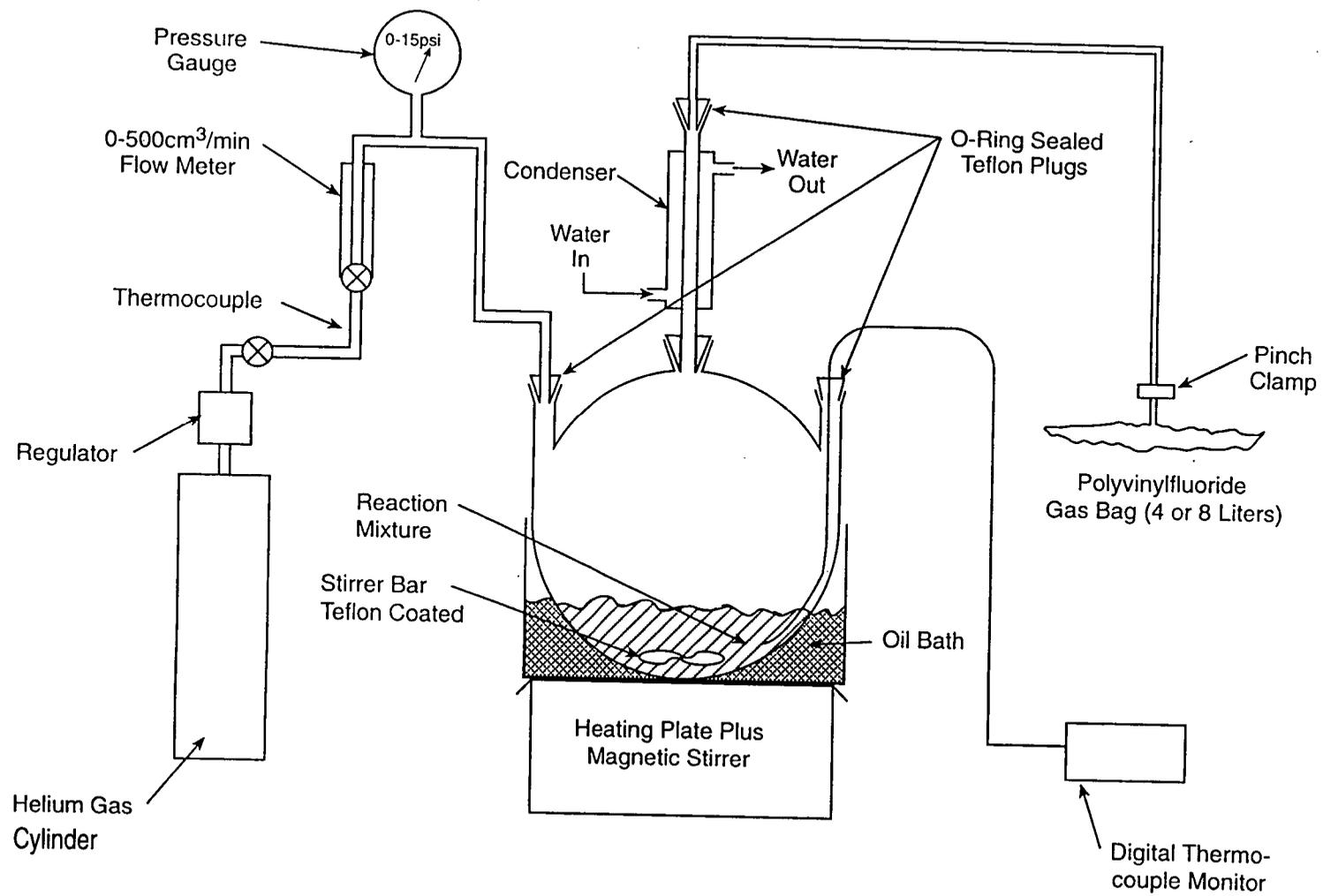


Figure 2. Schematic diagram of the experimental set-up used to react TNT, RDX and TNT + RDX with amines.

- 3) Assemble the reactor system shown in Figure 2 with the pinch clamp to the gas collection bag (not connected) closed.
- 4) Pressurize system to 2-3 psi and verify leak tightness.
- 5) Test gas bag for leaks by inflating and submersing in water.
- 6) Open pinch clamp to gas bag and purge system with helium at 100-200 mL/min for at least 10 minutes.
- 7) Turn on the condenser cooling water, magnetic stirrer and record reactor temperature for at least 10 minutes to ensure temperature stability ($\pm 2^{\circ}\text{C}$).
- 8) Weigh out the required amount of explosive in a small beaker.
- 9) When temperature stability in Item 7 is achieved, perform the following operation sequentially and quickly:
 - a) remove the taper joint containing the helium purge line
 - b) place a powder funnel in the taper joint and pour in the explosive
 - c) remove the powder funnel and replace the helium purge line
 - d) attached the gas collection bag to the system
 - e) turn off the helium purge gas flow
- 10) Continue to monitor the reactor temperature.
- 11) Approximately 10 minutes after addition of explosive, turn on the reaction flask heater plate to the required setting.
- 12) Continue to monitor reactor temperature and observe the degree of gas bag inflation.
- 13) If the gas bag becomes filled, quickly remove, seal and replace with a second or third bag as required.
- 14) When the reactor temperature maximizes and begins to cool, the heater plate is turned off and the system allowed to cool to ambient.
- 15) The gas collection bag is removed and a new bag attached. The helium purge gas flow is started and the residual reactor headspace gas collected.
- 16) As soon as is practical, (usually the same day) the collected gas is analyzed (see Section 1.2.3 on gas analysis by IR spectroscopy).
- 17) When the reactor has cooled to ambient temperature, it is dismantled from the system and weighed to determine the mass of reaction product remaining.

1.2.2 Materials Used in the Reactions.

- a) Monoethanolamine (MEA), $\text{HOC}_2\text{H}_4\text{NH}_2$, Sigma Aldrich-Chemical Co., purity, 99%
- b) Diethylenetriamine (DETA), $\text{H}_2\text{NC}_2\text{H}_4\text{NHC}_2\text{H}_4\text{NH}_2$, Sigma-Aldrich Chemical Co., purity 99%.
- c) Tributylamine (TBA), $(\text{C}_4\text{H}_9)_3\text{N}$, Fluka Chemical, purity 99%.
- d) TNT - Type 1, ICI Explosives, Canada. This is a flake material.
- e) RDX-3 Type 1, AI-water-wet (dried). This is a finely granulated material.

1.2.3 Analyses of Gas Samples by Infrared Spectroscopy.

1.2.3.1 Calibration of the IR Spectrophotometer. During the study, IR spectroscopy was used to identify and quantify gaseous species generated in the explosive-amine reactions. The following species were identified, nitrous oxide (N₂O), ammonia (NH₃), nitrogen dioxide (NO₂) and carbon dioxide (CO₂). IR spectra were recorded on a Perkin-Elmer Model 273 IR spectrophotometer using a 10 cm pathlength gas cell fitted with either KBr windows (N₂O, NH₃ and CO₂) or AgCl windows (NO₂ or any gas mixture containing NO₂). Calibration gases were introduced into the IR gas cell at known pressures using standard vacuum line techniques. The following gases were used:

- N₂O: supplied by AGA Gas Central, purity 99%
- NH₃: supplied by AGA Gas Central, purity 99.99%
- NO₂: supplied by Sigma-Aldrich Chemical Co., purity, 99.5+%
- CO₂: supplied by AGA Gas Central, purity 99.99%

Spectra of the pure gases at the pressures indicated, are shown in Figures 3 through 6. The balance of the pressure in the gas cell was made up to 760 mm of Hg with zero air.

The response of the spectrophotometer to the various gases was determined assuming a linear relationship:

$$\log I_0/I = P_x(\text{mm of Hg}) + C$$

where I_0/I is the ratio of the transmitted IR energy at a specified wavelength, with and without respectively, the gas (x) in the cell at a pressure of P_x mm of Hg. Experimental data were fitted to the above equation using a linear regression analysis and the correlation coefficient determined. Calibration equations were generated based on 3 to 6 data points. Calibration equations were considered satisfactory provided the correlation coefficient r was > 0.99 . The calibration equation was checked on each day of its use by comparing the actual instrument response to a given gas standard of known pressure with that calculated from the calibration equation. Providing the responses were within $\pm 10\%$ of the equation calculated values, the calibration equation was considered acceptable, if not a new calibration equation was generated. A set of experimental data used to calibrate the IR spectrophotometer with ammonia is shown in Figure 7. Typical calibration equations are shown below:

Table 1. IR spectrophotometer calibration data.

Gas	Equation	No. of Data Pts.	Correlation Coefficient (r)	Absorption ¹ Maximum (cm ⁻¹)	Pressure Range (mm of Hg)
N ₂ O	$\ln I_0/I = 0.2357P_{N_2O} + 0.1357$	5	0.9912	~ 2210	4.74 - 0.50
N ₂ O	$\ln I_0/I = 0.0455P_{N_2O} + 0.1940$	3	0.9976	~ 1275	25.0 - 8.19
NH ₃	$\ln I_0/I = 0.00588P_{NH_3} + 0.08831$	6	0.9962	~ 3340	120 - 21
NH ₃	$\ln I_0/I = 0.2234P_{NH_3} + 0.1657$	4	0.9993	~ 940	8.08 - 1.51
NO ₂	$\ln I_0/I = 0.2959P_{NO_2} + 0.1407$	5	0.9979	~ 1602	4.93 - 0.53
CO ₂	$\ln I_0/I = 0.1666P_{CO_2} - 0.0021$	6	0.9988	~ 2330	7.53 - 0.70

(1) Frequency of absorption band used in the calibration determination.

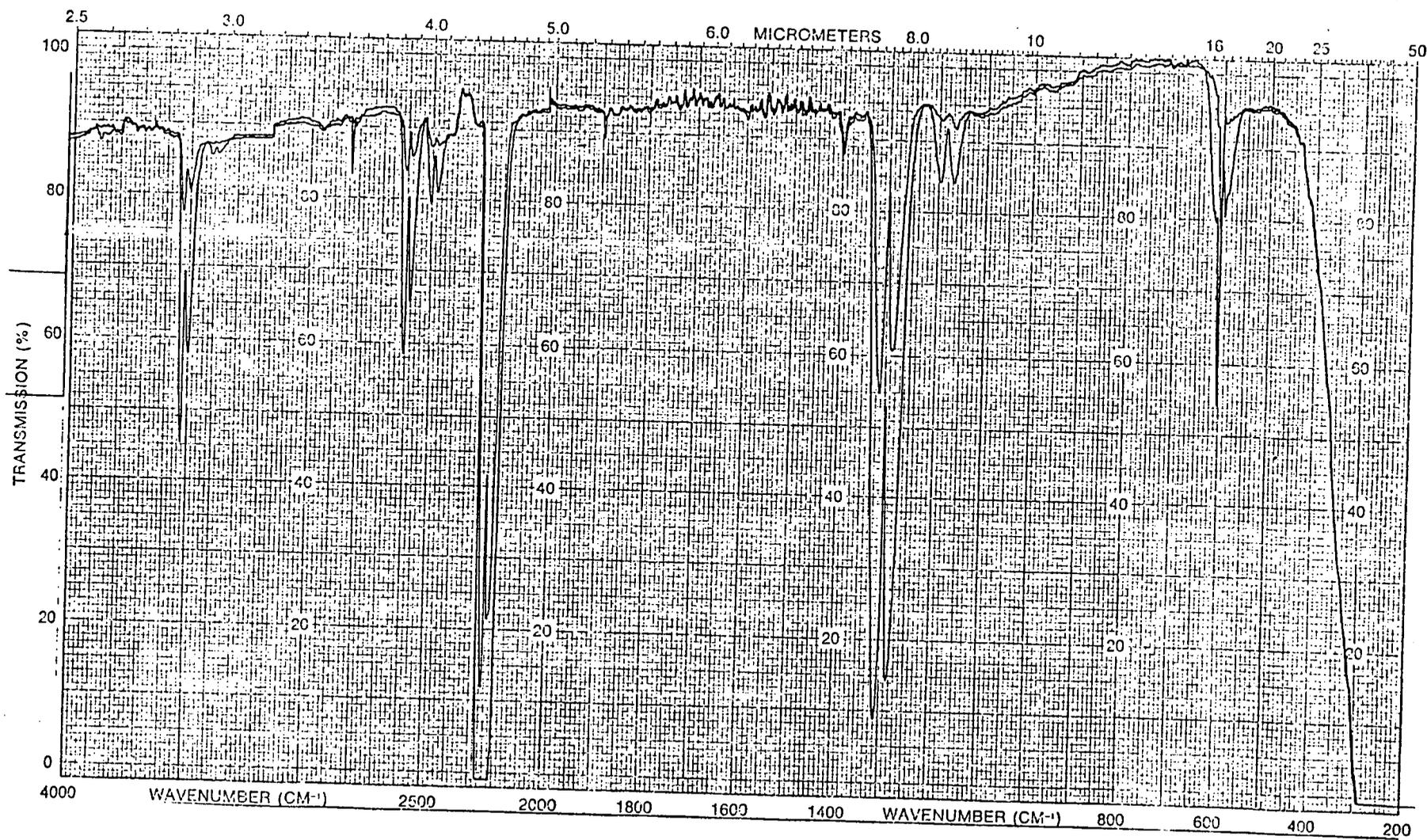


Figure 3. IR spectra of N_2O at pressures of 5 and 50 mm of Hg.

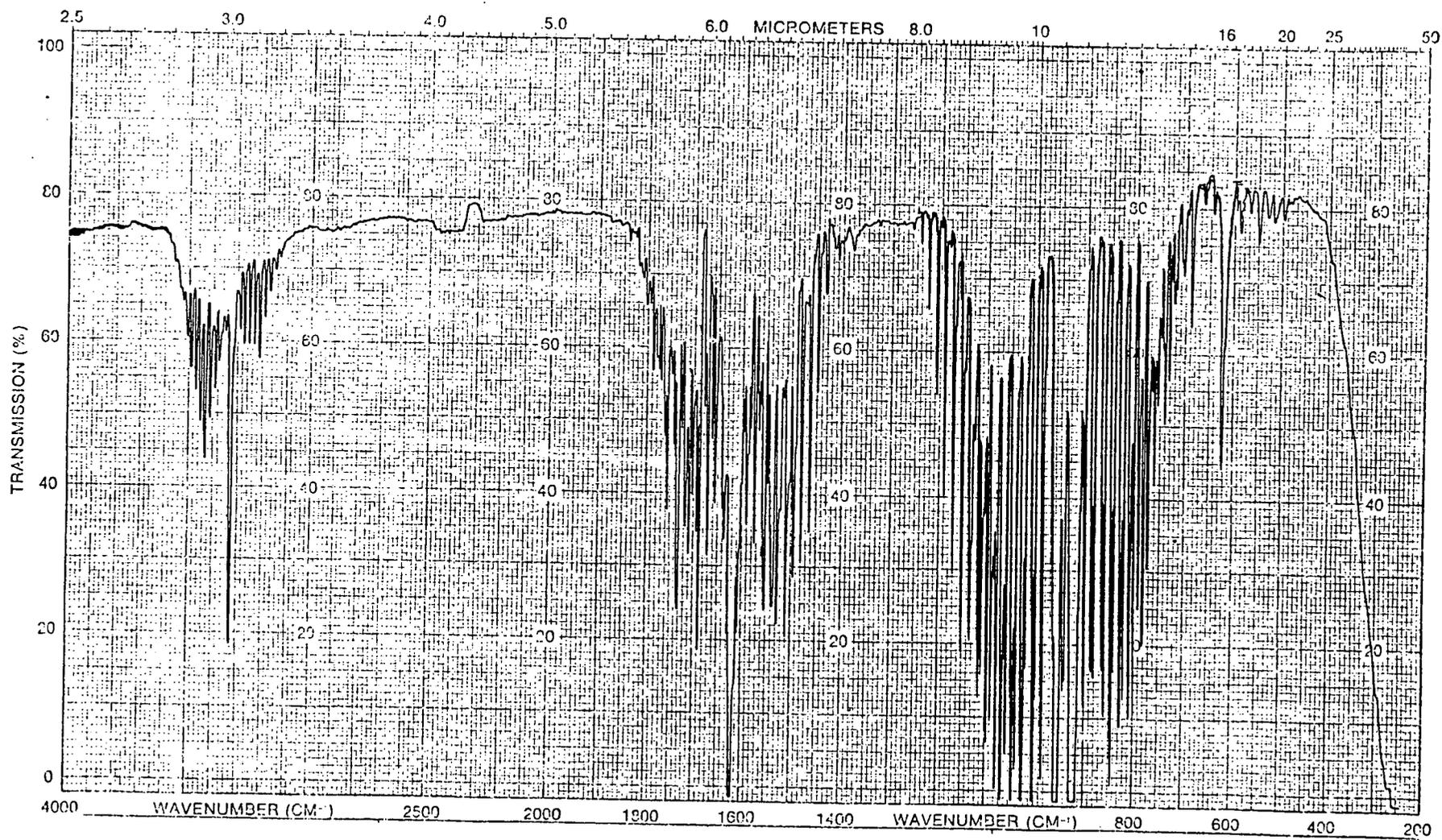


Figure 4. IR spectrum of NH₃ at a pressure of 10 mm of Hg.

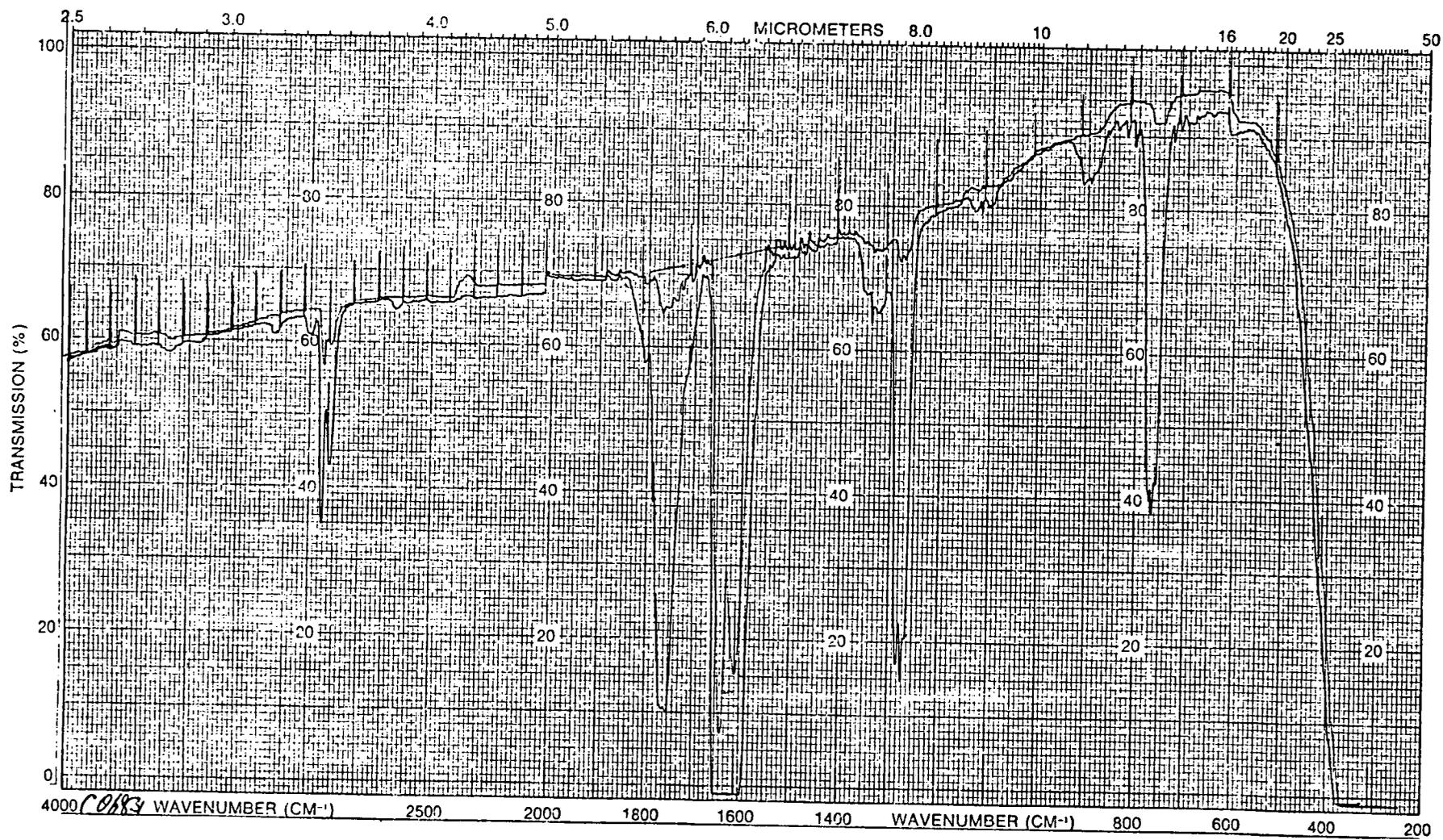


Figure 5. IR spectra of NO₂ at pressures of 4.9 and 25 mm of Hg.

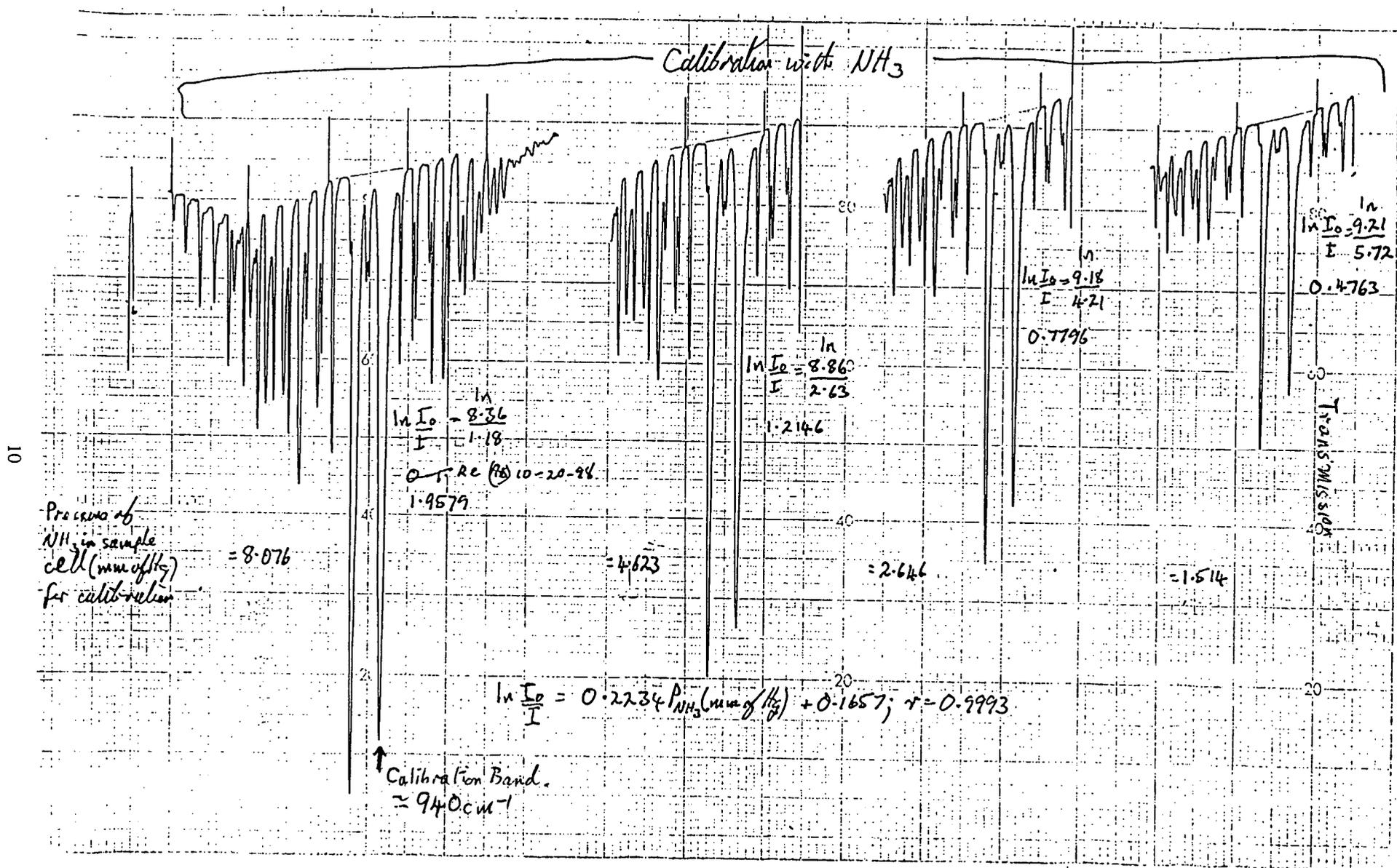


Figure 7. Experimental data used to calibrate the IR spectrometer response to ammonia gas at various pressures.

1.2.4 Quantitative Analyses of Explosive-Amine Gas Samples.

Gas bags, 8- or 4-liter capacity, containing gases generated from explosive-amine reactions were attached to a vacuum line containing a calibrated volume of $\approx 4200 \text{ cm}^3$. Standard vacuum line techniques were used to measure the volume of gas in collection bags using ideal gas PVT behavior. After determining the volume (moles) of gas in each bag, the IR cell was filled with a gas sample at as high a pressure as possible (≤ 1 atmosphere depending on the amount of gas collected) and a survey spectrum run to identify the species present. The pressure in the cell was then reduced to bring the $\log I_0/I$ absorbance values of each gas into the range of its calibration equation and the mole fraction of each gas present in the sample determined. These data were then used to determine the total amount of each gas present in the original gas sample collected.

1.2.5 Analysis of Amines in Liquid Explosive-Amine Reaction Product Matrices by Gas Chromatography with Flame Ionization Detection, GC/FID.

1.2.5.1 Calibration of the GC/FID. Analyses were performed on the liquid reaction product from the amine-explosive reactions to determine the amount of amine consumed. The analytical method selected was GC/FID. Analyses were performed on a Perkin-Elmer GC/FID Autosystem using an internal standard (IS) method. The GC/FID was run under the conditions shown in Table 2.

Standard solutions (a minimum of five concentration levels) of each of the amines with the internal standard were prepared in methanol for calibration of the GC/FID. Duplicate injections of each of these standards were used to generate GC/FID calibration equations in the form:

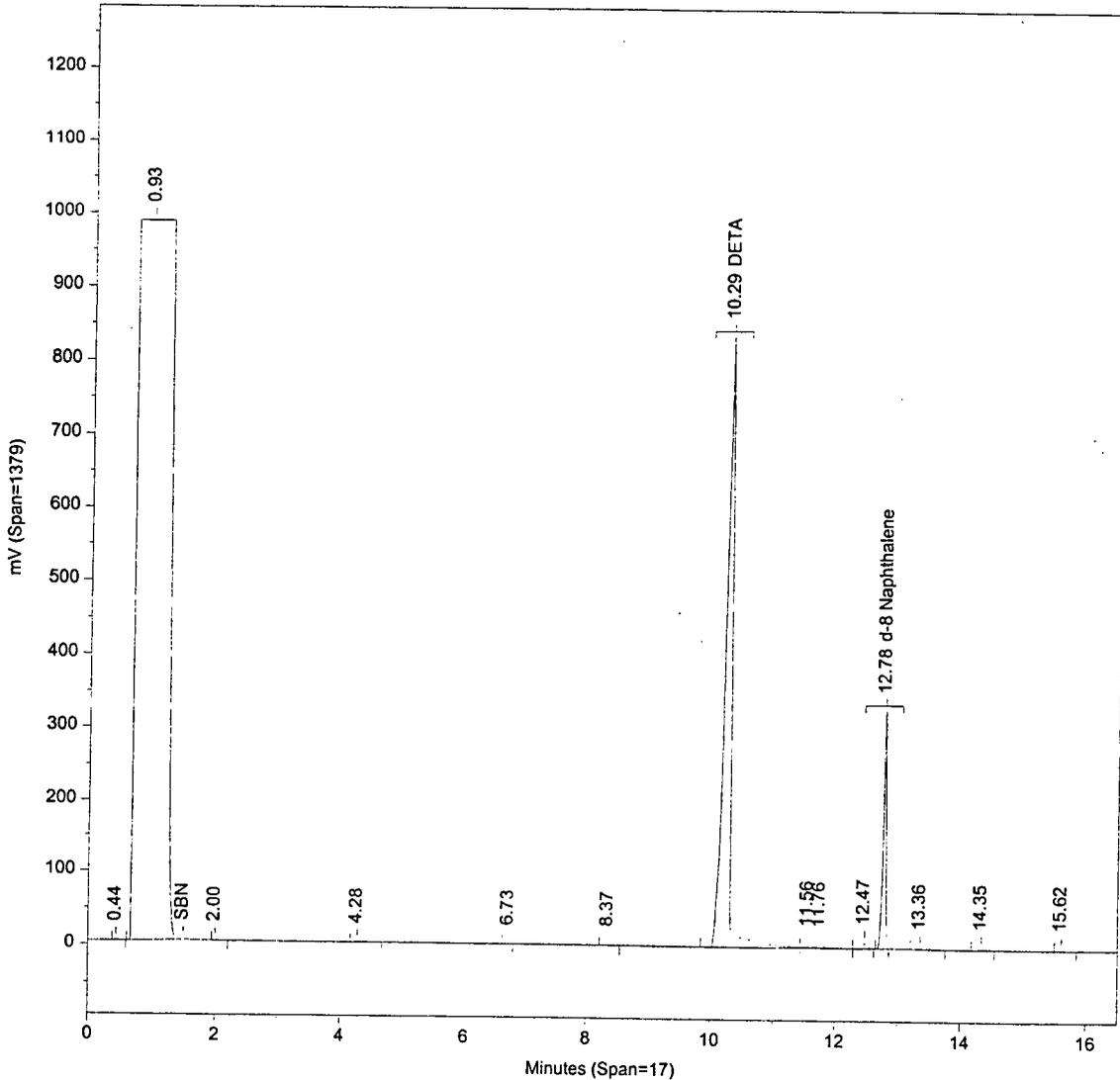
$$\frac{\text{Amine GC/FID area response}}{\text{IS GC/FID area response}} = \left[A \frac{\text{Conc. Amine } (\mu\text{g/mL})}{\text{Conc. IS } (\mu\text{g/mL})} \right] + B$$

where A and B are constants determined from a least squares analysis of the data. A typical chromatogram obtained in the calibration of the GC/FID with DETA is shown in Figure 8. Graphical plots of typical calibration equations are shown in Figures 9, 10 and 11. Calibration equations were considered acceptable if:

- a) r, the linear regression analysis correlation coefficient was ≥ 0.99
- b) Amine standard concentrations calculated from the GC/FID responses were within $\pm 25\%$ of the prepared values for all but the lowest standard used.

Table 2. GC/FID operating conditions for the determination of MEA, DETA and TBA in explosive reaction product matrices.

	MEA	DETA	TBA
Temp Program	35°C for 6 min. to 250°C @ 10 C/min	35°C for 4 min. to 250°C @ 10 C/min	35°C for 4 min. to 250°C @ 10 C/min
Inj. Temp.	250°C	250°C	250°C
FID	300°C	300°C	300°C
Range	1	1	1
Attn.	4	16	16
Column	AT-CAM: 30 M. .53 mm, 1.0 μm	RTX-5 Amine: 30 M. .53 mm, 1.0 μm	RTX-5 Amine: 30 M. .53 mm, 1.0 μm
Helium Flow	12.55 mL/min	11.68 mL/min	12.45 mL/min
Hydrogen Flow	52.33 mL/min	56.58 mL/min	63.04 mL/min
Air Flow	503.75 mL/min	509.15 mL/min	505.43 mL/min
Retention Time	MEA: 13.35 min IS: 17.92 min	DETA: 10.30 min IS: 12.78 min	TBA: 12.85 min IS: 14.43 min
Calibration Conc. Range	4000-500 μg/mL	4000-500 μg/mL	2000-1600 μg/mL
Conc. IS ¹	313.28	331.2	1565.2
(1) With MEA and DETA, d-8Naphthalene used as IS. For TBA, 2-methylnaphthalene used as IS.			



Sample Name: 4032.9 ug/mL DETA + 331.2 ug/mL Naph; 1.2 uL
 Acquired from PE-A--FID via port 2 on 11/3/98 11:18:19am by MG ; C06831
 RTX-5 Amine:30Mx.53mm,1.0um;35C,4m-250C@10C/m
 Inj 250C; FID 300C; Range 1; Attn 16

Data File: C:\CPWIN\DATA2\DETA1103.04R
 Date Stamp: 11/3/98 11:18:18am
 Method File: C:\CPWIN\DATA1\DETANAP.MET
 Version 4. Date Stamp: 11/3/98 10:22:44am
 Calibration File: C:\CPWIN\DATA1\DETA1102.CAL
 Version 2. Date Stamp: 11/3/98 10:22:36am

Run Time = 16.5 min Sample Rate = 3.0 per sec.
 Amount Inj. = 1.000 Dilution Factor = 0.000

C:\CPWIN\DATA2\DETA1103.04R

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Figure 8. GC/FID chromatogram of a calibration standard of DETA (4032.9 $\mu\text{g/mL}$) + IS(331.2 $\mu\text{g/mL}$) in methanol.

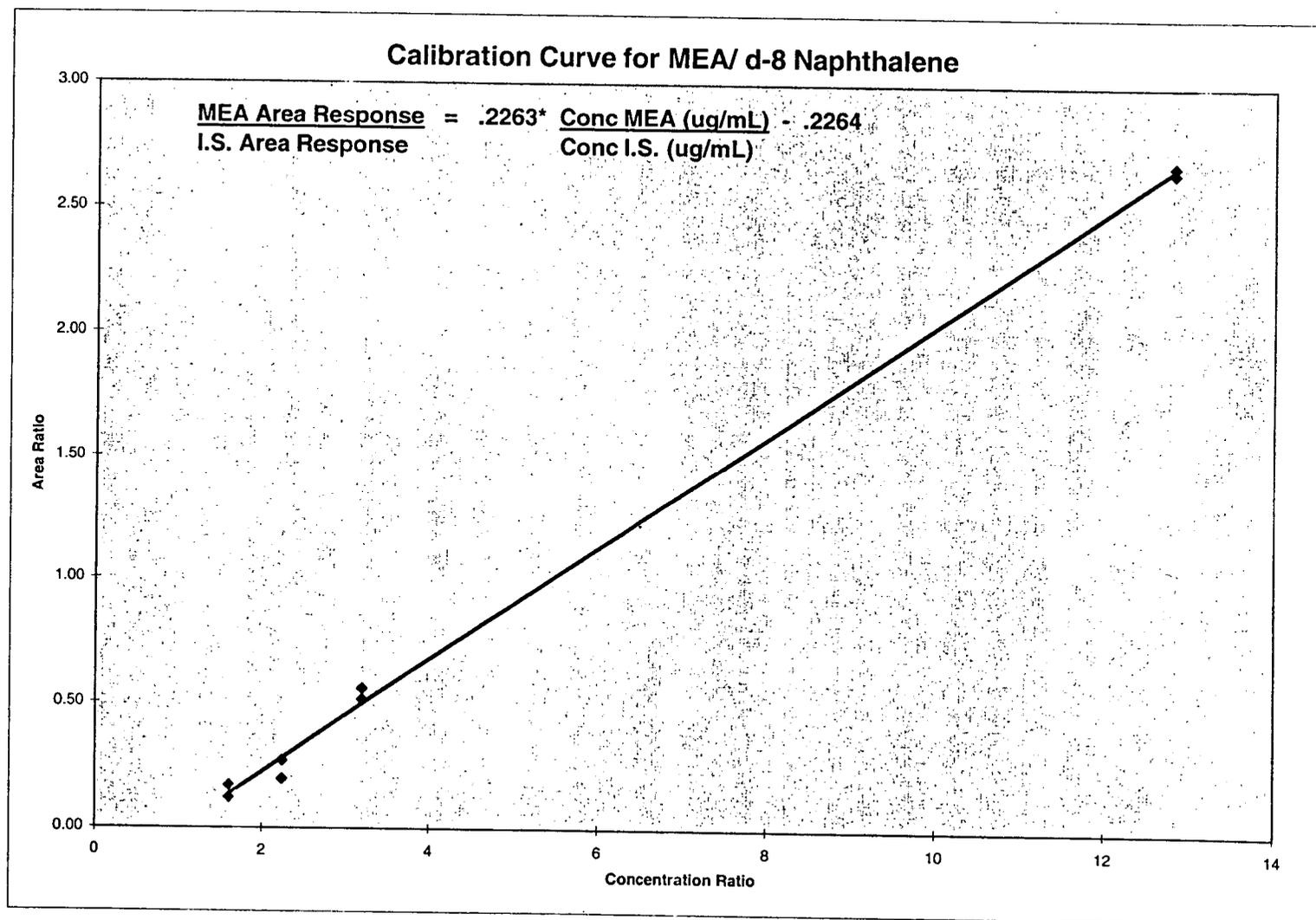
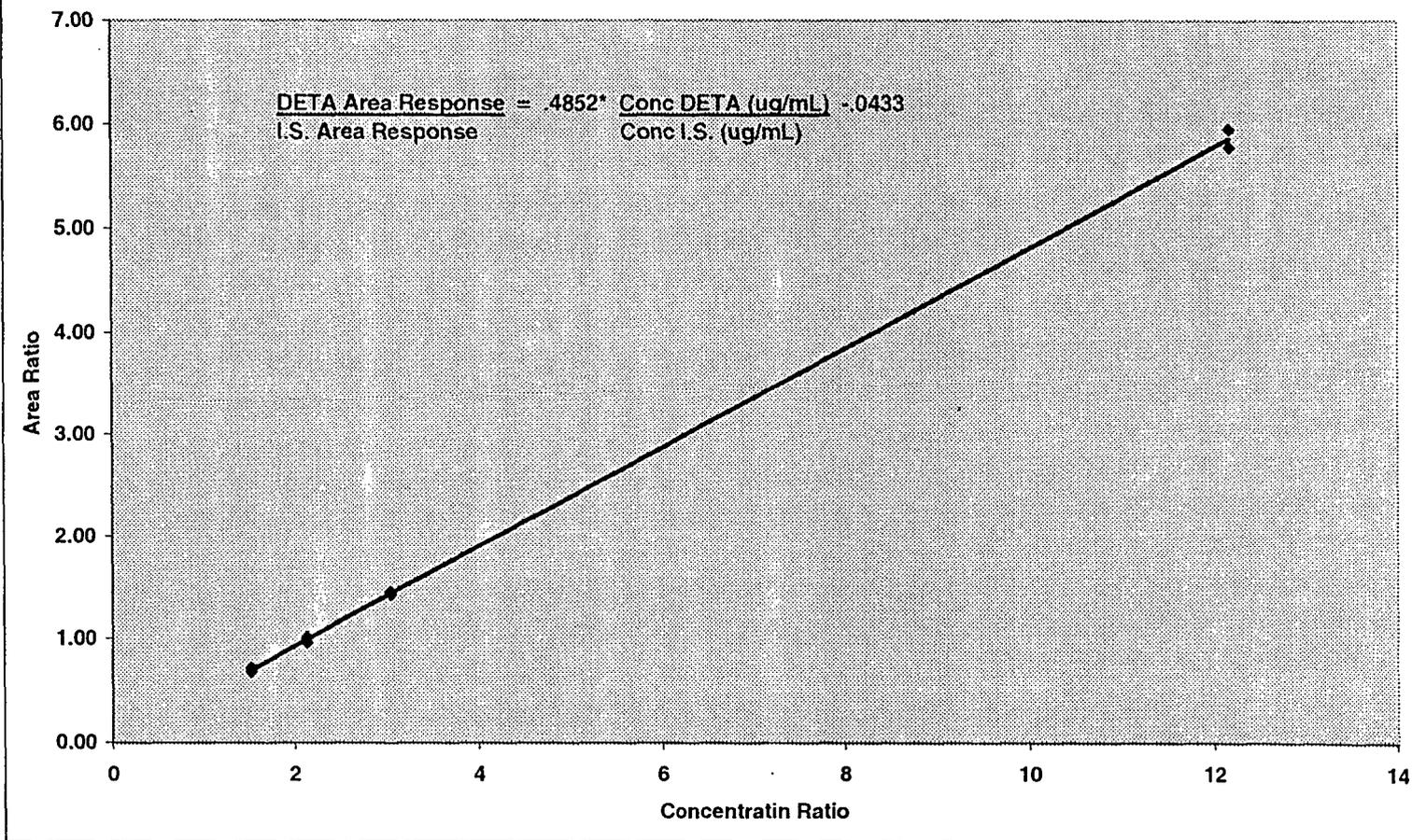


Figure 9. Graphical representation of GC/FID calibration data for MEA over the concentration range $\approx 4000\text{-}500 \mu\text{g/mL}$ in methanol. IS = d-8 naphthalene, concentration $313.28 \mu\text{g/mL}$.

Calibration Curve for DETA/ d-8 Naphthalene



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Figure 10. Graphical representation of GC/FID calibration data for DETA over the concentration range $\approx 4000\text{-}500 \mu\text{g/mL}$ in methanol. IS = d-8 naphthalene, concentration $331.2 \mu\text{g/mL}$.

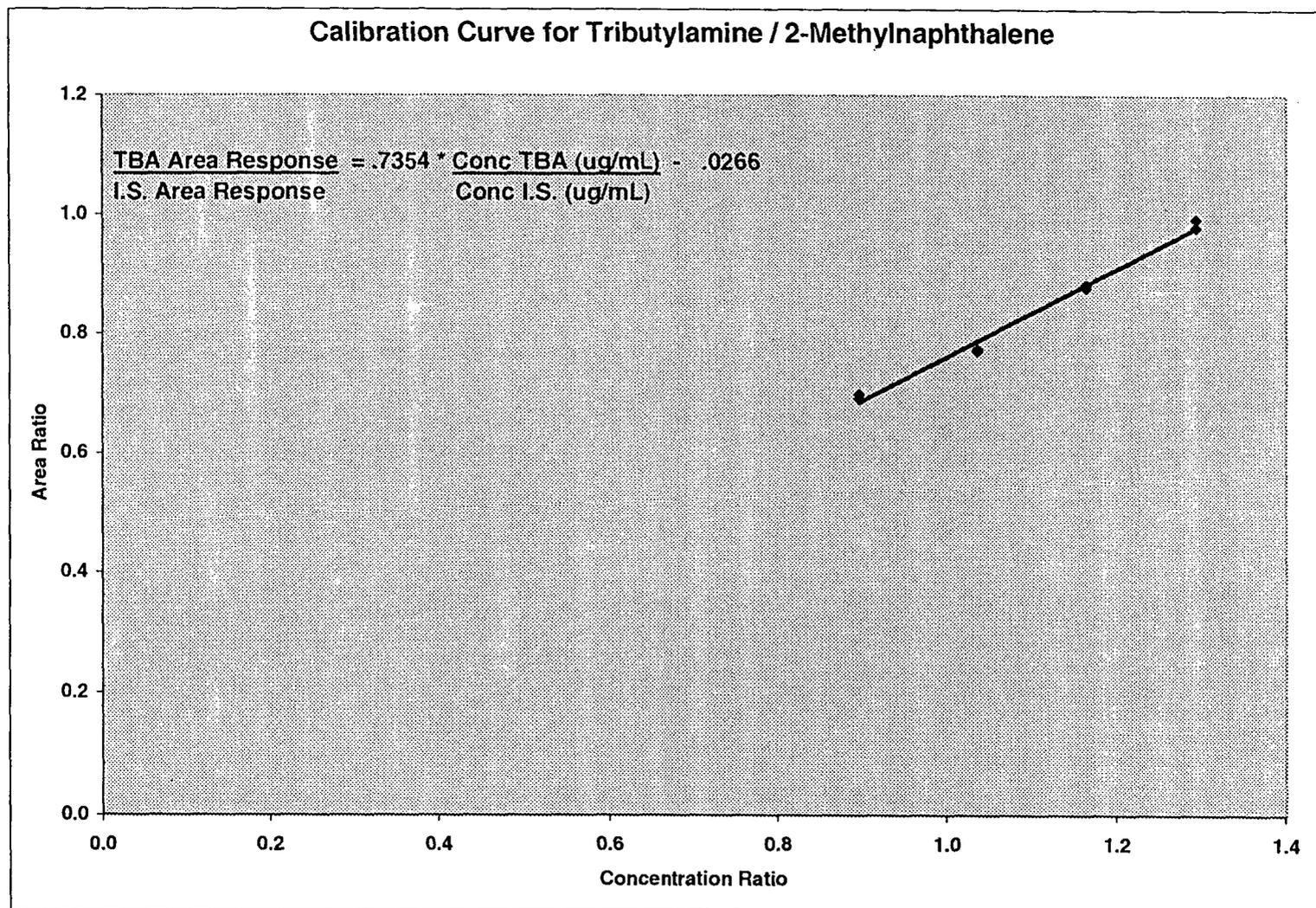


Figure 11. Graphical representation of GC/FID calibration data for TBA over the concentration range ~ 2000-1000 $\mu\text{g/mL}$ in methanol. IS = 2-methylnaphthalene, concentration 1565.2 $\mu\text{g/mL}$.

On subsequent use of the calibration equation, the responses of the GC/FID to the highest and second lowest calibration standards were determined and the calculated equivalent concentrations determined. If the calculated concentrations were not within $\pm 25\%$ of the actual values (they were generally within $\pm 10\%$) a new calibration equation was generated.

1.2.5.2 Determination of Amine Content of Explosive-Amine Reaction Product Matrices. The amine contents of the reaction product matrices were determined by preparing methanol solutions containing known masses of each of the matrices together with the internal standard. The amine concentrations in these solutions were adjusted by appropriate dilutions to fall within the range of the GC/FID calibration equations. From the determined amine matrix solution concentration, the total amount of amine present in the reaction product matrix was calculated.

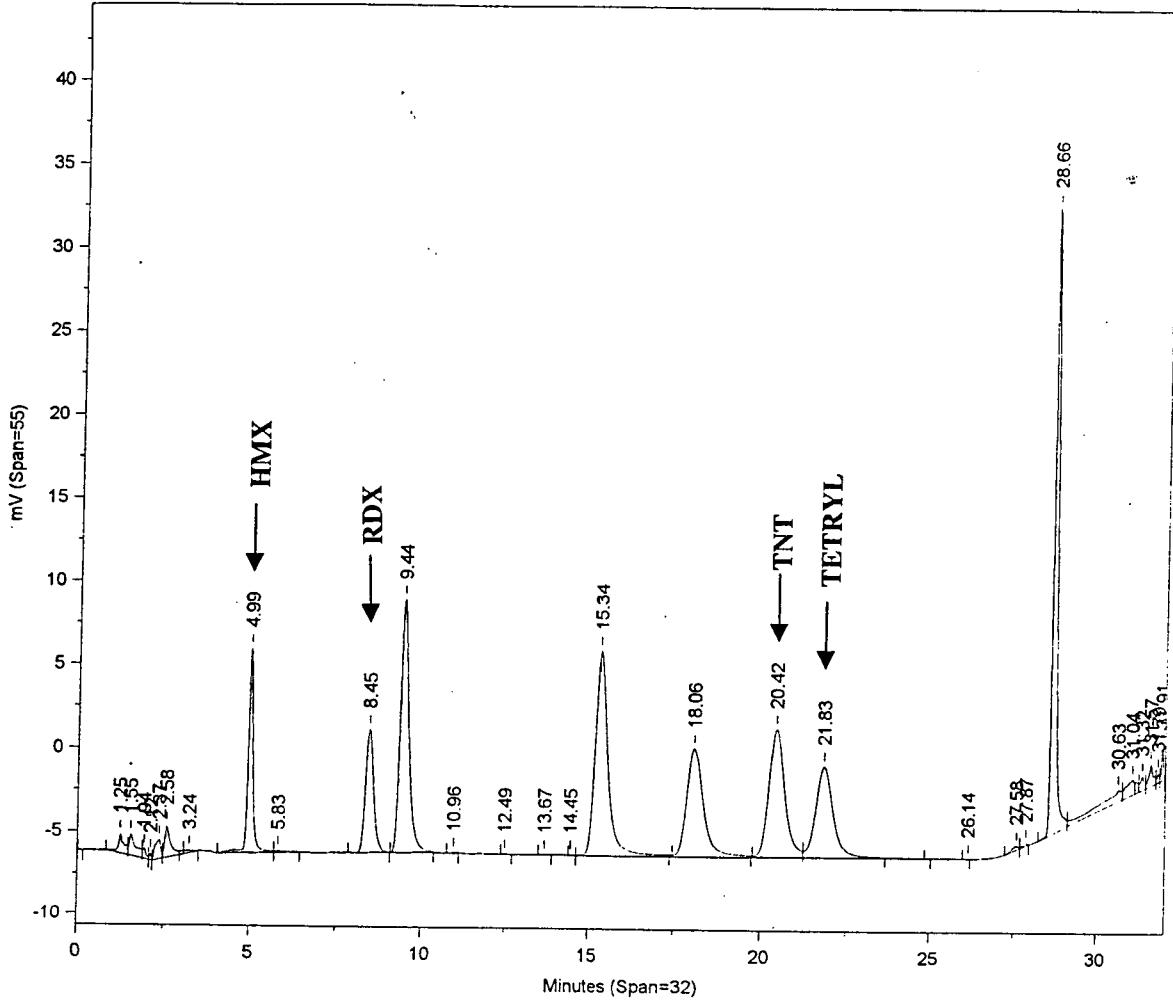
1.2.6 Analysis of TNT and RDX in Reaction Product Matrices by HPLC.

1.2.6.1 Calibration of HPLC. The EPA Method 8330 for analysis of nitroaromatics and nitramines by high performance chromatography (HPLC) in water, solid or sediment matrices, was modified for use in this study to accommodate the highly basic explosive-amine reaction product matrix.

The analyses were performed on a Waters HPLC using a LC-18 reverse phase column with UV detection at 254 nm. The instrument was calibrated in the 10-0.25 ppm range with the following mixture of explosives supplied by 1) Restek: HMX, RDX, 1,3,5-trinitrobenzene, 1,3-dinitrobenzene, nitrobenzene, TNT and 2,4-dinitrotoulene and 2) Supelco: tetryl. The above standards were prepared in acetonitrile (CH_3CN) and eluted using the following program: solvent (MeOH: H_2O , 25:75) for 20 minutes; then to 100% MeOH at 26 minutes; and hold for 6 minutes; flow rate 1.5 mL/min. A chromatogram of a 1-ppm mix of the explosive calibration standards is shown in Figure 12 using a 100 μL injection.

1.2.6.2 Determination of TNT and RDX Concentrations in Selected Explosive-Amine Matrices. Samples of the selected reaction product matrices were prepared as follows:

1. Add 3 ml amine matrix and 3 mL glacial acetic acid to 100-mL flask; mix on magnetic stirrer.
2. Add ~ 75 mL of 25g/100 mL NaCl/ H_2O solution to flask and stir. Add 18 mL ACN to flask and stir. Remove ACN layer - transfer to graduated cylinder.
3. Add 5 mL ACN to flask and stir. Remove ACN layer and transfer to graduated cylinder. Repeat.
4. To combine ACN extracts, add ACN to reach 18 mL ACN; transfer to new flask. Add 81 mL of 25g/100 mL NaCl/ H_2O solution and stir.
5. Remove ACN layer and transfer to graduated cylinder. Add an additional 1 mL ACN to flask and stir.
6. Combine ACN layers in graduated cylinder - record volume. Dilute to final volume with Milli-Q water and analyze.



Sample Name: **1PPM STD MIX-A AND TETRYL**
 Acquired from Chrom3--Det3A via port 3 on 10/9/98 10:11:45am by K BORCK
 UV254
 MEOH:H2O 25:75 FOR 20MIN THEN TO 100 MEOH AT 26 MIN HOLD 6

Data File: **C:\CPWIN\DATA1\DECT3\100998.01R**
 Date Stamp: 10/9/98 10:11:42am
 Method File: **C:\CPWIN\DATA1\HPEXP-A.MET**
 Version 3. Date Stamp: 9/22/98 09:28:12am
 Calibration File: **C:\CPWIN\DATA1\DECT3\EXP-1.CAL**
 Version 10. Date Stamp: 10/9/98 10:24:16am

Run Time = 32.0 min Sample Rate = 1.0 per sec.
 Amount Inj. = 100.000 Dilution Factor = 1.000
 Sample Weight = 1.000 Int Std Amount = 1.000

Starting Peak Width = 0.04 min. Peak Threshold = 0 Area Reject = 100

C:\CPWIN\DATA1\DECT3\100998.01R

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Figure 12. HPLC chromatogram of a 1 ppm mix of the explosive calibration standards.

1.3 EXPERIMENTAL RESULTS FOR THE EXPLOSIVE-AMINE REACTIONS.

1.3.1 Qualitative Analytical Results for Gaseous Products Formed in Explosive-Amine Reactions.

1.3.1.1 Identification of Gaseous Products from Reaction of MEA with TNT, RDX and TNT + RDX. Typical IR spectra of the gases generated in the MEA + TNT and MEA + RDX reactions are shown in Figures 13 and 14, respectively. Comparison of these spectra with those of N₂O and NH₃ reference spectra shown in Figure 3 and 4 allow assignment of all absorption bands in Figures 13 and 14 to either NH₃ or N₂O. In the MEA + TNT system, NH₃ is the major component with N₂O present as a minor constituent \approx 0.01 mole % relative to NH₃. In the MEA + RDX system, both gases are present at significant levels, in the approximate mole ratio NH₃:N₂O of 1:3. In the MEA + TNT + RDX reactions, NH₃ and N₂O were also the only gaseous species detected.

1.3.1.2 Identification of Gaseous Products From Reaction of DETA with TNT, RDX and TNT + RDX. NH₃ and N₂O were the only gaseous products identified in the DETA-explosive reactions. Their relative amounts were very similar to those found in the MEA-explosive reactions (Section 1.3.1.1 above).

1.3.1.3 Identification of Gaseous Products From Reaction of TBA with TNT and RDX. A typical IR spectrum of the gases generated in the TBA + RDX reaction is shown in Figure 15. Comparison of this spectrum with those of N₂O, NO₂ and CO₂ reference spectra in Figures 3, 5 and 7 allow assignment of all absorption bands in Figure 15 to these species. Similar results were obtained for the gaseous products formed in the TBA + TNT reaction.

1.3.1.4 Identification of Gaseous Products Formed on Heating MEA, DETA and TBA. Tests were made to determine if the amines used in the study underwent any decomposition when heated to temperatures of \approx 150°C typical of the above explosive-amine reaction. Approximately 100 g of amine was heated in the experimental set-up shown in Figure 2, under conditions typical of the explosive-amine reactions. Approximately 3-4 liters of headspace gas was collected by purging the septum with helium after the reactor cooled to ambient temperature. The gas was analyzed by IR spectroscopy. With MEA and DETA, very small amounts of NH₃ were detected, equivalent to \approx 0.05 and 0.015 mole %, respectively, in the volume of headspace gas collected. These amounts of ammonia are <1 % of those typically generated in MEA and DETA explosive reactions. With TBA, no NH₃ was detected in the headspace gas sample. With none of these amines were N₂O, NO₂ or CO₂ detected in the headspace gases.

1.3.2 Quantitative Analytical Results for Residual Amine Present in Explosive-Amine Reaction Product Matrices.

Reaction product matrices from the explosive-amine reactions were analyzed by GC/FID for their residual unreacted amine content. A chromatogram of a DETA + TNT reaction product matrix is shown in Figure 16. Apart from the large solvent injection peak, there are only two other major peaks present in the chromatogram, those of DETA and IS(d-8 naphthalene). Similar chromatograms were obtained for all amine-explosive reaction product matrices. Only those peaks attributable to the solvent amine and IS appeared at significant intensities. Data

obtained from these analyses are summarized in Tables 3, 4 and 5. In the MEA and DETA, reactions significant quantities of the amine, approximately 20-50% were consumed. In contrast, in the TBA + RDX and TBA + TNT reactions, within the precision of the analytical data, the amounts of residual TBA present in the reaction product matrices were determined at 99.35 ± 3.6 RSD% of the original amounts of TBA present initially in the reaction, i.e., within the precision of the data very little, if any, TBA was consumed in the reactions with the explosives.

1.3.3 Analytical Data On The Explosive-Amine Reaction Mass Balances.

Analytical data obtained for amounts of MEA, DETA and TBA consumed and amounts of products formed in the explosive-amine reactions studied are presented in Table 3, 4 and 5, respectively. The percentage mass balances were calculated as follows:

$$\% \text{ Mass Balance} = \left[\frac{\text{Mass of Liquid + Solid + Gaseous Reaction Products Formed (g)}}{\text{Mass of Amine + Explosive used in the Reaction(g)}} \right] \times 100$$

Average % mass balances obtained for the reactions studied are summarized in Table 6.

Table 6. Summary of data for mass balances obtained for the explosive amine reactions studied.

System	No. of Expts.	% Mass Balance	
		Average	± S.D.
MEA + TNT	4	98.98	0.64
MEA + RDX	6	99.18	0.75
MEA + TNT + RDX	2	99.53	0.05
DETA + TNT	2	98.72	1.10
DETA + RDX	3	98.75	1.45
DETA + TNT + RDX	1	99.94	--
TBA + TNT	1	98.68	--
TBA + RDX	1	98.52	--

In some of the above experiments, a small amount of liquid was observed to be present on the inside surfaces of the gas collection bags. This liquid was only noticeable when the bags were collapsed on evacuation to measure the collected gas volume. On prolonged evacuation, the amount of liquid appeared to decrease. It is possible the liquid may have been water. The mass of this liquid was probably small, but not known. For this reason, it was not included in the above mass balance calculation. Two gas samples generated in Test #: 12-10-29-98(TNT + MEA) and Test #: 13-10-26-98 (RDX + MEA) were analyzed for H₂, O₂ and N₂ at the Institute of Gas Technology with the following results:

Test Number	Mole %		
	H ₂	O ₂	N ₂
12	<0.04	0.05	0.41
13	<0.04	0.07	0.31

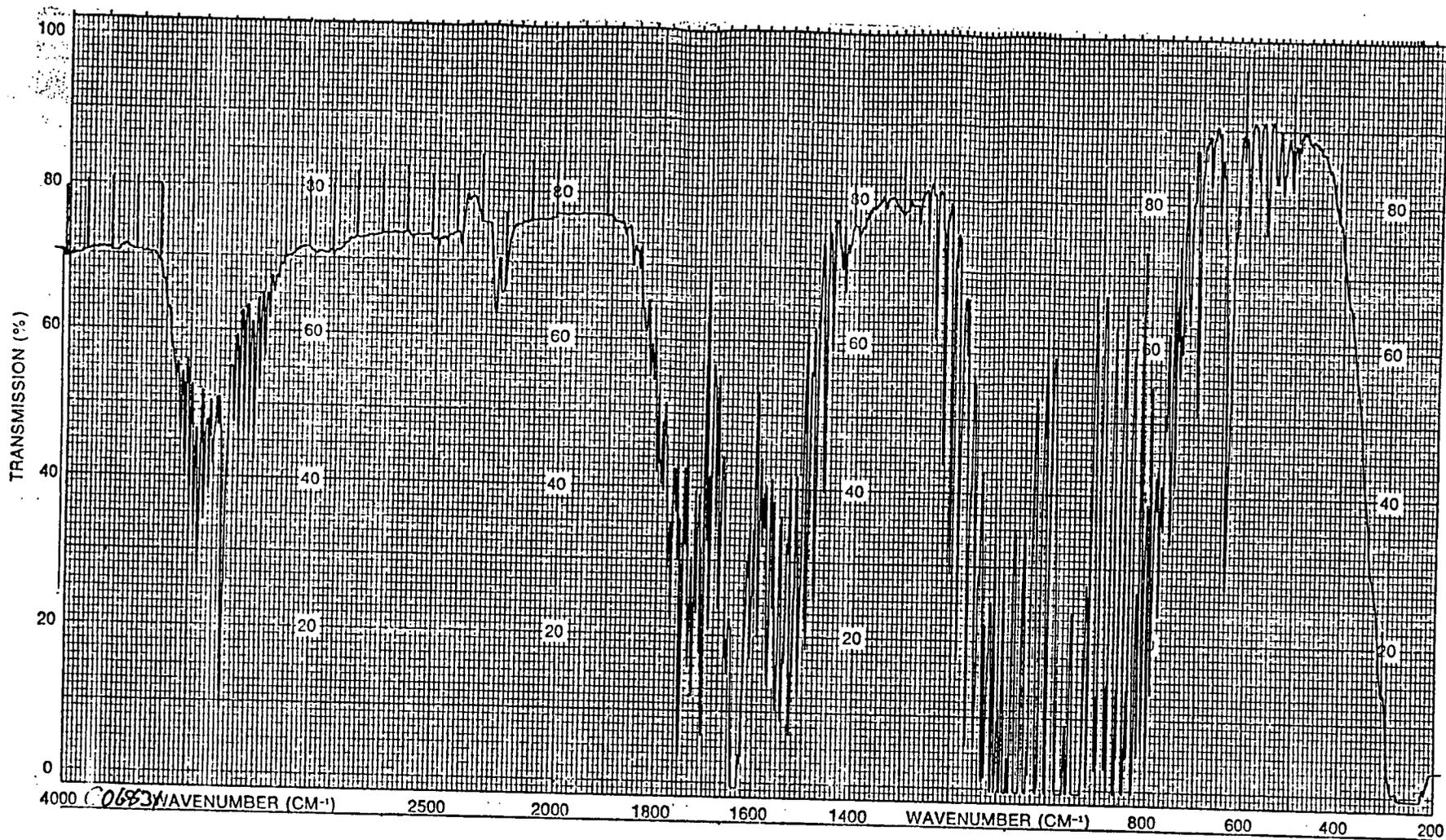


Figure 13. IR spectrum of gaseous reaction products generated in the MEA + TNT reaction, Test No. 8-10-20-98. Gas sample pressure, 400 mm of Hg.

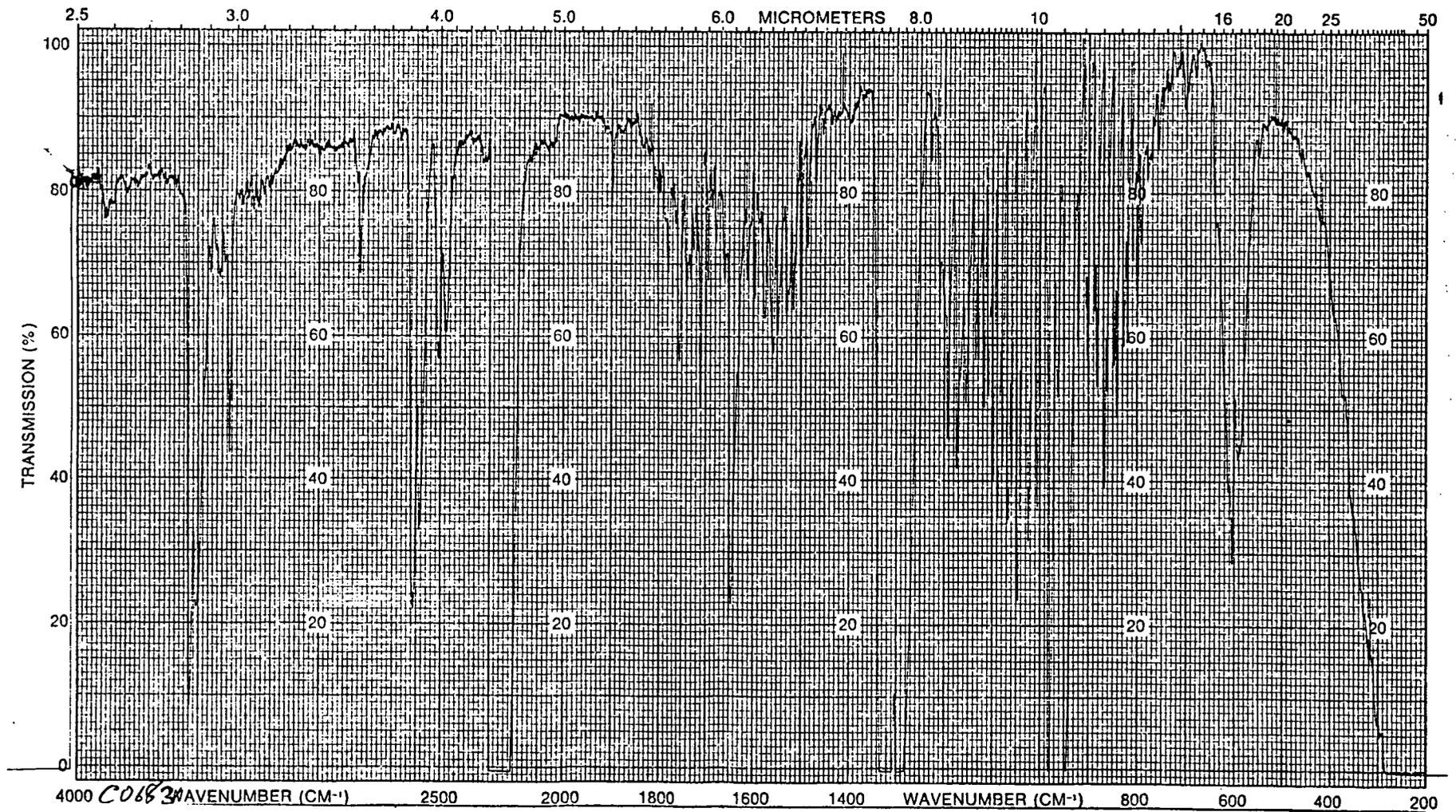


Figure 14. IR spectrum of gaseous reaction products generated in the MEA + RDX reaction, Test No. 4-10-05-98. Gas sample pressure, 740 mm of Hg.

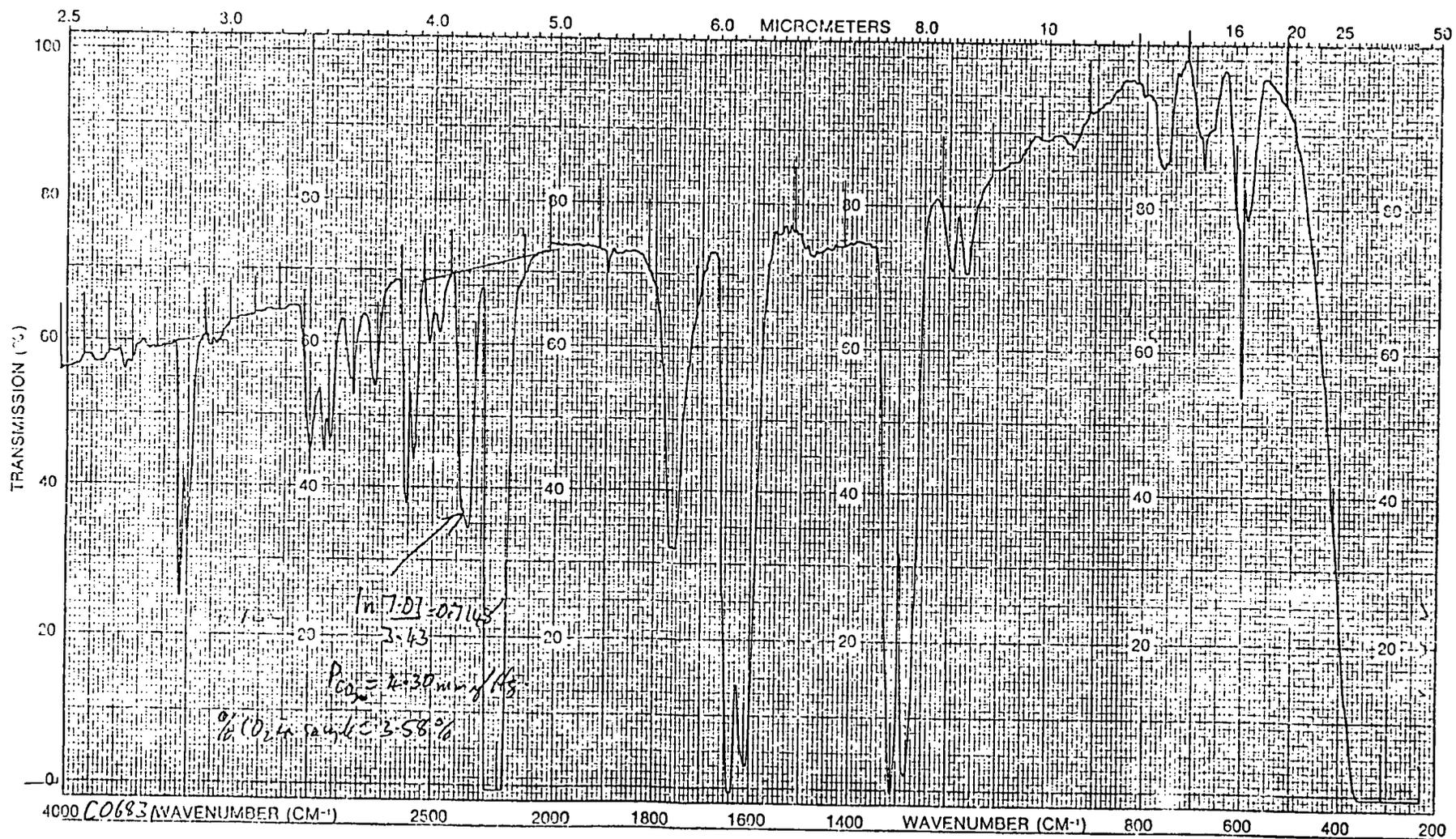


Figure 15. IR spectrum of gaseous reaction products generated in the TBA + RDX reaction, Test No. 27-12-18-98. Gas sample pressure, 120 mm of Hg.

Table 3. Summary of Analytical Data and Calculated Percentage Mass Balances for the Reaction of MEA with TNT, RDX and TNT + RDX.

Test Number	Initial Reactant Masses ¹			Initial Reactant Moles ¹			Mass of Liquid Reaction Product	Max. Reaction Temperature	Mass ² Balance
	MEA (g)	TNT (g)	RDX (g)	MEA	TNT	RDX	g	°C	%
1-08-26-98	100.31	10.00	--	1.6423	0.0440	--	109.26	101	99.47
2-10-02-98	100.4	15.01	--	1.6379	0.0661	--	113.19	129	98.90
3-10-03-98	99.92	15.06	--	1.6359	0.0663	--	111.39	139	98.10
4-10-05-98	100.66	--	10.07	1.6480	--	0.0453	106.16	86	99.59
5-10-06-98	101.32	--	15.45	1.6588	--	0.0696	109.60	100	97.85
6-10-19-98	100.11	--	20.62	1.6390	--	0.0928	111.00	131	99.69
7-10-20-98 ³	100.06	20.14	--	1.6382	0.0887	--	--	--	--
8-10-20-98	100.00	17.53	--	1.6372	0.0772	--	115.18	150	99.43
9-10-21-98	100.02	--	25.04	1.6375	--	0.1127	112.06	142	98.71
10-10-22-98	100.03	8.00	8.36	1.6377	0.0352	0.0376	112.80	118	99.56
11-10-23-98	100.19	--	15.05	1.6403	--	0.0678	108.58	90	99.65
12-10-24-98	100.26	8.05	8.14	1.6415	0.0354	0.0367	112.31	120	99.49
13-10-24-98	100.39	--	20.10	1.6436	--	0.0905	110.76	126	99.61

(1) Not corrected for reagent purity.

$$(2) \% \text{ Mass Balance} = \left[\frac{\text{Mass of Liquid + Gaseous Reaction Products Formed(g)}}{\text{Mass of Reactants Consumed(g)}} \right] \times 100$$

(3) Reaction too vigorous, no data obtained.

Table 3. Summary of Analytical Data and Calculated Percentage Mass Balances for the Reaction of MEA with TNT, RDX and TNT + RDX (continued).

Test Number	Composition Of Gaseous Reaction Products						Moles Of MEA Consumed Or NH ₃ And N ₂ O Formed, Per Mole Of TNT Or RDX In Reaction ¹		
	MEA		NH ₃		N ₂ O		MEA	NH ₃	N ₂ O
	g	moles	g	moles	g	moles			
1-08-26-98	70.68	1.1572	0.4700	0.0276	trace	trace	11.0165	0.6268	--
2-10-02-98	71.95	1.1780	0.5892	0.0346	trace	trace	6.9579	0.5235	--
3-10-03-98	72.14	1.1811	1.4084	0.0827	trace	trace	6.8579	1.2471	--
4-10-05-98	83.84	1.3726	0.4700	0.0276	3.6405	0.0827	6.0733	0.6087	1.8240
5-10-06-98	81.95	1.3417	0.4990	0.0293	4.1643	0.0946	4.5584	0.4212	1.3599
6-10-19-98	68.66	1.1242	1.5514	0.0911	7.8091	0.1774	5.5454	0.9812	1.9108
7-10-20-98 ²	--	--	--	--	--	--	--	--	--
8-10-20-98	63.76	1.0438	1.6826	0.0988	trace	trace	7.6874	1.2799	--
9-10-21-98	76.09	1.2458	1.6570	0.0973	9.7284	0.2210	3.4743	0.8630	1.9602
10-10-22-98	73.72	1.2069	0.4632	0.0272	2.6192	0.0595	5.9176	0.3733	1.5807
11-10-23-98	66.56	1.0897	0.7902	0.0464	5.4629	0.1241	8.1261	0.6847	1.8314
12-10-24-98	70.51	1.1544	0.8787	0.0516	2.6632	0.0605	6.7559	0.7157	1.6507
13-10-24-98	66.27	1.0850	1.3369	0.0785	7.9236	0.1800	6.1726	0.8674	1.9890

(1) In reactions containing both TNT and RDX: 1) the MEA consumed and NH₃ formed per mole of explosive in the reaction was determined relative to the sum of the moles of TNT and RDX present in the reaction, and 2) the N₂O formed per mole of explosive in reaction was based on the moles of RDX only in the reaction mixture since the TNT + MEA reaction did not produce significant amount of N₂O.

(2) This reaction was too vigorous and reactor liquor was transferred into the gas collection bag negating gas analyses and mass balance determinations.

Table 4. Summary of Analytical Data and Calculated Percentage Mass Balances for the Reaction of DETA with TNT, RDX and TNT + RDX.

Test Number	Initial Reactant Masses ¹			Initial Reactant Moles ¹			Mass of Liquid Reaction Product	Max. Reaction Temperature	Mass ² Balance
	DETA (g)	TNT (g)	RDX (g)	DETA	TNT	RDX	g	°C	%
15-10-28-98	100.68	10.08	--	0.9759	0.0444	--	108.93	156	99.49
16-10-29-98	100.38	20.01	--	0.9730	0.0881	--	115.18	157	97.94
17-10-30-98	100.18	--	10.01	0.9710	--	0.0451	105.55	141	97.08
18-10-31-98	100.88	--	10.30	0.9778	--	0.0464	106.56	> 101	99.50
19-10-31-98 ³	99.94	--	20.21	0.9687	--	0.0910	--	> 67	--
20-10-31-98	101.56	--	15.92	0.9844	--	0.0717	110.31	117	99.68
21-10-31-98	100.94	8.24	8.06	0.9784	0.0363	0.0363	113.17	126	99.94

(1) Not corrected for reagent purity.

(2) % Mass Balance =
$$\left[\frac{\text{Mass of Liquid + Gaseous Reaction Products Formed(g)}}{\text{Mass of Reactants Consumed(g)}} \right] \times 100$$

(3) Reaction too vigorous, data not obtained.

Table 4. Summary of Analytical Data and Calculated Percentage Mass Balances for the Reaction of DETA with TNT, RDX and TNT + RDX (continued).

Test Number	Composition Of Gaseous Reaction Products						Moles Of DETA Consumed Or NH ₃ And N ₂ O Formed Per Mole Of TNT Or RDX In Reaction ¹		
	DETA		NH ₃		N ₂ O		DETA	NH ₃	N ₂ O
	g	moles	g	moles	g	moles			
15-10-28-98	60.22	0.5837	1.2704	0.0746	trace	trace	8.8355	1.6807	--
16-10-29-98	43.93	0.4258	2.7333	0.1605	trace	trace	6.2101	1.8216	--
17-10-30-98	77.63	0.7525	0.2623	0.0154	1.1577	0.0263	4.8491	0.3417	0.5835
18-10-31-98	72.84	0.7061	0.6795	0.0399	3.3895	0.0770	5.8598	0.8604	1.6604
19-10-31-98 ²	--	--	--	--	--	--	--	--	--
20-10-31-98	64.87	0.6287	1.2483	0.0733	5.5465	0.1260	4.9618	1.0226	1.7578
21-10-31-98	63.78	0.6182	1.2040	0.0707	2.7997	0.0636	4.9625	0.9742	1.7526

(1) In reactions containing both TNT and RDX: 1) the DETA consumed and NH₃ formed per mole of explosive in the reaction was determined relative to the sum of the moles of TNT and RDX present in the reaction, and 2) the N₂O formed per mole of explosive in reaction was based on the moles of RDX only in the reaction mixture since the TNT + MEA reaction did not produce significant amounts of N₂O.

(2) Reaction too vigorous, data not obtained.

Table 5. Summary of Analytical Data and Calculated Percentage Mass Balances for the Reaction of TBA with TNT and RDX.

Test Number	Initial Reactant Masses ¹			Initial Reactant Moles ¹			Mass of Liquid/Solid Reaction Product	Max. Reaction Temperature	Mass Balance
	TBA (g)	TNT (g)	RDX (g)	TBA	TNT	RDX	g	°C	%
22-11-10-98	100.01	10.02	--	0.5396	0.04412	--	108.74	152.2	98.83
23-11-13-98	101.02	--	9.77	0.5450	--	0.04399	107.22	152.5	96.78
24-11-16-98	100.20	--	9.78	0.5406	--	0.04403	104.80	163.0	95.29
26-12-17-98	100.00	10.00	--	0.5395	0.04403	--	108.00	160.0	98.68
27-12-17-98	100.50	--	15.00	0.5422	--	0.06754	110.13	166.3	98.52

(1) Not corrected for reagent purity.

Table 5. Summary of Analytical Data and Calculated Percentage Mass Balances for the Reaction of TBA with TNT and RDX (continued).

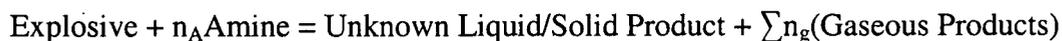
Test	Composition Of Gaseous Reaction Products								Moles Of TBA Consumed Or N ₂ O, NO ₂ And CO ₂ Formed Per Mole Of TNT Or RDX In Reaction			
	TBA		N ₂ O		NO ₂		CO ₂		TBA	N ₂ O	NO ₂	CO ₂
Number	g	moles	g	moles	g	moles	g	moles				
22-11-10-98 ¹	100.70	0.5433	--	--	--	--	--	--	-0.0846	--	--	--
23-11-13-98 ¹	97.77	0.5275	--	--	--	--	--	--	+0.3981	--	--	--
24-11-16-98 ¹	94.70	0.5109	--	--	--	--	--	--	+0.6740	--	--	--
26-12-17-98	103.63	0.5591	0.0132	0.0003	0.3588	0.0078	0.1760	0.0040	-0.4444	0.00681	0.17714	0.09084
27-12-17-98	101.65	0.5484	2.9669	0.0674	0.4508	0.0098	0.2421	0.0055	-0.0915	0.99797	0.14511	0.08144

(1) Analytical data on gaseous products formed not obtained.

The small amounts of the gases detected indicate they are not significant species generated by the explosive-MEA reaction. It is more likely they represent contamination of the experimental set-up with air, incompletely removed by the helium purging.

The reported mass balances, together with the above observations, strongly suggest that the only significant gaseous species generated in the amine-explosive reactions studied have been identified i.e., NH₃, N₂O, NO₂ and CO₂.

From data presented in Tables 3 through 5, approximate stoichiometries for the amine-explosive reactions were derived for the reactions written in the form:



where n_A is the number of moles of amine consumed by 1 mole of explosive to produce n_g moles of gaseous products. The resulting equations are shown in Table 7.

Table 7. Approximate stoichiometries of explosive-amine reactions studied.

No. of Expts.	REACTION	CALCULATED MOLES					
4 ⁽¹⁾	TNT + MEA	1	8.1±2.0 ⁽²⁾	Liquid Product	+ NH ₃	+ N ₂ O	
				-----	0.9±0.4	(trace)	
6	RDX + MEA	1	5.7±1.6	Liquid Product	+ NH ₃	+ N ₂ O	
				-----	0.7±0.2	1.8±0.2	
2	TNT + RDX + MEA	0.5	0.5	5.9±0.5	Liquid Product	+ NH ₃	+ N ₂ O
					-----	1.0±0.2	0.8±0.0
2	TNT + DETA	1	7.5±1.9	Liquid Product	+ NH ₃	+ N ₂ O	
				-----	1.8±0.1	(trace)	
3	RDX + DETA	1	5.2±0.6	Liquid Product	+ NH ₃	+ N ₂ O	
				-----	0.7±0.4	1.3±0.6	
1	TNT + RDX + DETA	0.5	0.5	5.0	Liquid Product	+ NH ₃	+ N ₂ O
					-----	1.94	0.9
2 ⁽³⁾	TNT + TBA	1	-0.3±0.3	Liquid Product ⁽⁴⁾	+ N ₂ O	+ NO ₂	+ CO ₂
				-----	0.007	0.18	0.09
3 ⁽³⁾	RDX + TBA	1	0.4±0.3	Liquid Product ⁽⁵⁾	+ N ₂ O	+ NO ₂	+ CO ₂
				-----	1.0	0.14	0.08

(1) Number of experiments used in generating data.
(2) Mean ± standard deviation.
(3) Number of experiments used to generate data for number of moles of TBA used per mole of TNT or RDX reacted. The data for moles of gaseous product formed are from single experiments.
(4) This liquid sample contained a solid pitch-like material. The liquid phase constituted ≈ 73 weight % of the reaction product.
(5) This liquid sample contained two immiscible liquid phases in the mass ratio ≈ 11:1.

The stoichiometries in the MEA and DETA explosive reactions show a number of similarities leading to the following conclusions:

- a) Within the precision of the data the amounts of MEA and DETA consumed in reactions with the TNT and RDX are essentially identical.
- b) Based on the amounts of MEA or DETA consumed and gaseous products formed, reaction mixtures containing TNT + RDX appear to react with the amine independently of the presence of each other in the mixture.
- c) Within the precision of the data the amounts of NH_3 and N_2O formed in the RDX + MEA and RDX + DETA reaction are identical.
- d) Within the precision of the experimental data, approximately twice as much NH_3 is formed in the DETA + TNT reaction as in the MEA + TNT reaction.

The reactions of TBA with TNT or RDX are clearly different from the analogous reactions of the explosives with MEA and DETA:

- a) With TBA, the gaseous reaction products are N_2O , NO_2 and CO_2 rather than N_2O and NH_3 with MEA and DETA.
- b) With TBA, the amount of amine consumed per mole of TNT or RDX is close to zero, whereas with MEA or DETA 5 to 8 moles of the amine are consumed.

1.3.4 Analyses Of Representative Explosive-Amine Reaction Product Matrices For Residual Explosive By HPLC.

In deriving the stoichiometries for the explosive-amine reactions above, it was tacitly assumed that the explosives were completely consumed in the reaction. The assumption was arrived at based on analyses of the following representative reaction product matrices for their TNT or RDX contents.

Test #: 1-08-26-98	MEA (100.31g) + TNT (10.00g)
Test #: 2-10-02-98	MEA (100.04g) + TNT (15.01g)
Test #: 3-10-03-98	MEA (99.92g) + TNT (15.06g)
Test #: 4-10-05-98	MEA (100.66g) + RDX (10.07g)
Test #: 5-10-06-98	MEA (101.32g) + RDX (15.45g)
Test #: 16-10-29-98	DETA (100.38g) + TNT (20.01g)
Test #: 17-10-31-98	DETA (100.18g) + RDX (10.01g)
Test #: 26-12-17-98	TBA (100.00g) + TNT (10.00g)
Test #: 27-12-18-98	TBA (100.50g) + RDX (15.00g)

Typical chromatograms obtained for MEA and TNT and MEA and RDX matrices are shown in Figure 17 and 18. A summary of the experimental data for these matrices (Tests #1 through #5) is presented in Table 8. TNT and RDX recovery data were not obtained when these analyses were made. During subsequent analyses of DETA and TBA matrices, some explosive recovery data were obtained suggesting values in the 10-15% range maybe assumed for the MEA matrices. For the matrices shown in Table 8, residual TNT and RDX concentrations, assuming the 10-15% recovery are estimated at less than 5 ppm and may be < 1 ppm.

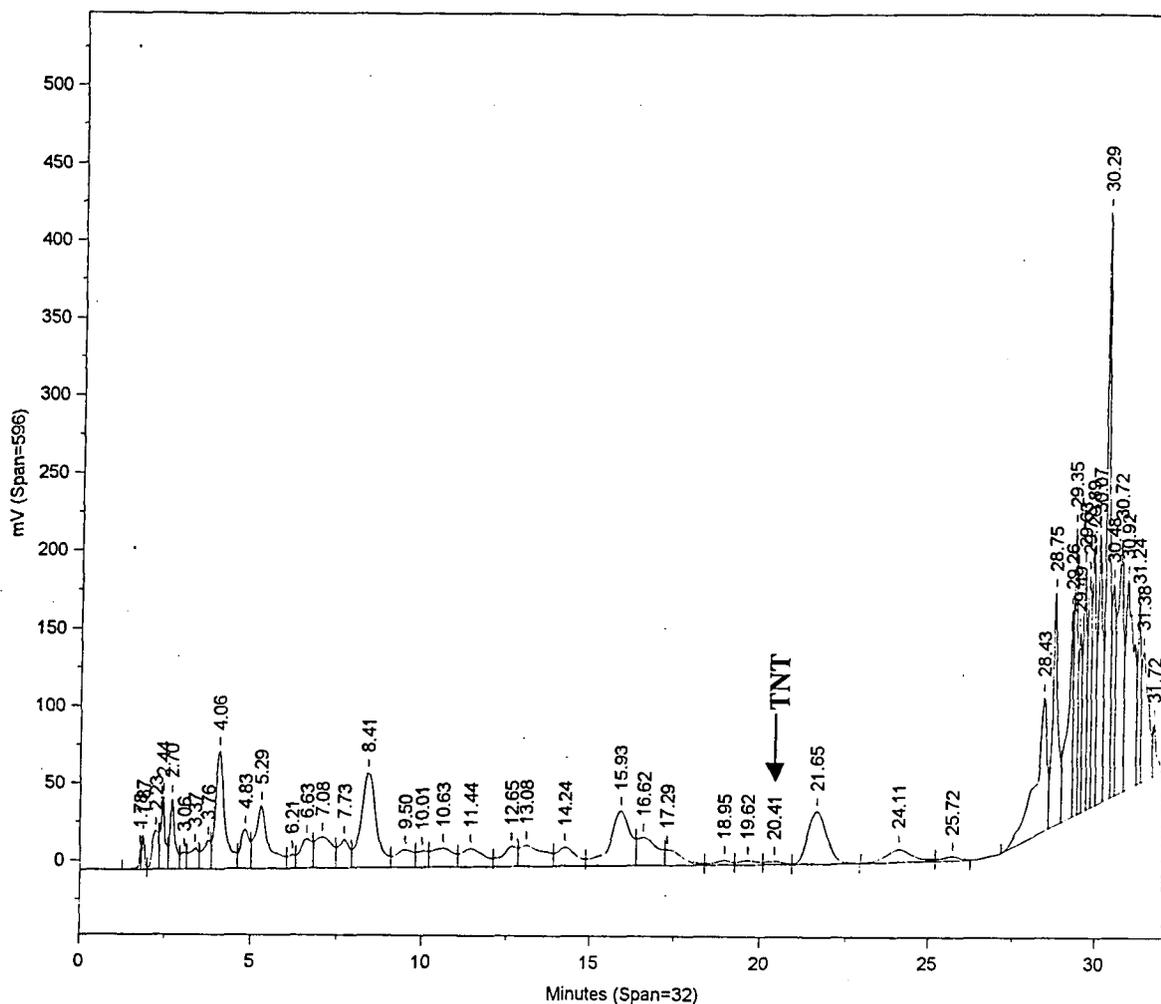
Similar analyses were performed on DETA and TBA liquid matrices to determine their residual TNT and RDX contents. Although these data have not been completely reduced, preliminary results strongly suggest low residual TNT and RDX levels for these matrices. In the TNT + TBA reaction, the condensed phase matrix consisted of liquid, = 73 weight % and a pitch-like solid = 27 weight %. The condensed phase in the RDX + TBA reaction consisted of two immiscible liquids, present at a mass ratio of = 11:1. The explosive contents of the pitch-like solid (TNT + TBA) and the minor liquid phase (RDX + TBA) were not determined by HPLC. Qualitative analyses of these samples by IR spectroscopy indicate that small amounts of residual explosive may be present.

1.3.5 Time-Temperature Profiles In The Explosive-Amine Reactions.

When performing the explosive-amine reactions, time-temperature profiles of the tests were obtained. Typical curves obtained for TNT + MEA and RDX + MEA reactions are shown in Figures 19 and 20. In both reactions, on addition of the explosive, there were small temperature rises in the reaction mix (exotherm), the magnitude of the temperature rise increasing as the mass of explosive added increased. For the amounts of explosive and MEA used in these tests, the initial temperature rise was < 10°C. Unless external heat was applied, the reaction matrix cooled to ambient temperature. For this reason, external heat was applied to the reaction. Time-temperature profiles shown in Figures 19 and 20 indicate both the TNT and RDX/MEA reaction rates accelerate markedly in the 40-50°C temperature range, resulting in a significant temperature increase in the reaction mixture.

Time-temperature profiles for TNT and RDX reactions with DETA were similar to those observed with MEA, indicating a moderately exothermic reaction. The accelerating phase of the reaction with DETA systems occurred in the 30-40°C temperature range, some 10°C lower than for the analogous MEA reactions.

Time-temperature profiles observed in TNT and RDX reactions with TBA are shown in Figures 21 and 22. In contrast to the analogous reactions with MEA and DETA, no exotherms were observed on the initial addition of either TNT or RDX to TBA at ambient temperatures. On heating the reaction mixtures, weak exotherms with both TNT and RDX did not occur until the temperature of the matrix was in the 120-140°C range, some = 100°C higher than that observed for the MEA and DETA reactions.



Sample Name: **Test 2-1 unspiked 10-7-98 (5ml)**
 Acquired from Chrom3--Det3A via port 3 on 10/9/98 12:31:02pm by K BORCK
 UV254
 MEOH:H2O 25:75 FOR 20MIN THEN TO 100 MEOH AT 26 MIN HOLD 6

Data File: **C:\CPWINDATA1\DECT3\100998.04R**
 Date Stamp: 10/9/98 12:31:00pm
 Method File: **C:\CPWINDATA1\HPEXP-A.MET**
 Version 3. Date Stamp: 9/22/98 09:28:12am
 Calibration File: **C:\CPWINDATA1\DECT3\EXP-1.CAL**
 Version 10. Date Stamp: 10/9/98 10:24:16am

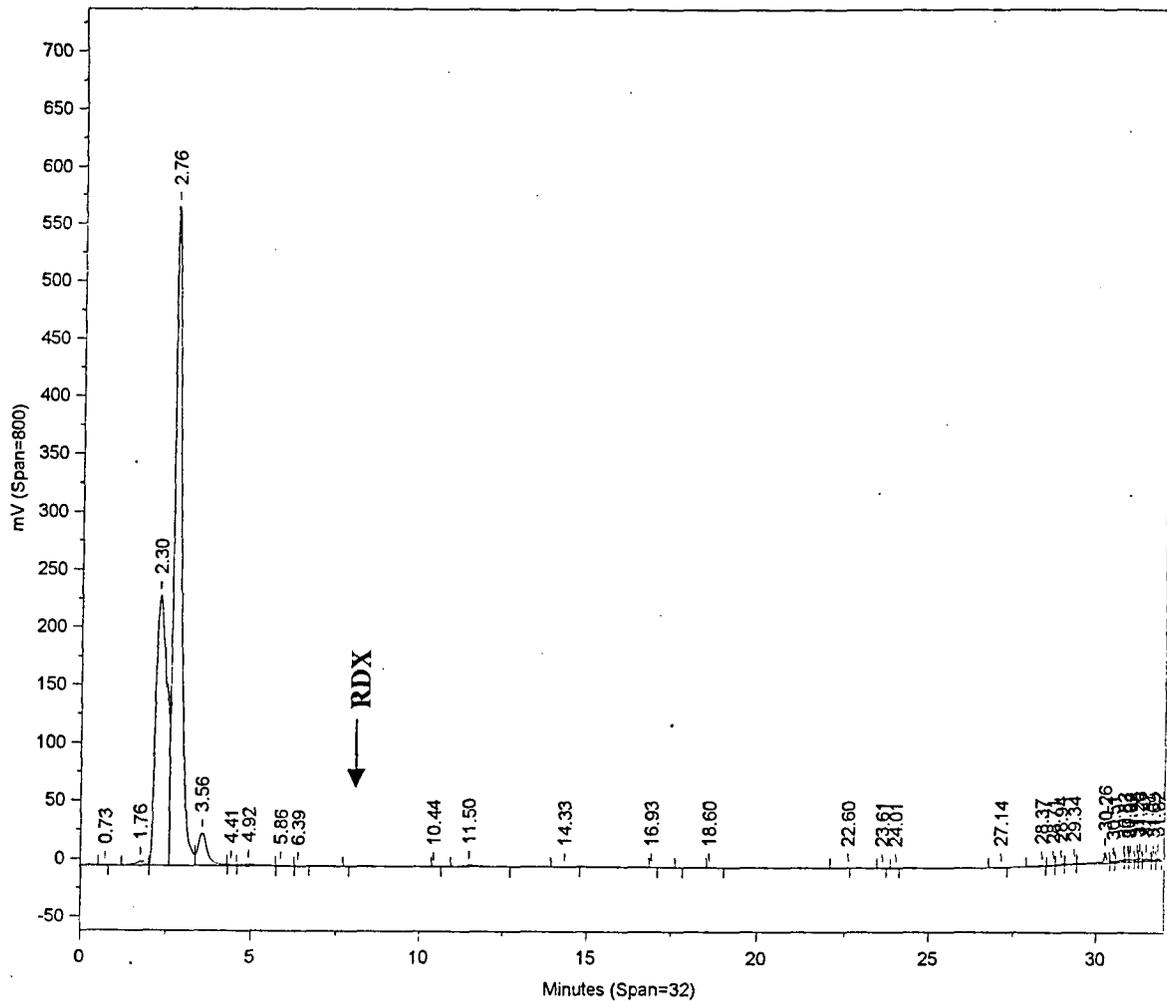
Run Time = 32.0 min Sample Rate = 1.0 per sec.
 Amount Inj. = 100.000 Dilution Factor = 1.000
 Sample Weight = 1.000 Int Std Amount = 1.000

Starting Peak Width = 0.04 min. Peak Threshold = 0 Area Reject = 100

C:\CPWINDATA1\DECT3\100998.04R

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Figure 17. Test No. 2-10-02-98, HPLC chromatogram of a MEA + TNT reaction product extract used in determination of the residual TNT content of the matrix.



Sample Name: **Test 4-1 unspiked 10-7-98 (5ml)**
 Acquired from Chrom3--Det3A via port 3 on 10/12/98 12:04:13pm by K BORCK
 UV254
 MEOH:H2O 25:75 FOR 20MIN THEN TO 100 MEOH AT 26 MIN HOLD 6

Data File: **C:\CPWINDATA\DECT3\101298.02R**
 Date Stamp: 10/12/98 12:04:10pm
 Method File: **C:\CPWINDATA\HPEXP-A.MET**
 Version 3. Date Stamp: 9/22/98 09:28:12am
 Calibration File: **C:\CPWINDATA\DECT3\EXP-1.CAL**
 Version 11. Date Stamp: 10/12/98 11:28:10am

Run Time = 32.0 min Sample Rate = 1.0 per sec.
 Amount Inj. = 100.000 Dilution Factor = 1.000
 Sample Weight = 1.000 Int Std Amount = 1.000

Starting Peak Width = 0.04 min. Peak Threshold = 0 Area Reject = 100

C:\CPWINDATA\DECT3\101298.02R

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Figure 18. Test No. 4-10-05-98, HPLC chromatogram of a RDX + MEA reaction product extract used in determination of the residual RDX content of the matrix.

Table 8. Summary of HPLC data for determination of residual TNT and RDX contents in MEA + TNT and MEA + RDX matrices.

File ID No.	Sample Name	TNT Retention Time (min.)	Calc. Matrix Conc. ($\mu\text{g/mL}$)
100998.01	1 ppm Std Mix A + Tetryl ⁽¹⁾	20.42	(1.0591) ⁽¹⁾
100998.02	Test 1-08-26-98-1 ⁽²⁾	20.43	0.0913
100998.03	Test 1-08-26-98-2 ⁽²⁾	20.11	0.1663
100998.04	Test 2-10-02-98-1 ⁽²⁾	20.41	0.2173
100998.05	Test 2-10-02-98-2 ⁽²⁾	19.50	0.7461 ⁽³⁾
100998.06	1 ppm Std Mix A + Tetryl ⁽¹⁾	19.87	(1.0275) ⁽¹⁾
100998.08	Test 3-10-03-98-1 ⁽²⁾	19.79	0.1000
100998.09	Test 3-10-03-98-1 ⁽²⁾	19.67	0.0899
100998.10	5 ppm Std Mix A + Tetryl ⁽¹⁾	19.71	(5.2197) ⁽¹⁾
		RDX Retention Time (min.)	
101298.01	1 ppm Std. Mix A + Tetryl ⁽¹⁾	7.92	(1.0228) ⁽¹⁾
101298.02	Test 4-10-05-98-1 ⁽²⁾	--	ND
101298.03	Test 4-10-05-98-2 ⁽²⁾	--	ND
101298.05	Test 5-10-06-98-1 ⁽²⁾	--	ND
101298.06	Test 5-10-06-98-2 ⁽²⁾	7.69	0.001
101298.07	5 ppm Std. Mix A + Tetryl ⁽¹⁾	7.58	(5.0997) ⁽¹⁾
<p>(1) Injection used to verify instrument calibration. (2) Separate extractions of the same matrix. (3) Probably not TNT based on low retention time.</p>			

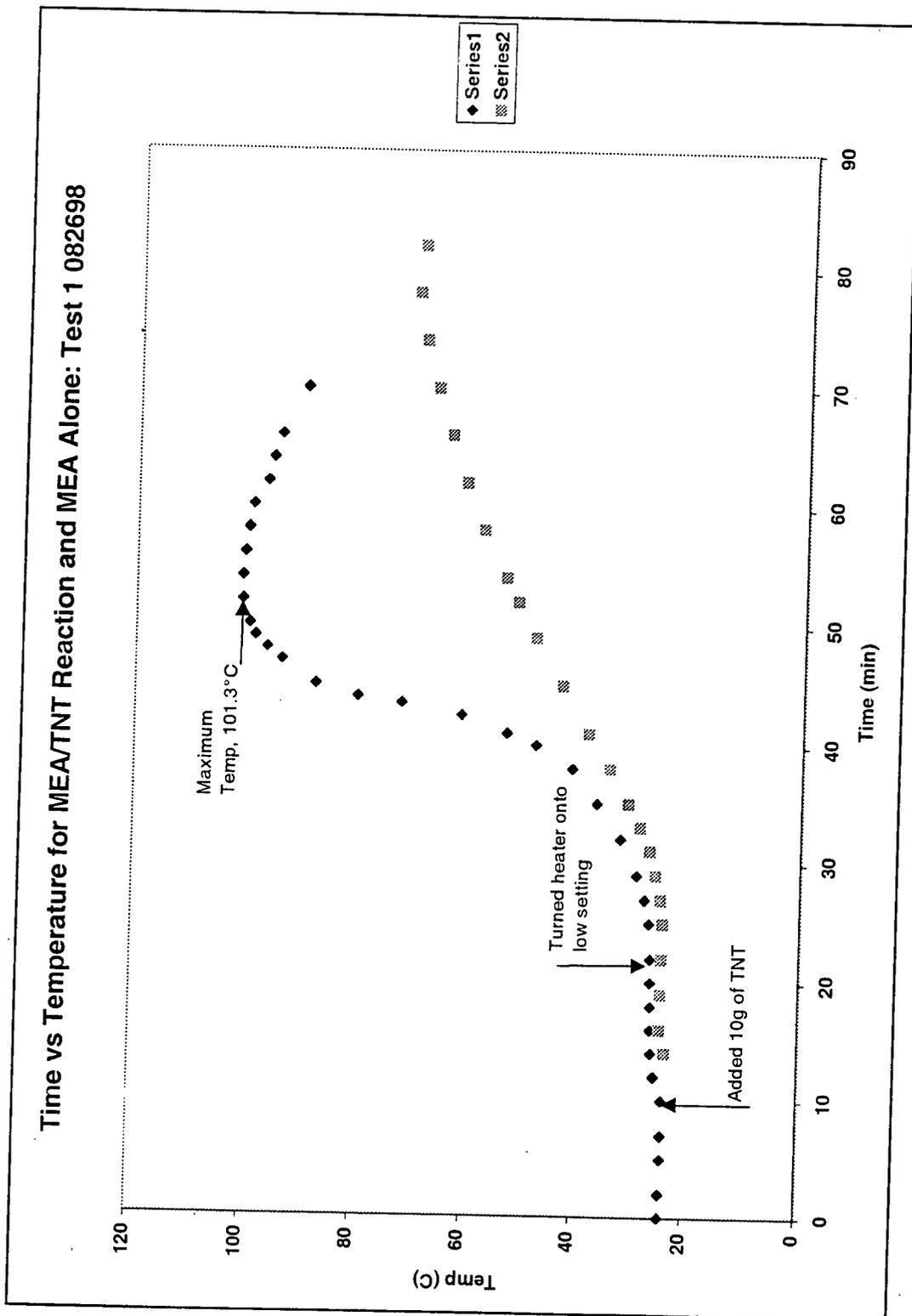


Figure 19. Test No. 1-08-26-98. Time versus temperature profiles generated for an MEA(100.31g) + TNT(10.00g) reaction matrix (black diamonds) and for a heated blank MEA(100g) reference matrix (grey squares).

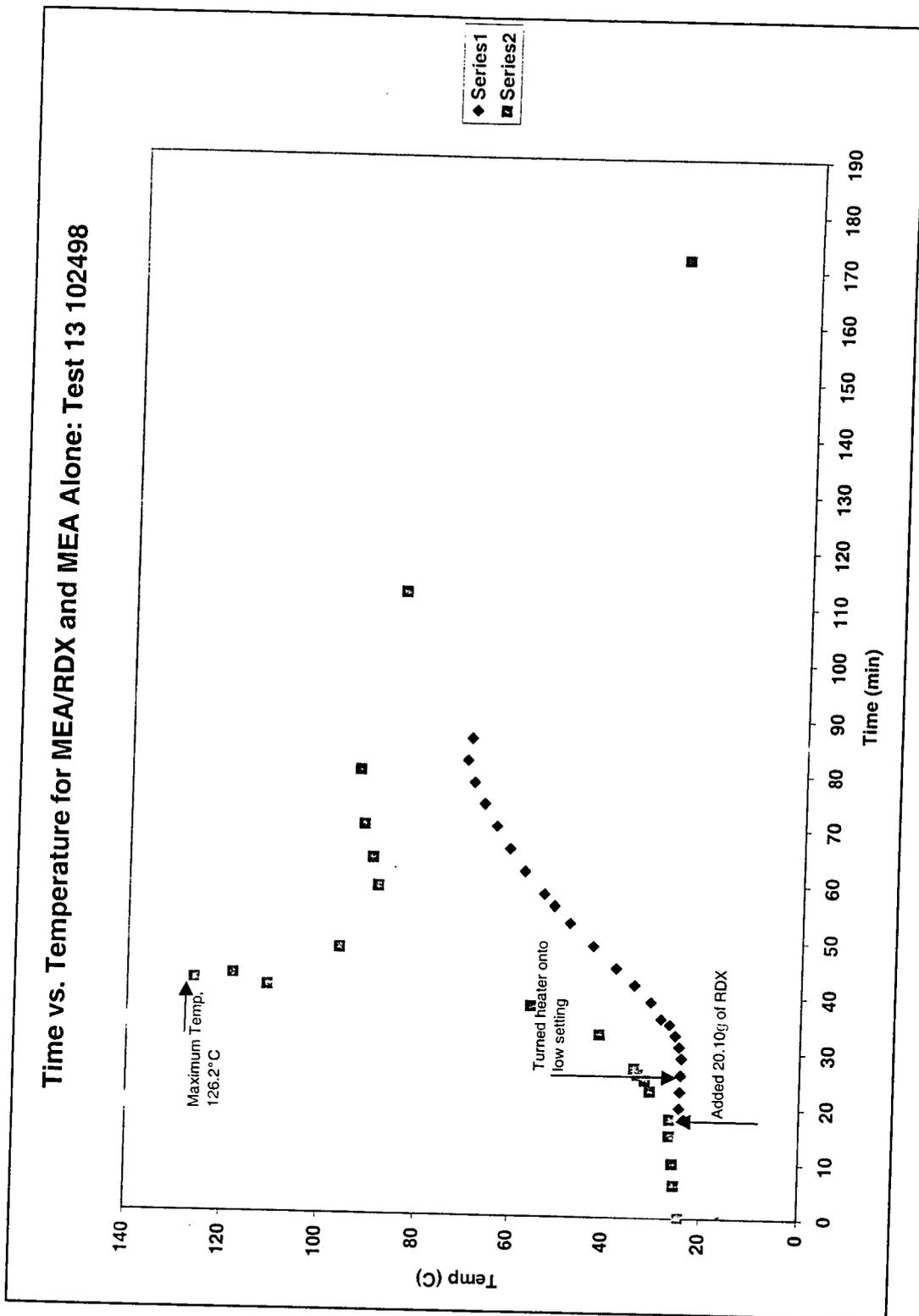


Figure 20. Test No. 13-10-26-98. Time versus temperature profiles generated for an MEA(100.39g) + RDX(20.10g) reaction matrix (grey squares) and for a heated blank MEA(100g) reference matrix (black diamonds).

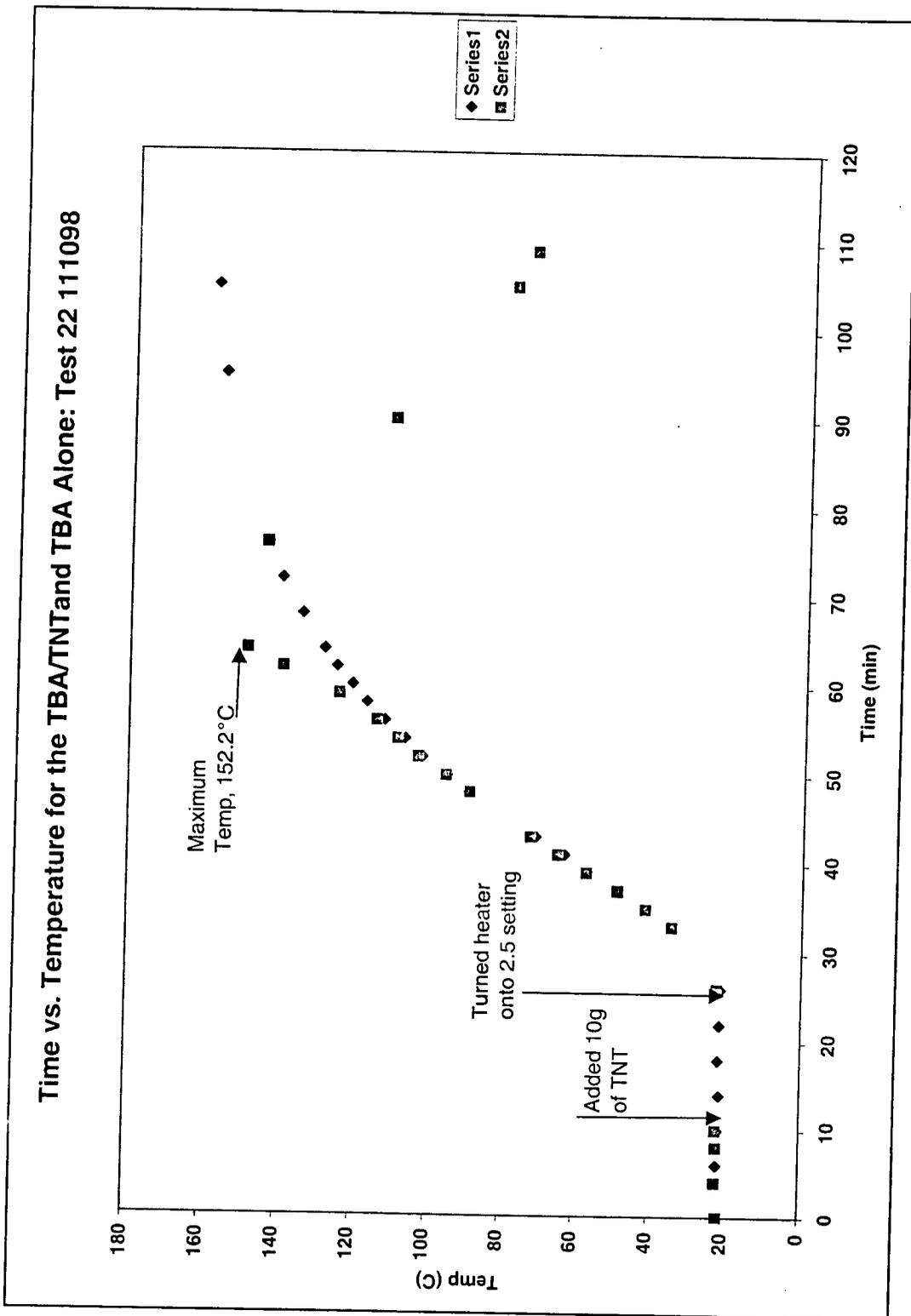


Figure 21. Test No. 22-11-10-98. Time versus temperature profiles generated for a TBA(100.00g) + TNT(10.00g) reaction matrix (grey squares) and for a heated TBA(100g) blank reference matrix (black diamonds).

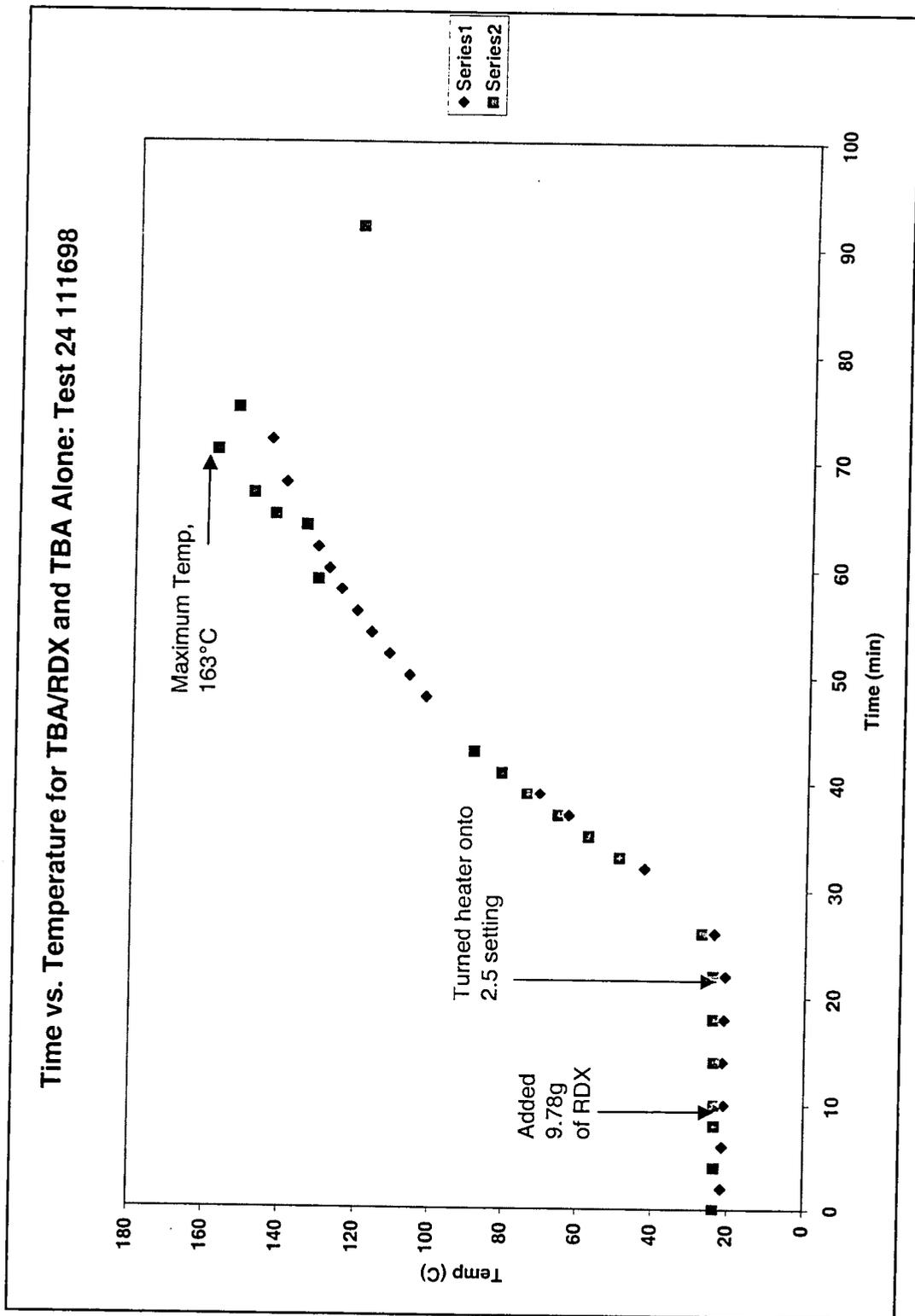


Figure 22. Test No. 23-11-11-98. Time versus temperature profiles generated for a TBA(100.50g) + RDX(15.00g) reaction matrix (grey squares) and for a TBA(100g) blank reference matrix (black diamonds).

1.3.6 General Observations On The Explosive-Amine Reactions.

- 1) Addition of TNT to stirred MEA and DETA in the 500-mL reaction flask at ambient temperature resulted in the immediate appearance of an intense purple red coloration in the liquid phase. Due to the intense color of the solution it was not possible to determine if the bulk of the TNT dissolved at the TNT:MEA or DETA ratios used in the study (Tables 3 and 4) prior to heating. On sonicating TNT:MEA (1 g:10 mL) and TNT:DETA (1g:10 mL) mixtures in a 25 mL vial for \approx 30 minutes at a temperature of \approx 30°C, all the TNT dissolved. This observation suggests that the bulk of the TNT was probably in solution in the early phase of the reaction when heat was applied to the reactor.
- 2) Addition of TNT to stirred TBA at ambient temperature resulted in the solution taking on a light brown color with the bulk of the solid remaining intact.
- 3) Addition of RDX to stirred MEA, DETA or TBA at ambient temperature did not cause any immediate color change in the liquid. On sonicating RDX:amine (1 g:10 mL) mixtures for \approx 30 minutes at \approx 30°C, the bulk of the RDX did not dissolve. These samples were left standing without sonification overnight, again the bulk of the solid RDX remained intact. These observations suggest that the RDX-amine reactions performed in the study were probably heterogeneous.
- 4) The reaction product matrices generated using TNT with MEA or DETA (Tables 3 and 4) were dark black-brown colored solutions, that were somewhat more viscous than the original amines used in their preparation. The solutions did not appear to contain undissolved solid material. The matrices appeared to be completely miscible with water, and after much dilution formed a transparent pale brown solution, in which no suspended solids were observed to be present.
- 5) Reaction product matrices generated in using RDX with MEA or DETA (Tables 3 and 4) were clear to pale-yellow-brown colored solutions, not noticeably more viscous than the starting amines. The matrices were completely miscible with water.
- 6) TNT + TBA reaction product matrices, (Table 5) were medium brown-red in color. There was, in addition in the flask, a dark black-brown solid which adhered to the flask walls. The liquid phase did not appear to contain any finely divided solid matter. The liquid matrix viscosity was not noticeably different than that of the neat amine. The liquid matrix was only slightly soluble in water. The dark solid was only partially water soluble, but was completely soluble in acetone.
- 7) The reaction product matrix from the TBA + RDX reaction contained two immiscible liquid phases; the major fraction with a light red-brown color and a minor fraction with a dark black-brown color. The major liquid fraction was largely non-water soluble. The minor liquid fraction appeared to be completely soluble in a water/acetone mixture.

1.3.7 Reaction Of TNT With MEA Using A Nominal Reaction Stoichiometry Of TNT + 7MEA → Products (Test #25-11-25-98)

The explosive-amine reactions run thus far were all made with a large excess of amine relative to explosive. In the MEA reaction system, TNT:MEA and RDX:MEA mole ratios ranged from 18-37:1 with the object of preventing uncontrollable exotherms occurring in the reaction mixture. The purpose of this test was to determine how well the TNT + MEA reaction occurred when run at the approximate stoichiometry indicated in Table 7, i.e., TNT + 7MEA → Products.

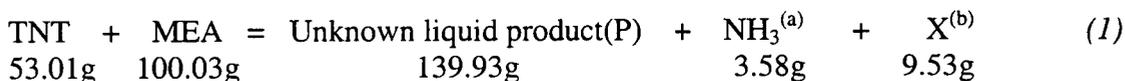
The reaction was run in the equipment shown in Figure 2 using the following amounts of reactants, TNT (53.01g) and MEA (100.01g). To control the reaction temperature, the TNT was added in 1-5 gram increments. A maximum temperature of 133°C was recorded during the reaction. At the end of the reaction, after allowing the flask to cool to ambient temperature, the weight of product in the flask was determined at 139.83g. The reaction product, an intense black color, was observed to be extremely viscous at ambient temperature. A small quantity, 7.08g was removed from the flask for testing. No attempt was made collect all the gas generated from the reaction, since incremental addition of the TNT required opening the reactor flask to the atmosphere. A small sample of gas from the reaction was obtained, analyzed by IR and shown to contain NH₃ together with a trace of N₂O. A similar composition was found in the MEA + TNT reactions run at MEA:TNT mole ratios of ≈ 18-37:1

After performing the above reaction, the reactor system was modified to permit distillation of volatile material from the reaction mixture under a reduced pressure of ≈ 0.3 atmosphere. In a two-stage distillation, the first at atmospheric pressure and the second at reduced pressure, the reaction flask containing the matrix lost 22.23 g and 6.10 g, respectively of volatile material. Samples of the volatiles were condensed in an ice-cooled receiver. Their water content was analyzed by TEI Analytical, Niles, Illinois at 90.0 wt% (larger sample) and 98.3 wt% (smaller sample). After distillation, the final weight of product from the initial reaction was determined at 104.52 g. This material had a pitch-like consistency at ambient temperature. A sample of the material was sent to Desert Analytics of Tucson, Arizona for an elemental, C, H, N and O analysis. Two samples were analyzed with the following results:

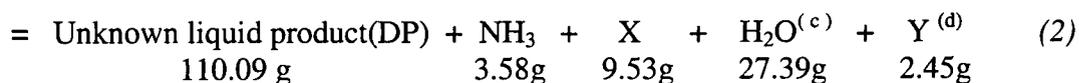
Wt%	%C	%H	%N	%O
	53.72	6.69	19.32	20.15
	53.97	6.62	19.30	20.65

A second sample of the pitch-like material was dissolved in water and analyzed by HPLC for its TNT content. A value estimated at < 5 ppm was determined. The experimental data for the TNT + 7MEA reaction followed by distillation are summarized in the following equations:

Initial Reaction:



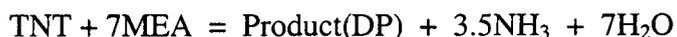
Final Reaction Product after distillation:



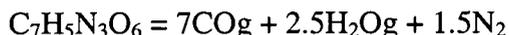
- a) Empirical estimate of ammonia generated in the reaction, based on data in Table 7, 1 mole of TNT = 0.9 moles of NH₃;
- b) Amount of unknown material required to maintain mass balance;
- c) Mass of water distilled off liquid product (P) and
- d) Mass of unknown liquid (not H₂O) distilled of liquid product (P).

Data for the overall elemental mass balances starting with the reactants in (1) and going to final reaction products in (2) are presented in Table 9. For carbon, the calculated percentage mass balance at 100.5% is satisfactory and strongly suggests that volatile carbon species are not produced in any significant amount in the reaction. For H, N and O, the mass balances found imply that volatile or semi-volatile specie(s) have not been accounted for. It is possible that the N(8.54g) and O(1.82g) deficits in the elemental mass balances are due largely to 1) the amount of NH₃ formed in the reaction being underestimated and 2) a small quantity of liquid water being experimentally not quantified. If these assumptions are correct, the N and O deficits, in terms of NH₃ and H₂O respectively, would require an additional 1.72g of hydrogen to be added to the elemental mass balance. This amount of hydrogen is consistent with the calculated hydrogen deficit at 1.69g (Table 9).

Based on the above assumption for the elemental N, O and H deficits, the stoichiometry for the TNT/MEA reaction may be written as:



The elemental stoichiometry of the combined initial reactants (MEA + TNT) and final product(DP) are calculated at C₂₁H₅₄N₁₀O₁₃ and C_{21.1}H_{31.1}N_{6.5}O_{6.0}, respectively. Relative to TNT as an explosive, the final reaction product from the MEA reaction is highly oxygen deficient. For simplicity, the high temperature detonation reaction of TNT may be assumed to produce the following products:



requiring 4.75 moles of oxygen for the reaction as written, equivalent to an oxygen deficiency of 36.8%. If the same products are assumed to be formed from the MEA/TNT reaction product (DP), the calculated oxygen deficiency is 83.6%. It is highly unlikely that this material will be an effective explosive.

Table 9. Reaction TNT(53.01g) + MEA(100.03g) = Products. Elemental Mass Balances.

Reactants ⁽¹⁾			Final Product(PD) ⁽²⁾ (Mass=110.09g)			H ₂ O ⁽³⁾ (27.39g)	NH ₃ ⁽⁴⁾ (3.58g)	∑ PE ⁽⁵⁾	Elemental Mass Balance ⁽⁶⁾	%Elemental Mass Balance ⁽⁷⁾
Elements	%	Mass (g)	Elements	% ± SD ⁽⁸⁾	Mass (g)	Mass (g)	Mass (g)	Mass (g)		
C	38.53	58.96	C	53.85 ± 0.18	59.28	--	--	59.28	-0.32	100.5
H	8.32	12.73	H	6.66 ± 0.05	7.33	3.07	0.64	11.04	1.69	86.72
N	21.40	32.74	N	19.31 ± 0.01	21.26	--	2.94	24.20	8.54	73.92
O	31.76	48.50	O	20.40 ± 0.35	22.46	24.32	--	46.78	1.82	96.26
∑ = 153.03g						∑ = 141.03g				

(1) Elemental composition of reactants (MEA & TNT) not corrected for purity.

(2) Reaction product after distillation of volatiles.

(3) Mass of water distilled off reaction product.

(4) Empirical estimate of ammonia generated in reaction.

(5) Sum of masses of indicated elements in PD, H₂O and NH₃ = ∑PE.

(6) Elemental mass balance calculated as: Mass of each element in reactants - ∑PE for each element.

(7) % Elemental Mass Balance = (∑PE for each element in product/mass of each element in reactant mixture) X 100.

(8) Elemental % composition for final product (PD) determined by Desert Analytics. SD = standard deviation of analysis.

1.3.8 Speciation of the Amine-Explosive Liquid/Solid Reaction Product Matrices.

Chemical speciation of the reaction product matrices was attempted in the following ways:

- a) Reaction product matrices were diluted in methanol and analyzed by GC/MSD. In some of these samples, a moderate number of peaks were present in the chromatograms, however none of these peaks represented major species that could reasonably be expected to be formed in the reactions.
- b) On the possibility that some of the major species formed in the amine-explosive reactions contained NH_2 , OH and COOH groupings in which hydrogen bonding may reduce volatility, the matrices were derivatized with BSTAF to form the more volatile trimethylsilyl derivatives. This did not produce any significant increase in the number of species appearing in the resulting GC/MSD chromatograms.
- c) IR spectroscopy was used to characterize some of the reaction product matrices, but failed to produce any definitive results.
- d) Preliminary attempts have been made to use NMR spectroscopy to analyze the matrices; the approach shows some promise and will be investigated further.

In summary, to date the speciation of the explosive-amine reaction product matrices have not proved successful.

SECTION 2

RESULTS TO DATE ON TASK 3

2.1 INTRODUCTION.

TNT is known to react with DETA¹. Under certain conditions, the reactions can lead to the spontaneous destruction of the TNT in a highly exothermic reaction, which may or may not result in the visible ignition of the TNT when the reaction is performed in air. The nature of this spontaneously induced decomposition of the TNT is poorly understood. There is evidence that after the initial TNT-DETA induced decomposition reaction is completed, the remaining neat TNT will spontaneously decompose in a reaction that does not produce large amounts of carbon typical of free burning solid TNT in air.

The purpose in this task is to determine if the chemical initiation of the TNT decomposition reaction produces different gaseous reaction products than those that are produced in the thermally induced TNT decomposition reaction. It was hoped that this task could be performed in the laboratory, using small amounts of explosive (≤ 10 g) burned in the cigarette mode, such that the evolved gas (not too large) could be easily sampled for analysis by GC/MSD, GC/TCD and IR.

Preliminary tests to initiate sustained reaction in small amounts of flake or powdered flake TNT < 10 g using either thermal (gas-oxygen flame) or chemical (a few drops of DETA) were not successful. Reaction occurred only in those areas directly contacted by either the flame or the DETA and did not propagate into the bulk of the material. Tests with pelletized (≈ 12 mm diameter x 1 cm long) TNT initiated thermally and chemically (DETA) were similarly unsuccessful. The method finally selected with some success involved activating the TNT powder, followed by pelletizing and initiating the reaction either thermally or chemically (DETA).

2.2 EXPERIMENTAL.

2.2.1 Activation of TNT (ATNT) Powder.

The following procedure was adopted for preparation of TNT powder activated with DETA:

- 1) Weigh ≈ 2 g of powdered TNT (flake TNT ground in pestle and mortar) to nearest 0.01 g and place in a 50 mL Pyrex beaker.
- 2) Weigh ≈ 1 g of DETA to nearest 0.01 g in a 100 mL volumetric flask and make up to volume with hexane and sonicate.
- 3) Add 15 mL of 1 weight % DETA in hexane to 2 g of TNT in beaker. Stir for ≈ 20 sec.
- 4) Add ≈ 50 mL of hexane to the beaker and stir for ≈ 20 sec. Allow solid to settle ≈ 1 minute and decant off excess hexane.
- 5) Repeat washings with ≈ 50 -mL aliquots of hexane twice.

- 6) Place beaker with drained activated TNT in vacuum desiccator and pump off residual solvent (\approx 10 minutes).

The resulting material, a very dark red-brown in color, was a free flowing powder

2.2.2. TNT Pellet Preparation and Cigarette Burning Designs.

Cylindrical pellets of powdered and activated powdered TNT were prepared using an infrared pellet press. Approximately 2 g or less of TNT were poured into the press and pelletized at pressures of \approx 100,000 lb/in². A pellet \approx 1.22-cm diameter and \approx 1 cm long weighed \approx 2 g, indicating the pellet had a density close to that of bulk TNT at \approx 1.66 g/cm³.

Pellets of TNT so prepared were burned in two configurations:

- 1) For reaction in the presence of air, the pellet(s) was (were) wrapped with a few turns of aluminum foil and assembled with thermocouples (Type K stainless steel clad, 0.080" diameter) positioned as shown in Figure 23. The assembly was supported by a clamp around the "crumpled" aluminum foil sealing the base of the cigarette. Approximately 0.1 g of powdered TNT was placed on the exposed top surface of the pellet. The system was ignited by adding a few drops of DETA to the powder.
- 2) For reaction in the absence of air (run under argon) the experimental set-up shown in Figure 24 was assembled allowing evacuation of the system, establishment of an argon atmosphere over the sample, and if required collection of evolved gases generated by the reaction. The reaction in the TNT pellet was initiated by addition of a few drops of DETA to the powdered TNT on the top of the pellet. Temperatures in these reactions were either monitored on a digital or strip chart recorder.

2.2.3. Results.

The results obtained to date are largely qualitative in nature and are summarized below.

- 1) Attempts to initiate sustained reaction in activated TNT (ATNT) pellets failed when the pellets were contained in Pyrex glass tubular holders. It was concluded that the reaction was probably being quenched on the cold Pyrex glass containment walls.
- 2) Sustained reaction in single ATNT pellets (\approx 2 g as shown in Figure 23) wrapped in aluminum foil and initiated with TNT powder plus a few drops of DETA were repeatedly obtained. On addition of DETA, there was an initial emission of a red-brown colored gas/aerosol cloud. After \approx 6 seconds, a visible somewhat smoky flame appeared. Maximum temperatures (upper thermocouple in Figure 23) in the 800-900°C range were recorded with the vigorous reaction being sustained for \approx 20-25 seconds. A substantial amount of black char was found in the base of the aluminum foil holder. This char was ground up with a small amount of acetone and analyzed for TNT by GC/MSD. Qualitatively, low levels of residual TNT were detected in several such chars analyzed from reaction of ATNT pellets.

- 3) Tests as in (2) above were repeated with ATNT powder activated using 0.2 weight % DETA in hexane (rather than 1 weight % DETA in hexane). Although reaction was initiated with these pellets on addition of DETA, it was not sustained, a large fraction of the original pellet remaining intact. The result suggests that the degree of surface activation of the TNT pellet is critical to obtaining sustained reaction.
- 4) A time-temperature (upper thermocouple) profile obtained with a single ATNT pellet burned in the configuration shown in Figure 23 are shown in Figure 25.
- 5) Several tests were made using the two-pellet set-up shown in Figure 23. The results from these tests were variable. In some tests both pellets would completely react, in other tests the reaction would terminate part way through the lower TNT pellet. A time-temperature (upper thermocouple) profile from a test in which both pellets were completely reacted is shown in Figure 26. During this test, initially, the system inflamed with a production of fairly smoky flame. The visible flame after a short while extinguished and the reaction continued thereafter with the emission of a white smoke. On examination of the pellet holder, complete reaction of both pellets appeared to have occurred.
- 6) A single test was made in which an aluminum foil wrapped single pellet of ATNT (≈ 2 g) was placed in a glass containment vessel similar to that shown in Figure 24 and initiated with a few drops of DETA. On examination of the pellet holder after removal from the glass containment vessel, the pellet appeared to have been completely consumed. The time-temperature profile for the reaction is shown in Figure 27.

2.3 CONCLUSIONS.

A technique has been developed for initiating sustained reaction in pellets of activated TNT (ATNT). By contacting an ATNT pellet with a TNT pellet (as in Figure 23) sustained reaction in the non-activated TNT pellet can be achieved; though not reproducibly for reasons unknown.

The reaction occurring in the pellets appear to be capable of occurring in two modes: one, which produces a visible fairly smoky (black) flame and a second mode in which a visible flame, present initially, extinguishes and is replaced by emission of a white smoke plume. In both cases complete reaction in the non-activated TNT pellet may occur. The cause of the apparent change in the reaction modes is not known.

Initiation of the DETA-TNT reaction, and propagation into an ATNT pellet with sustained reaction to completion is not dependent on the presence of air at the reaction site.

Finally, although the use of activated TNT shows promise for initiating and sustaining the self-propagating high temperature decomposition of TNT; the method needs further development to insure its reliability.

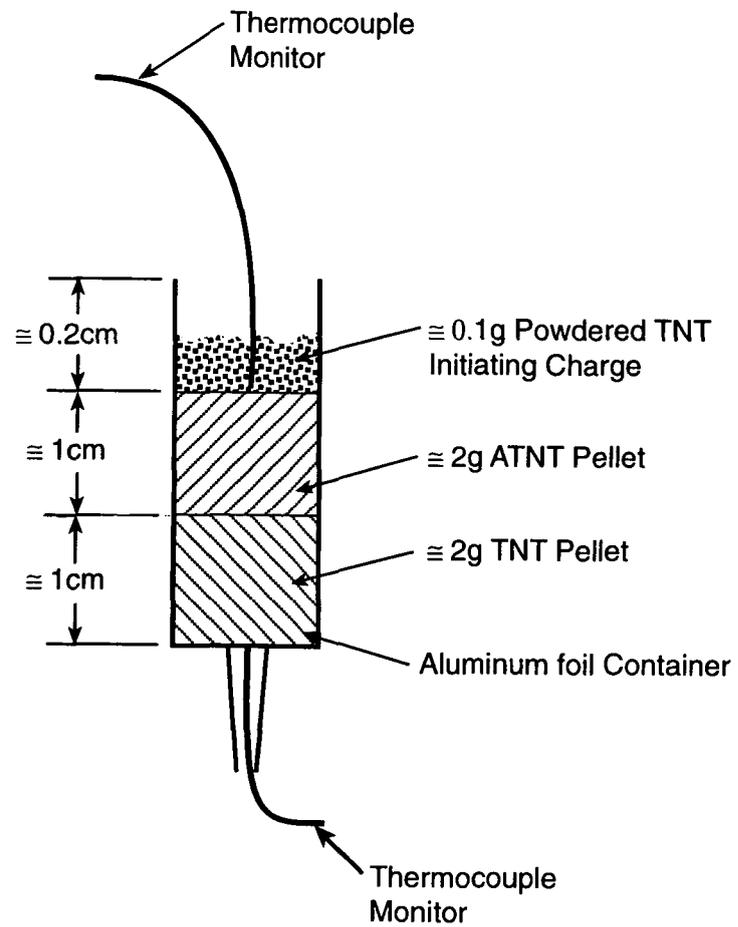


Figure 23. Representative experimental set-up used for the "cigarette" burning of ATNT and TNT pellets in air.

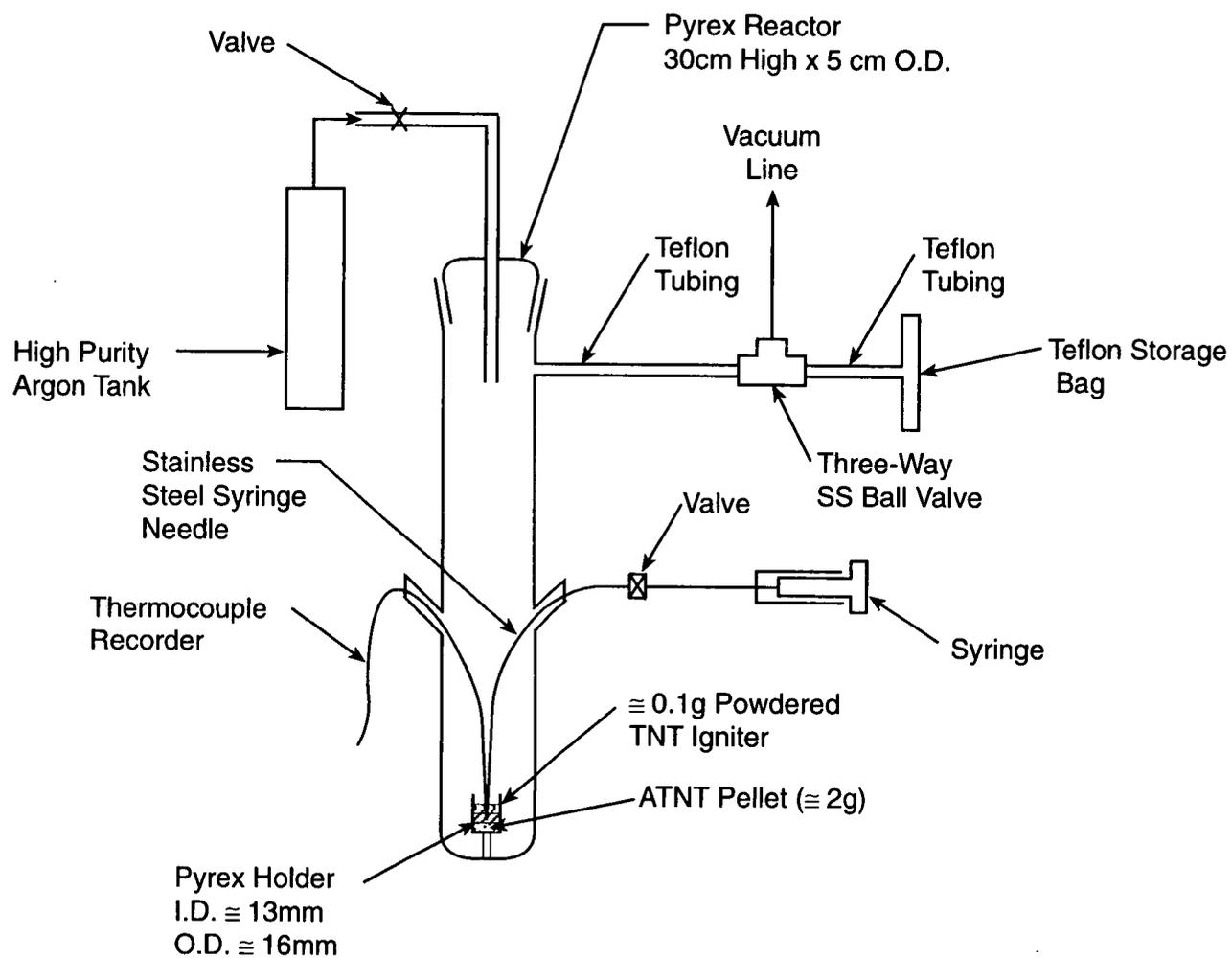


Figure 24. Representative experimental set-up used for the "cigarette" burning of ATNT and TNT pellets in an argon atmosphere.

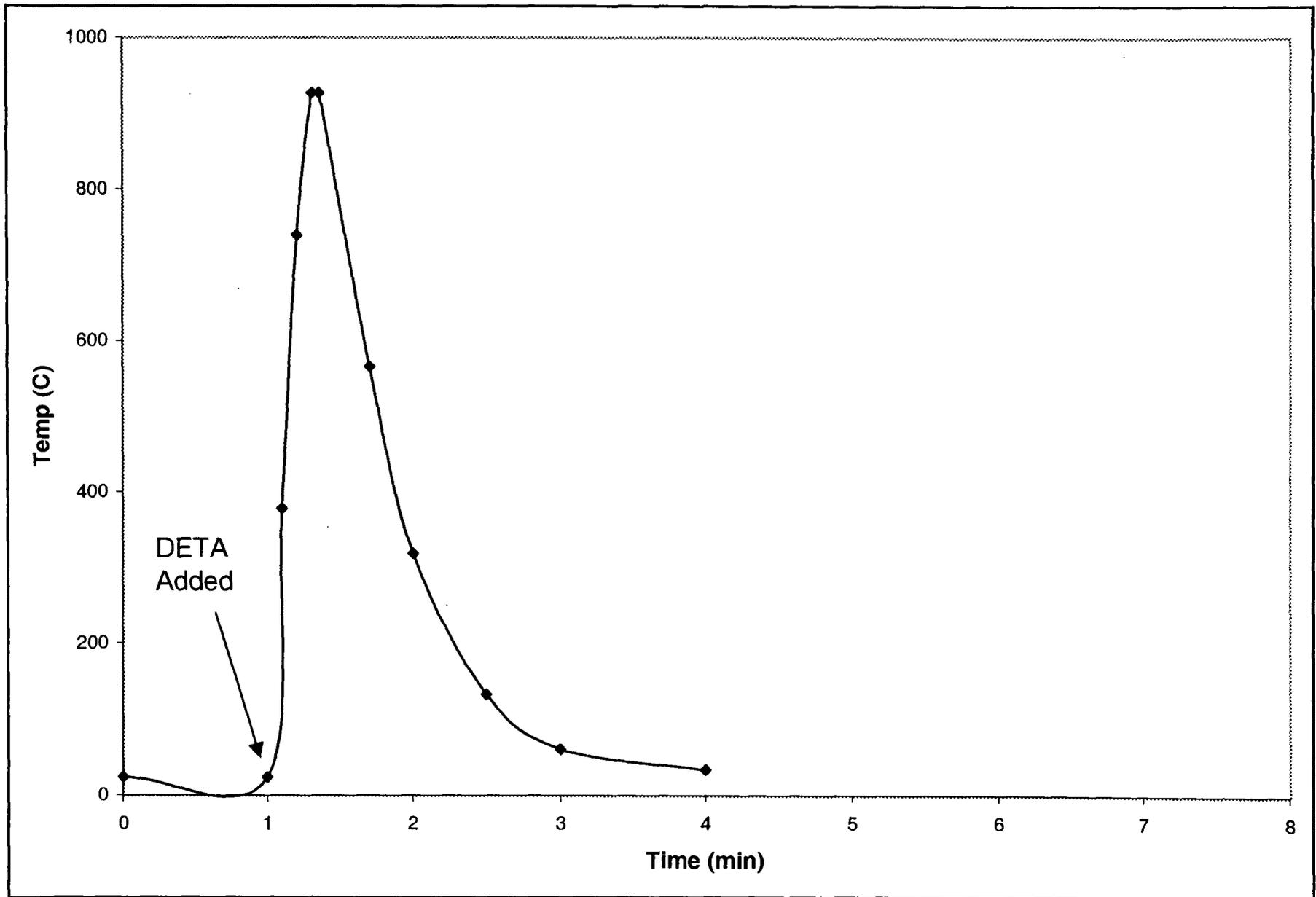


Figure 25. Time-temperature profile of a single ATNT pellet (≈ 2 g) reacted in the cigarette burning mode in air. Temperature probe just above pellet top surface.

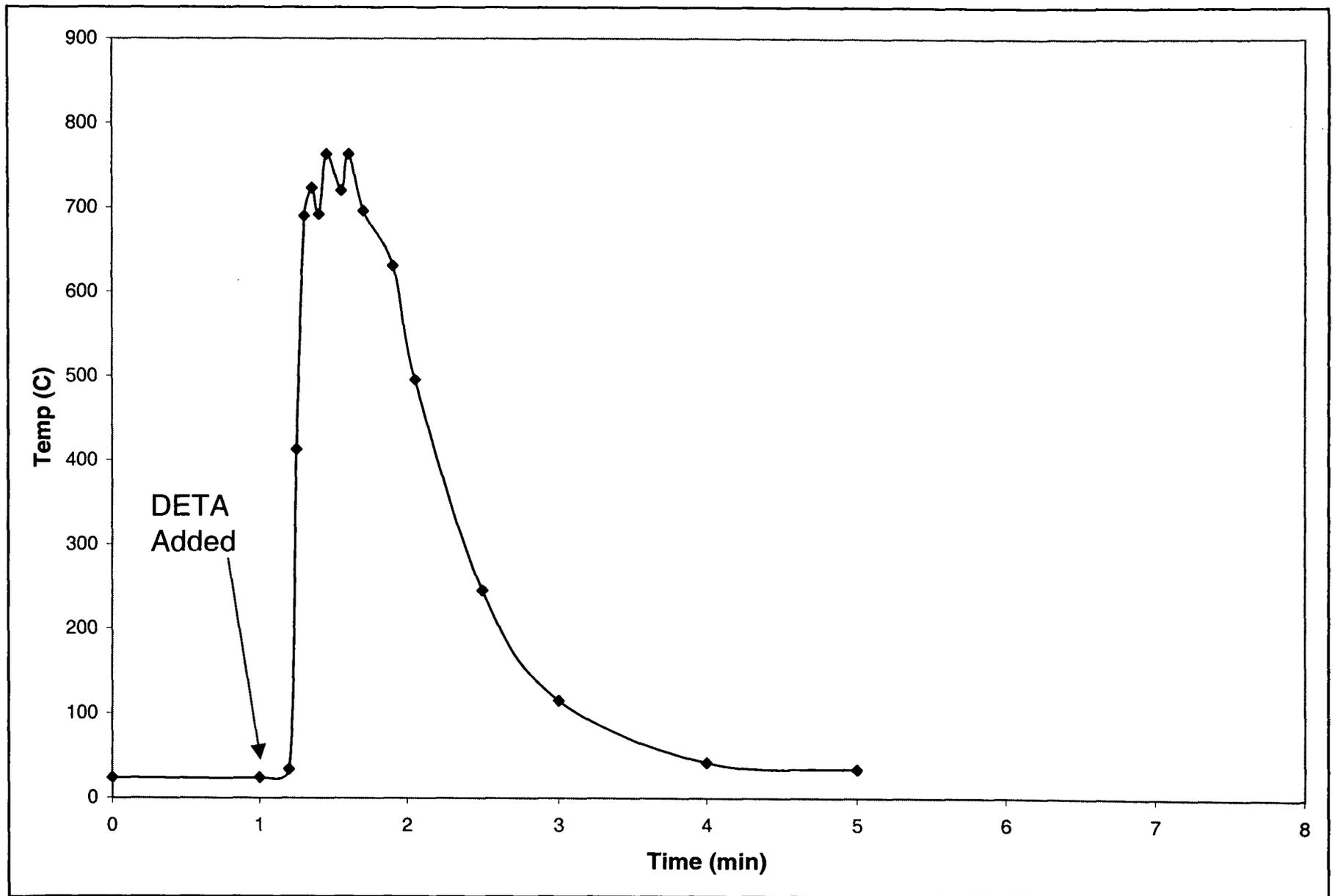


Figure 26. Time-temperature profile of a single ATNT pellet (≈ 2 g) mounted on top of a TNT pellet (≈ 2 g) reacted in the cigarette burning mode in air. Temperature probe just above top surface of upper pellet.

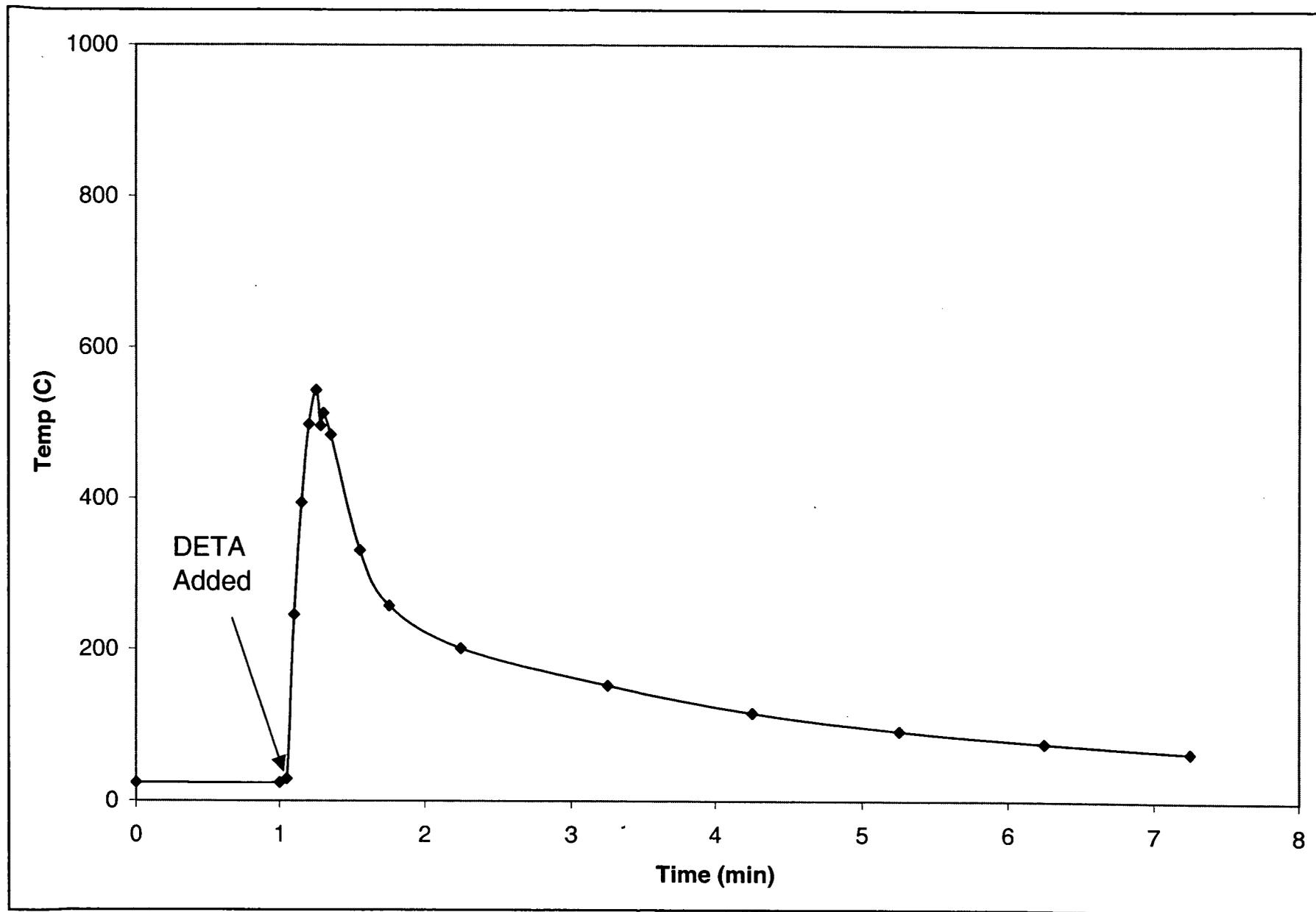
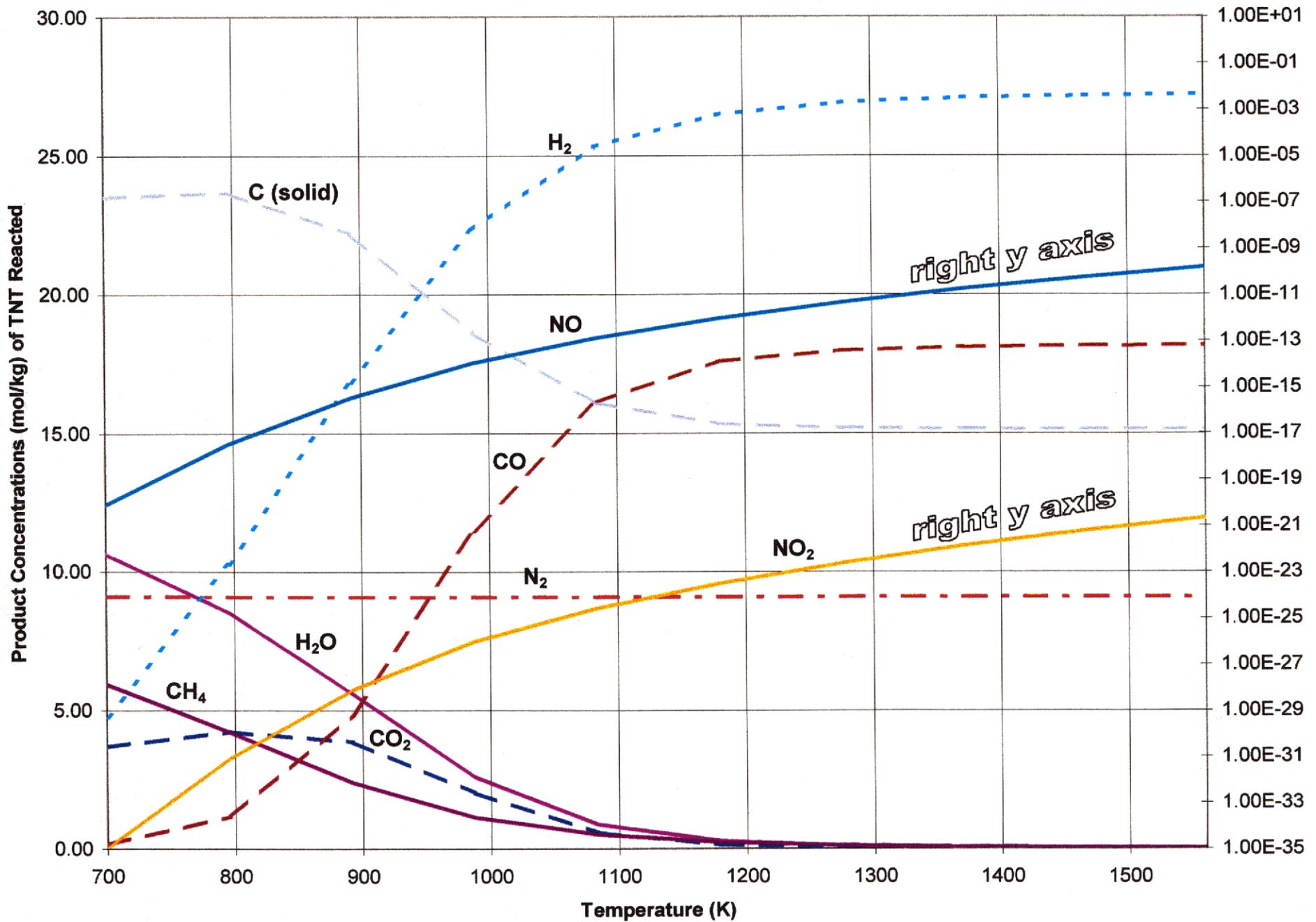
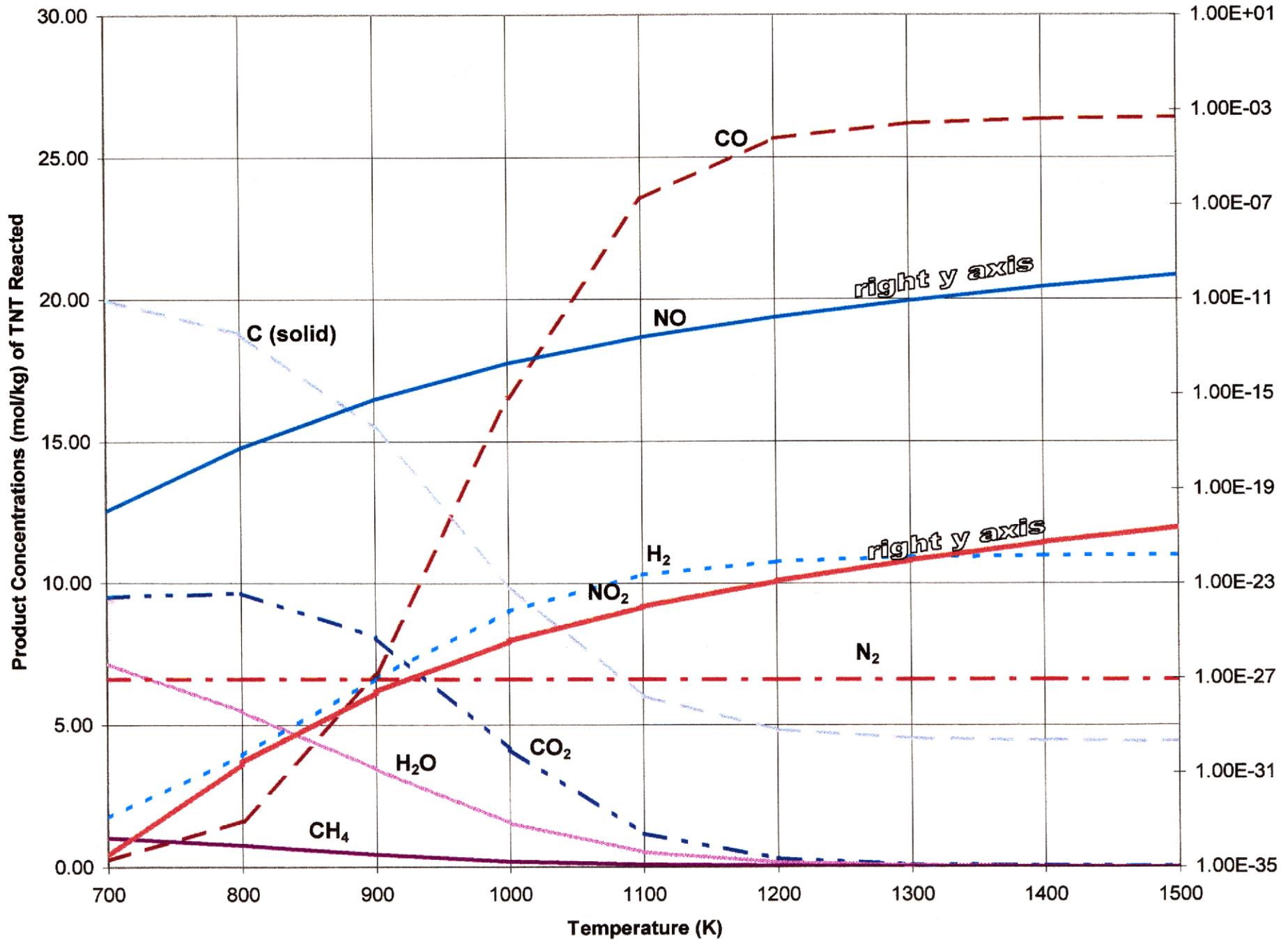


Figure 27. Time-temperature profile of an ATNT pellet (~ 2 g) reacted in the cigarette burning mode in argon. Temperature probe just above top surface of pellet.

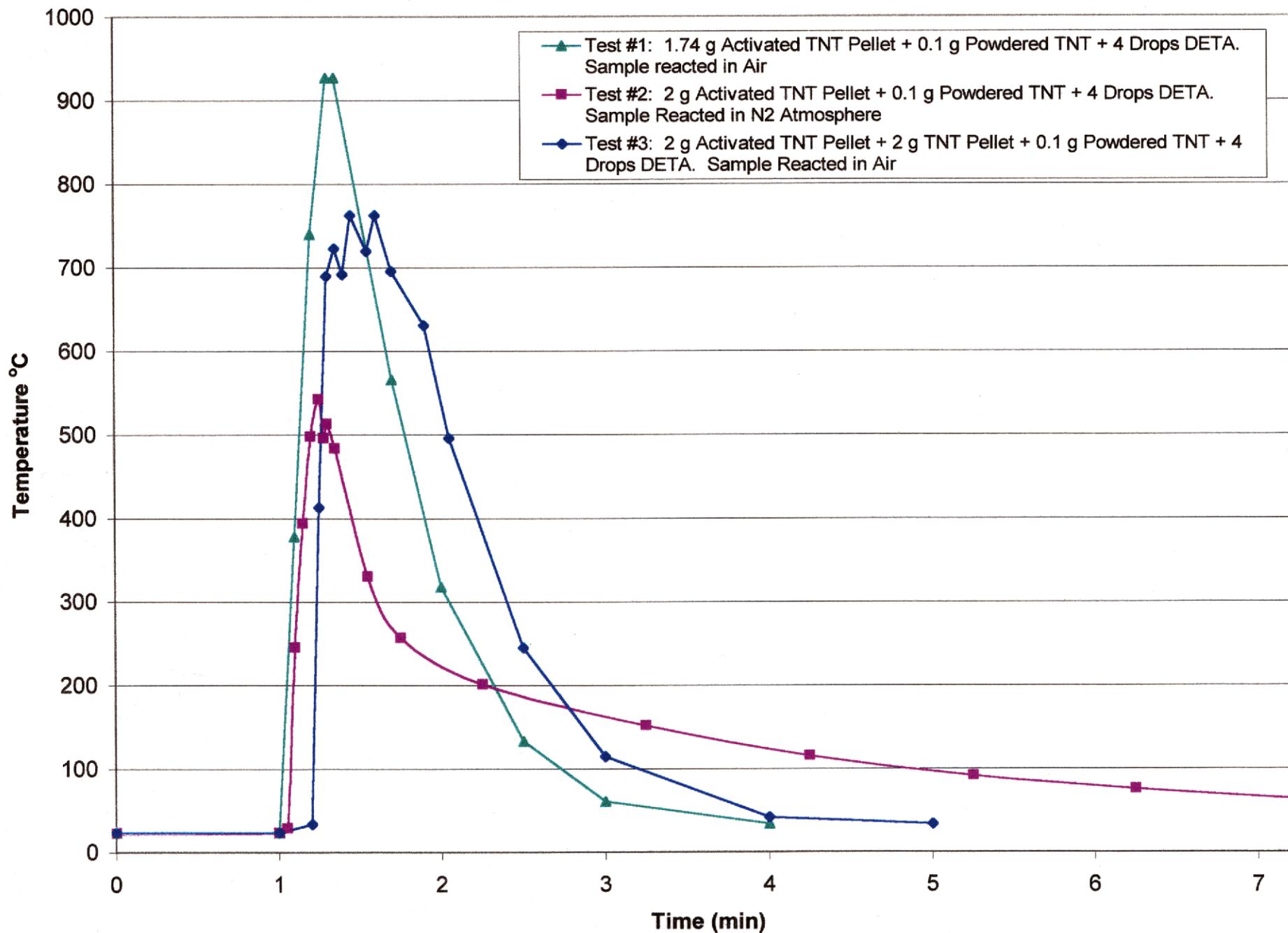
TNT:DETA 50:50 mole percent Calculated Equilibrium Product Distribution for Selected Temperatures at 1 atm Pressure



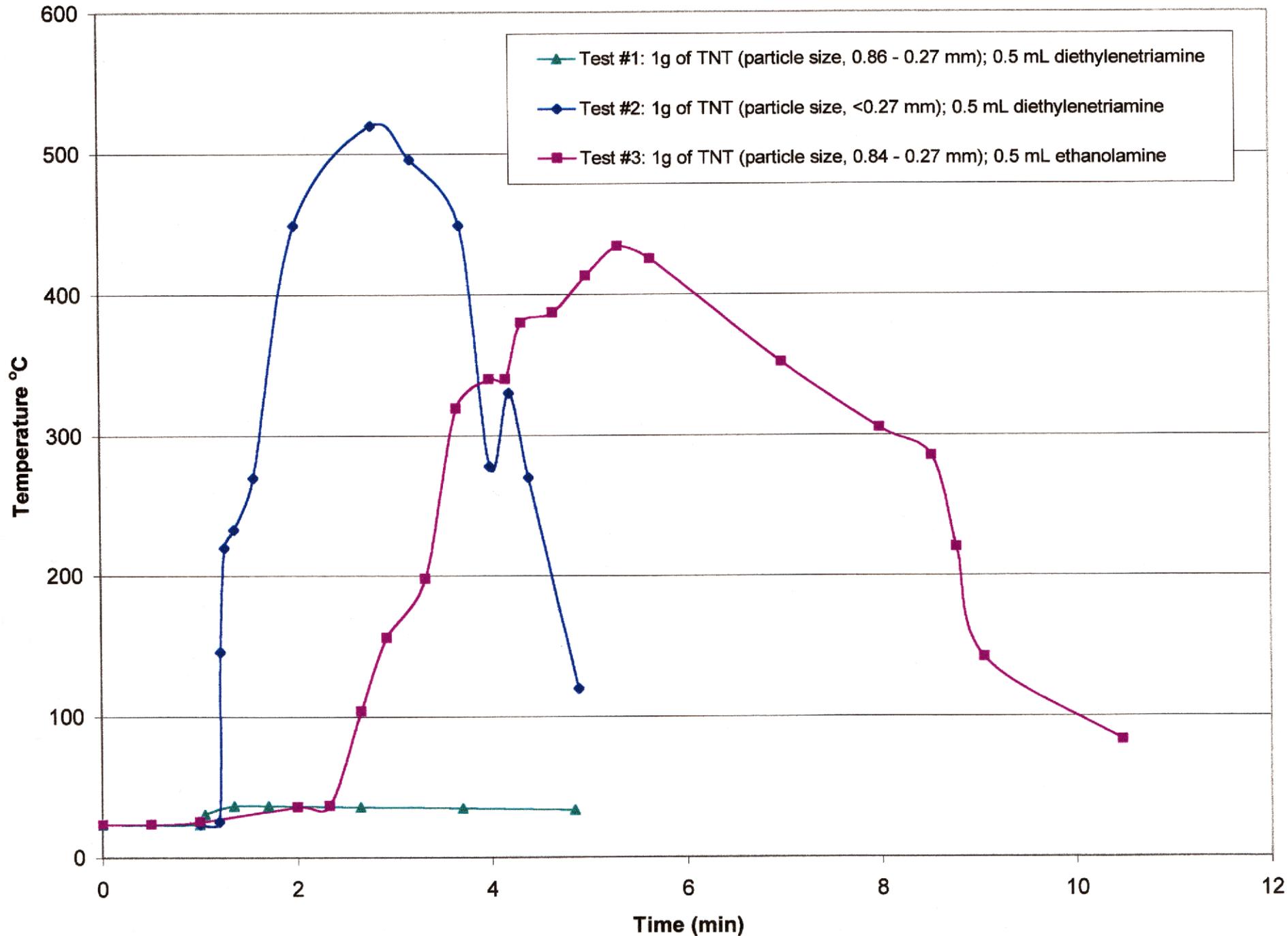
TNT Calculated Equilibrium Product Distribution for Selected Temperatures at 1 atm Pressure



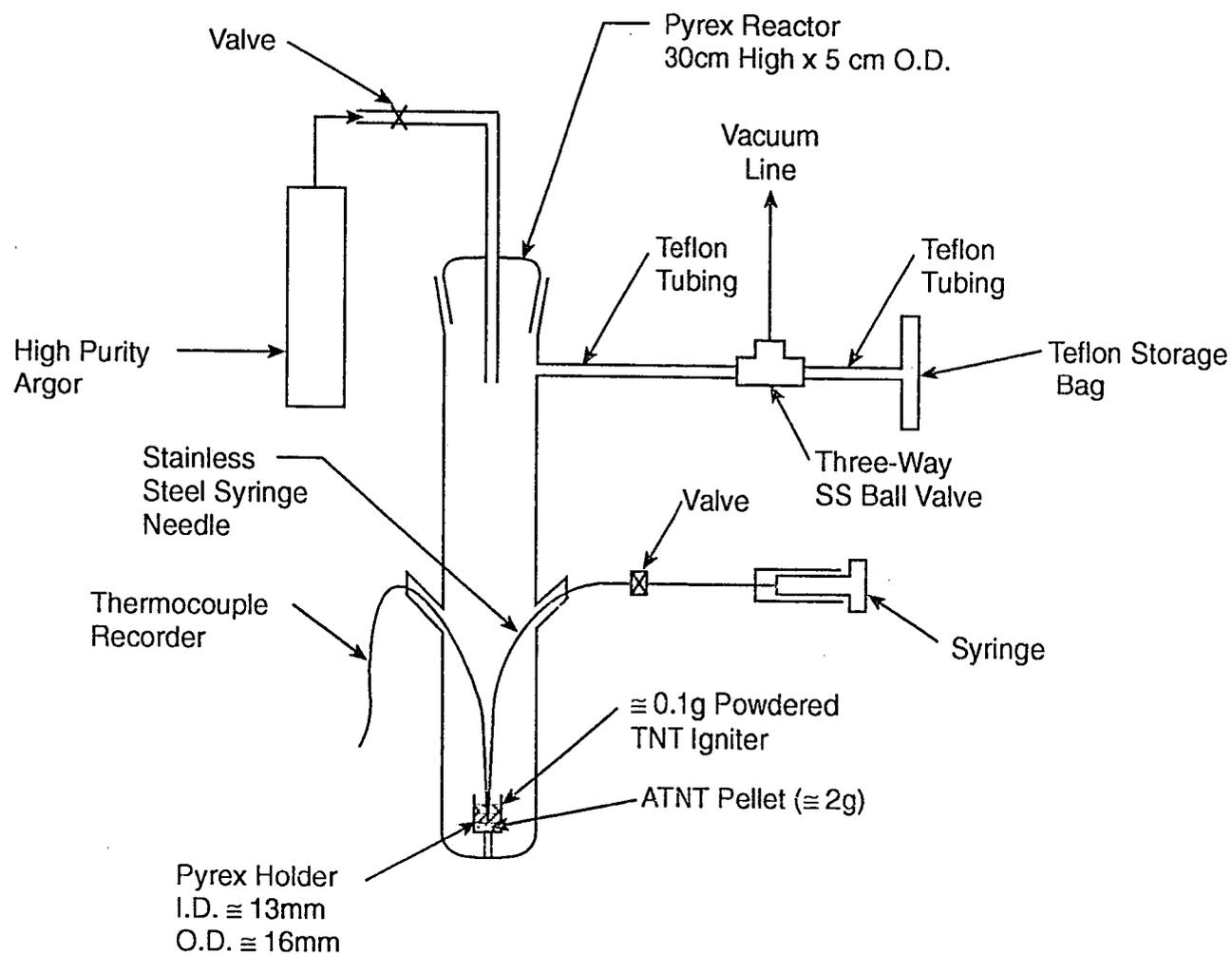
Time-Temperature Profiles in The Hypogolic Reactions of Solid Pelletized TNT with Diethylenetriamine in Air and Nitrogen Atmospheres

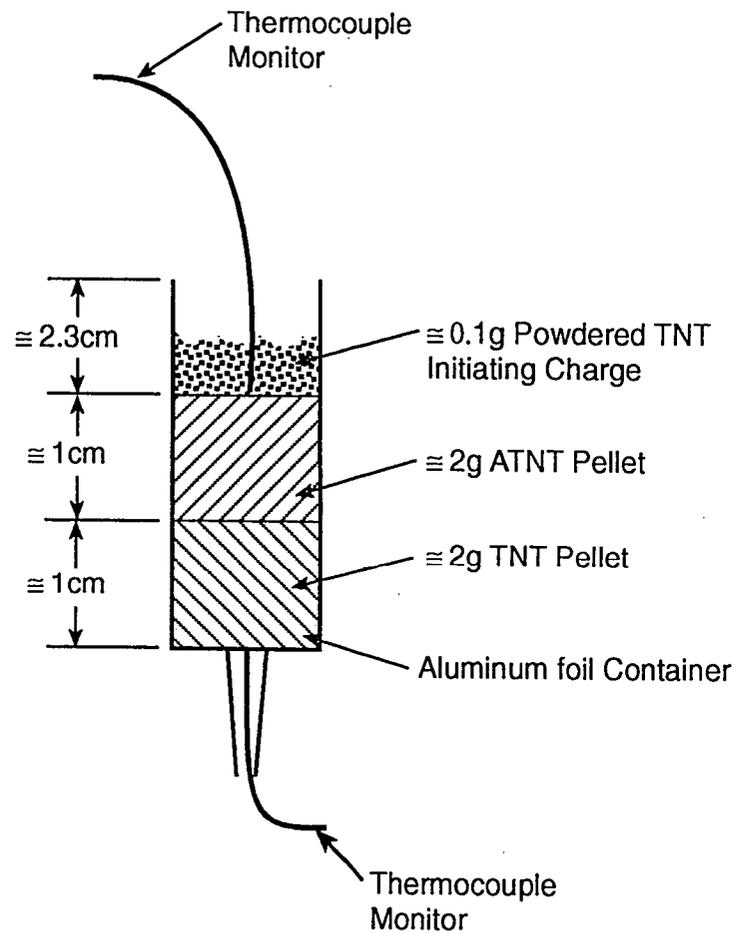


Time-Temperature Profiles in The Hypogolic Reactions of Powdered TNT with Selected Amines



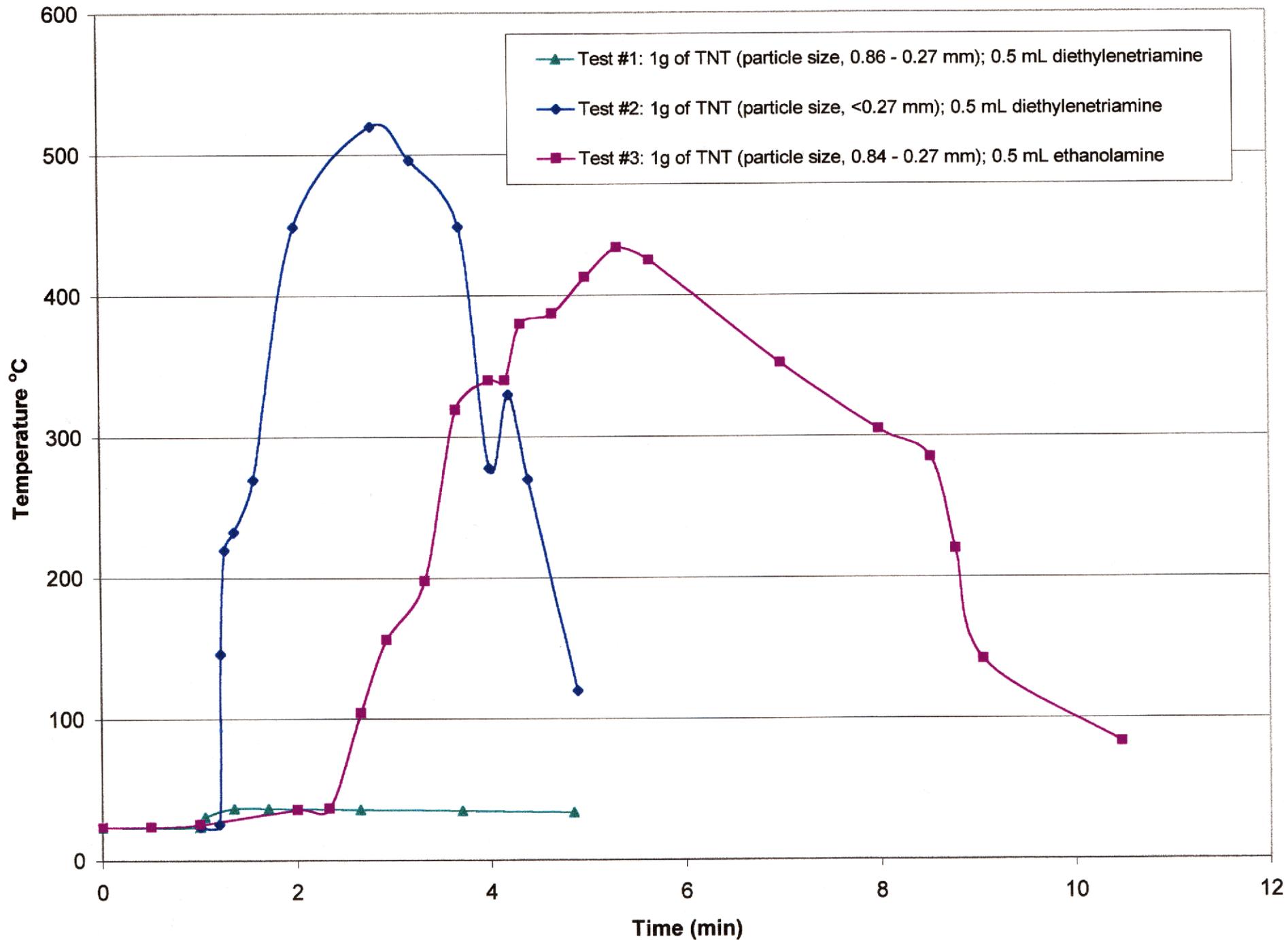
Experiment Set-up for Hypergolic Reaction of TNT with Amines in a Control Atmosphere



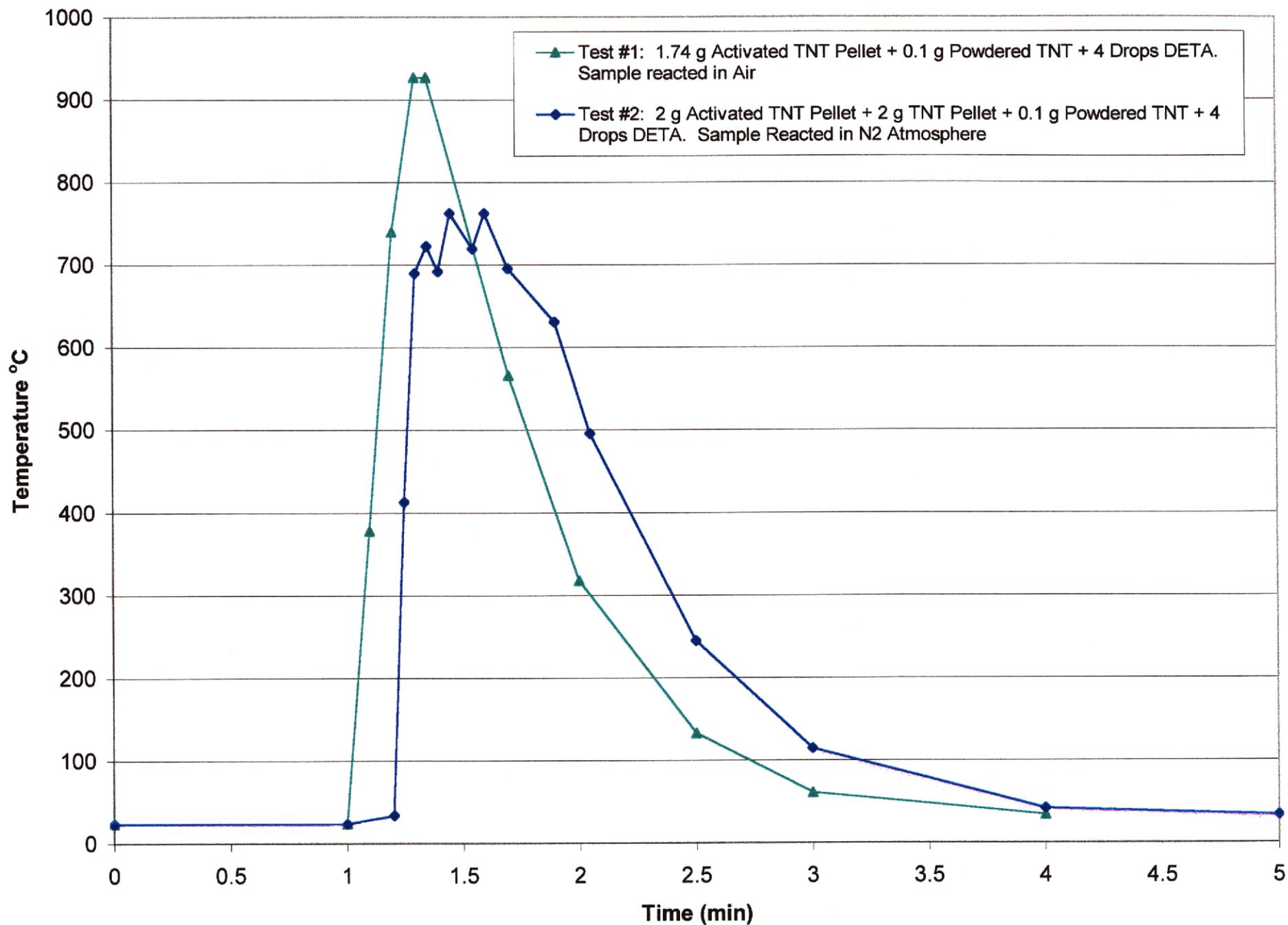


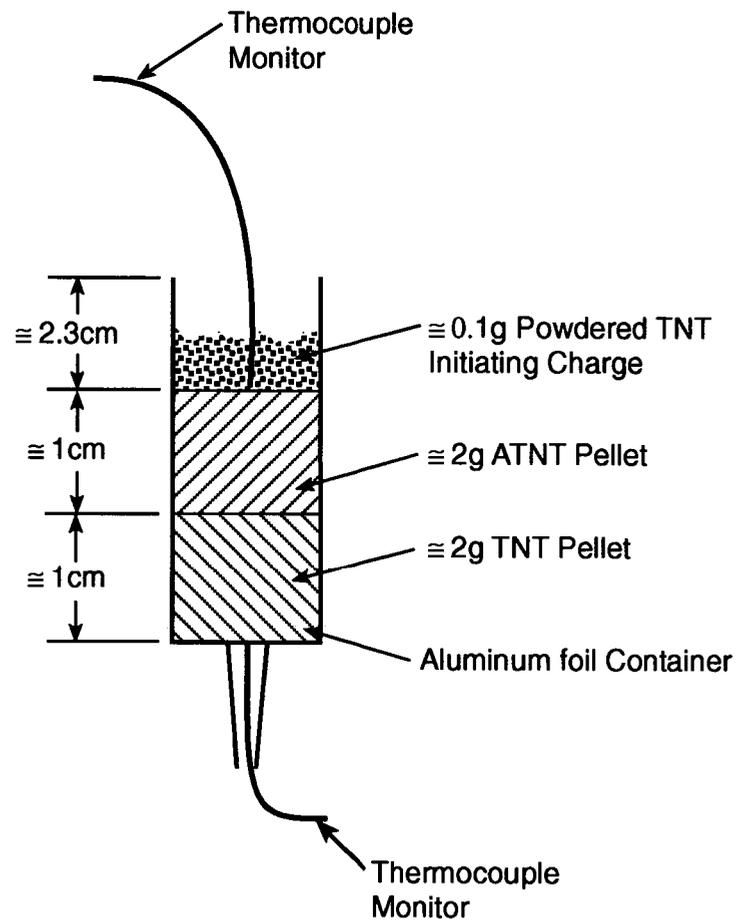
Experimental Set-up for Hypergolic
Reaction of TNT Pellets with Amines in Air

Time-Temperature Profiles in The Hypogolic Reactions of Powdered TNT with Selected Amines



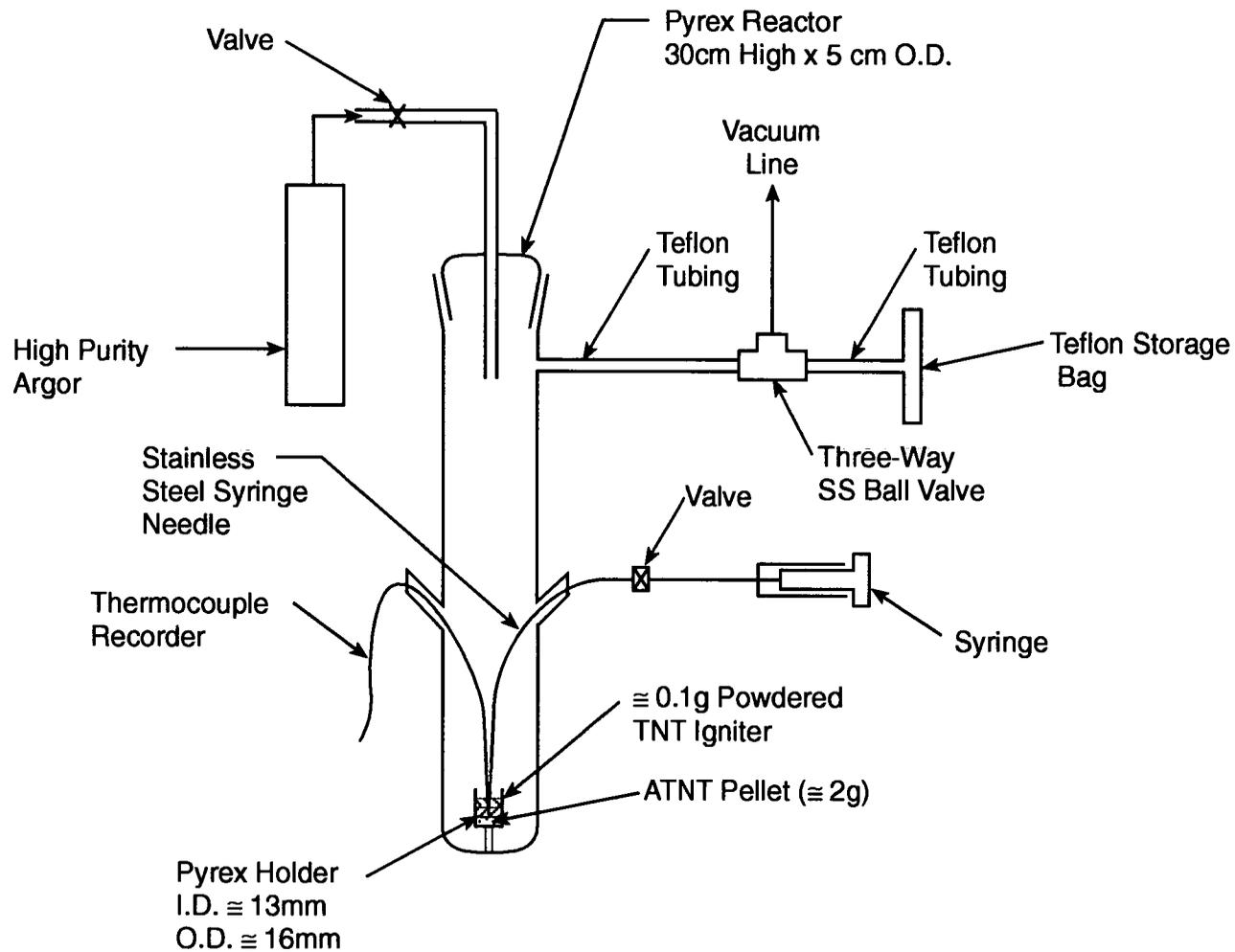
Time-Temperature Profiles in The Hypogolic Reactions of Solid Pelletized TNT with Diethylenetriamine in Air and Nitrogen Atmospheres



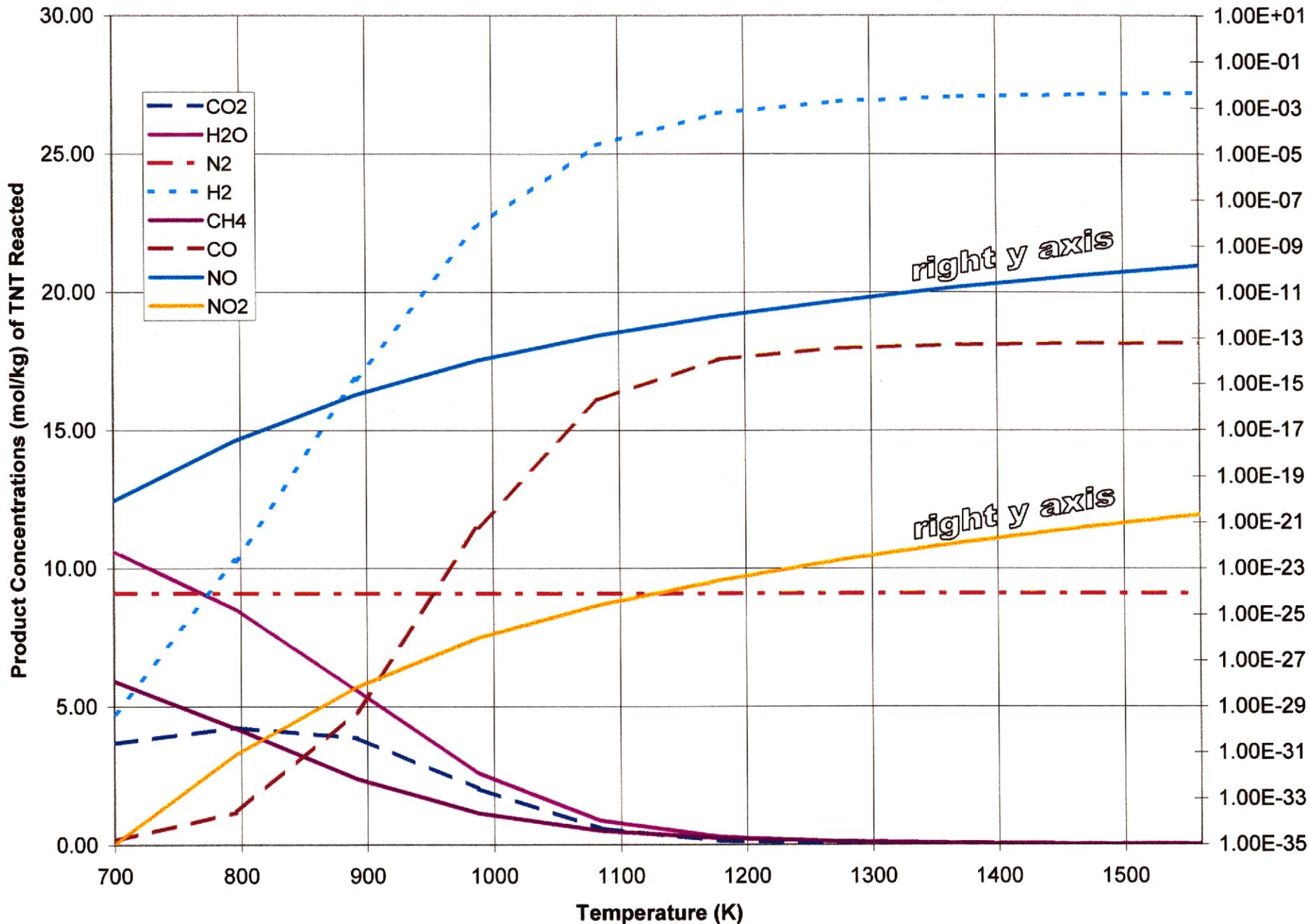


Experimental Set-up for Hypergolic Reaction of TNT Pellets with Amines in Air

Experiment Set-up for Hypergolic Reaction of TNT with Amines in a Control Atmosphere



TNT:DETA 50:50 mole percent Calculated Equilibrium Product Distribution for Selected Temperatures at 1 atm Pressure



7.0 Appendix B – Commerce Business Daily Ad

[Commerce Business Daily: Posted in CBDNet on June 8, 2000]
From the Commerce Business Daily Online via GPO Access
[cbdnet.access.gpo.gov]

PART: SPECIAL NOTICES

OFFADD: Sandia National Laboratories, Technology Partnerships
Dept., PO Box 5800-MS1380, Albuquerque, NM 87185-1380

SUBJECT: MODIFIED “JEFFAMINE” T-403” AMINE CURING AGENT
FOR EPOXY FORMULATIONS

DESC: Sandia National Laboratories has a laboratory-scale chemical process which produces a by-product of modified “Jeffamine” T-403” (commercial product of the Huntsman Corp.). “Jeffamine” T-403” is a trifunctional amine used as a curing agent for epoxies such as Epon 828. Sandia’s patented process utilizes the virgin “Jeffamine” T-403” to degrade explosives such as TNT and Comp B into safe products. “Jeffamine” T-403” is used as a reactant in the chemical reaction, then, after reacting, the modified-“Jeffamine” becomes part of the waste stream. This non-explosive, off-color, viscous “Jeffamine” by-product can still be used to make epoxy for use in applications which do not require virgin “Jeffamine.” Epoxies made with this modified “Jeffamine” have altered mechanical properties, such as lower glass transition temperatures. However, the mechanical properties can be tailored for use in the final epoxy application.

This chemical process is one of military interest. The Department of Defense and Department of Energy have funding to dispose of hundreds of thousands of tons of ammunition during the next decade. About 100,000 tons/year of new materials are added to this inventory. The huge inventory of obsolete military explosives are available for this process and will provide many tons of modified “Jeffamine” T-403” for commercial applications.

Sandia is interested in identifying potential users of the modified “Jeffamine” T-403” amine curing agent and/or partnering with a commercial company to scale up the operation from laboratory scale to industrial proportions. Demilled explosives are available from Army Ammunition Plants to demonstrate the process and scale-up.

EMAILADD: slpound@sandia.gov

EMAILDESC: Sheila L. Pounds

CITE: (W-160 SN462822)

8.0 Appendix C – CFD Research Final Report

DEVELOPMENT OF A NUMERICAL SIMULATION TOOL FOR THE SANDIA ENERGETIC MATERIAL NEUTRALIZATION PROCESS

Final Report

By

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CFD Research Corporation
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April 2001

CFDRC No.: 8313/2

**Submitted to
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Albuquerque, NM 87123**

ACKNOWLEDGMENTS

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1. BACKGROUND

Sandia National Labs is investigating an alternative environmental technology to replace open burn/open detonation (OB/OD) operations for the destruction and disposal of obsolete, excess, and off-spec energetic materials. Organic amines have been found to chemically react with explosives like TNT, RDX and Composition B (60%RDX, 40%TNT, wax), safely breaking them down without detonation. The reaction creates liquid products that are effective curing agents for conventional epoxy resins. These epoxies are safe and non-detonable and their commercial use will be explored to complete the recycle of the explosives.

In support of this project, CFD Research Corporation has developed a model of the above neutralization process. This model has been used to analyze the effects of scale-up and operating condition on the maximum temperature obtained during the reaction. The maximum temperature and time are two critical parameter since it indicates the potential for explosion. The model development and conclusions are presented in this report.

2. TECHNICAL APPROACH

The modeling in this project was to adapt the multi-component chemistry option in the CFD-ACE to simulate the foaming reaction in the Sandia reactor. The code computes the flow, heat generation, heat transfer and mass transport in the system as part of the solution. The reaction mechanisms were developed and calibrated based on experimental data from Sandia. A series of simulations was subsequently performed to investigate the effects of geometry, initial conditions, and boundary conditions on the reaction process.

3. EMPIRICAL DATA

Sandia National Laboratories have been experimentally investigating the neutralization of explosives using Jeffamine. A partial overview of these experiments, as they relate to the modeling effort, is provided in this report.

Sandia's initial work in FY99 was on a laboratory-scale. This work confirmed that the commercially available "Jeffamine T-403" (product of Huntsman Corp.), an amine curing agent used in 2-part epoxies, is effective in decomposing explosives such as RDX, TNT, and Comp B. The experimental investigation was performed in a 1000-milliliter tall pyrex beaker. After Jeffamine was heated to 130C and stirred with a magnetic stirrer, a small quantity of fine powdered explosive (up to 20g) was added either incrementally or "all-at-once". Different scenarios were tested to determine the possibility of a worst-case thermal run-away that leads to detonation of the mixture. Such scenarios (behavior of the exothermic reaction) are directly related to the safety of the scale-up process that is needed for the effective decomposition of the explosives. The laboratory-scale experiments revealed a complicated sequence of events that led to intense foaming, and the production of gaseous and liquid products. Differences in the final color of the liquid products seem to indicate that the chemical pathway and final products are affected by the type of explosive added to the Jeffamine. Gaseous products have been collected and

analyzed using gas chromatography. Typical results for the reaction of RDX and Jeffamine are presented in Fig. 1.

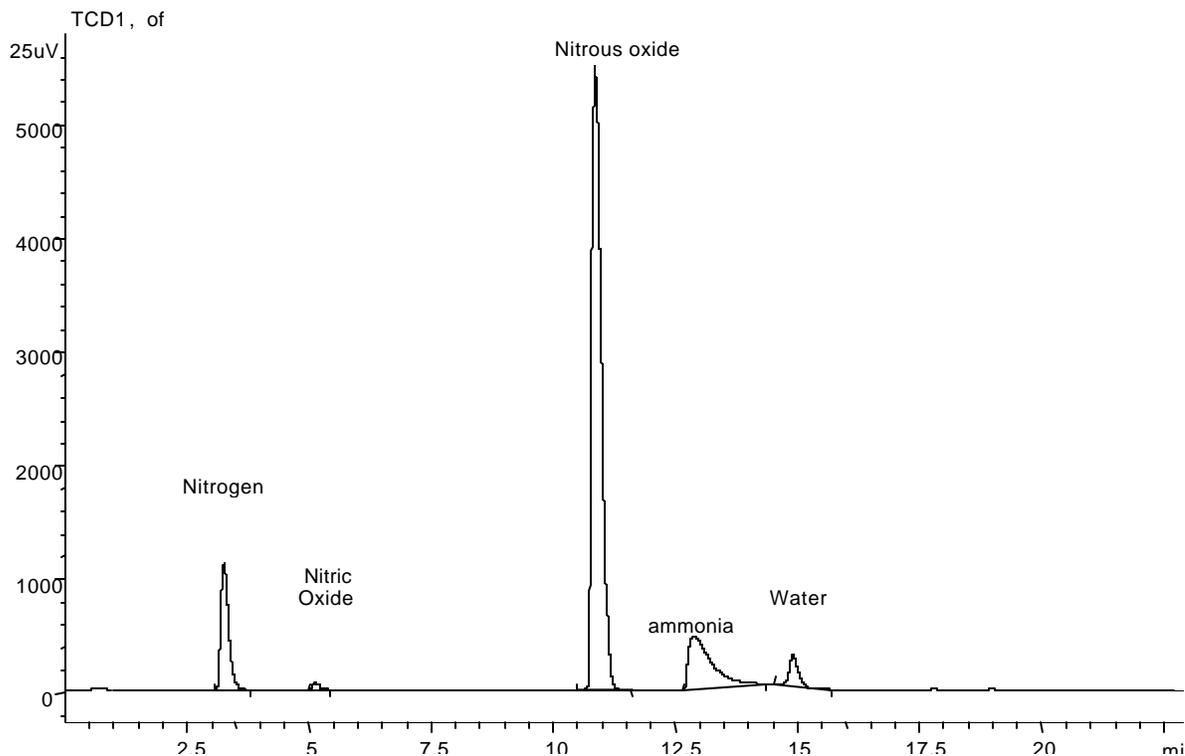


Figure 1. Reactant Products for the Reaction of RDX and Jeffamine

Following the FY99 experiments, additional experiments were conducted for “chunks” of Composition B and TNT dropped into pre-heated Jeffamine. Table 1 provides the test matrix for one of these tests series. As before, the experimental investigation was performed in a 1000-milliliter tall pyrex beaker. After Jeffamine was heated to 130C using a hotplate, the chunks were dropped into the heated liquid. Throughout the process, the mixture is stirred with a magnetic stirrer. The addition of the room temperature chunks temporarily lowers the average temperature of the Jeffamine. As the chunks melt and the temperature of the liquid mixture re-establishes 130C, the hotplate is turned off. Figure 2 shows a schematic of this experiment. Figure 3 provides the temperature profiles for the four cases in Table 1 based on a thermocouple dipped into the liquid.

Table 1. Test Matrix for the Reduction of TNT and Compound B in Jeffamine

Curve	Explosive Material	Diameter of Chunk	Mass (in grams)
A	Comp B	1 inch rod	23.8
B	Comp B	1 inch rod	26.6
C	Comp B	Wafer like	23.8
D	Comp B	1 inch rod	29.9

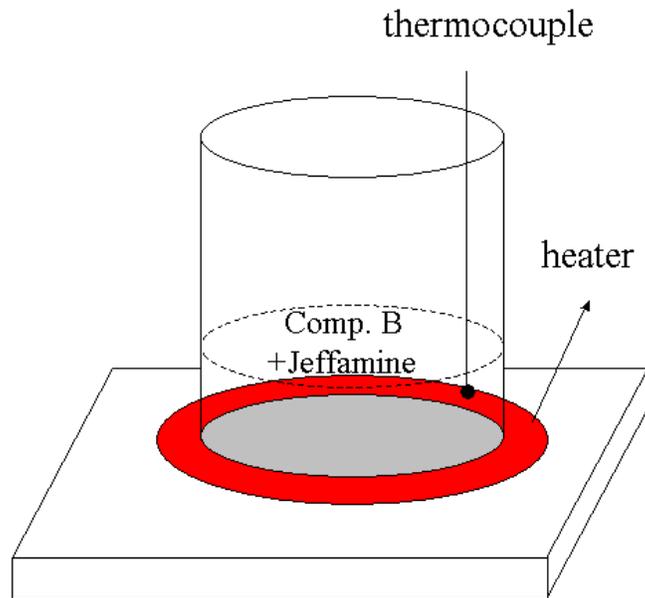


Figure 2. Schematic for the Reduction of TNT and Comp. B

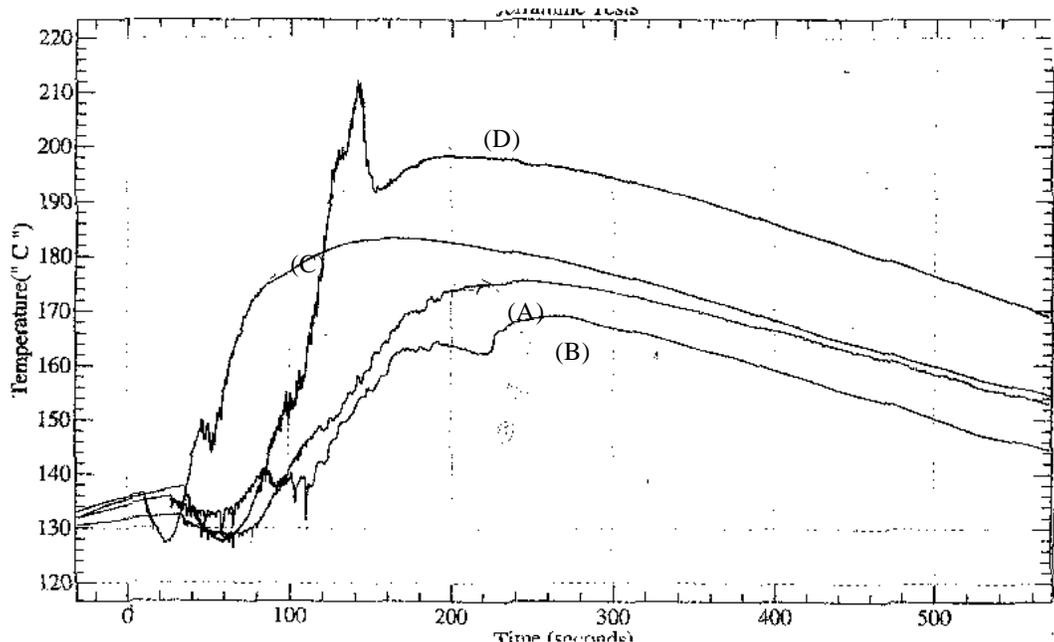


Figure 3. Thermal histories for reduction of Comp. B

The procedure used in the above experiments is similar to the proposed procedure for the full-scale process. However, it is too complex to facilitate model calibration in the sense that too many processes occur simultaneously. For example, the chunks are being stirred and melt as the reaction occurs. At the same time, the hot plate is providing heat to the beaker in an uncontrolled manner. This makes the problem a three-phase reaction with unknown boundary conditions. In order to simplify the modeling calibration, Sandia National Labs conducted a more controlled experiment. This experiment was described as follows:

“This was another glass beaker experiment, with 100 grams of Jeffamine heated to 77C. Then 20 grams of powdered Comp B were added while the hot plate was still on. Once the temperature of the reacting solution reached 130C, the heater/stirrer was turned off.

There were 4 thermocouples in place: one in the reacting solution, one at the 425 ml level (of the 1000 ml beaker), one at the 600 ml level, and one tucked under the edge of the beaker and taped to the hot plate. Some of the reaction took place between 77 and 130C, so the foaming was not as severe as in previous experiments.”

The results of the experiment are provided in Figure 4.

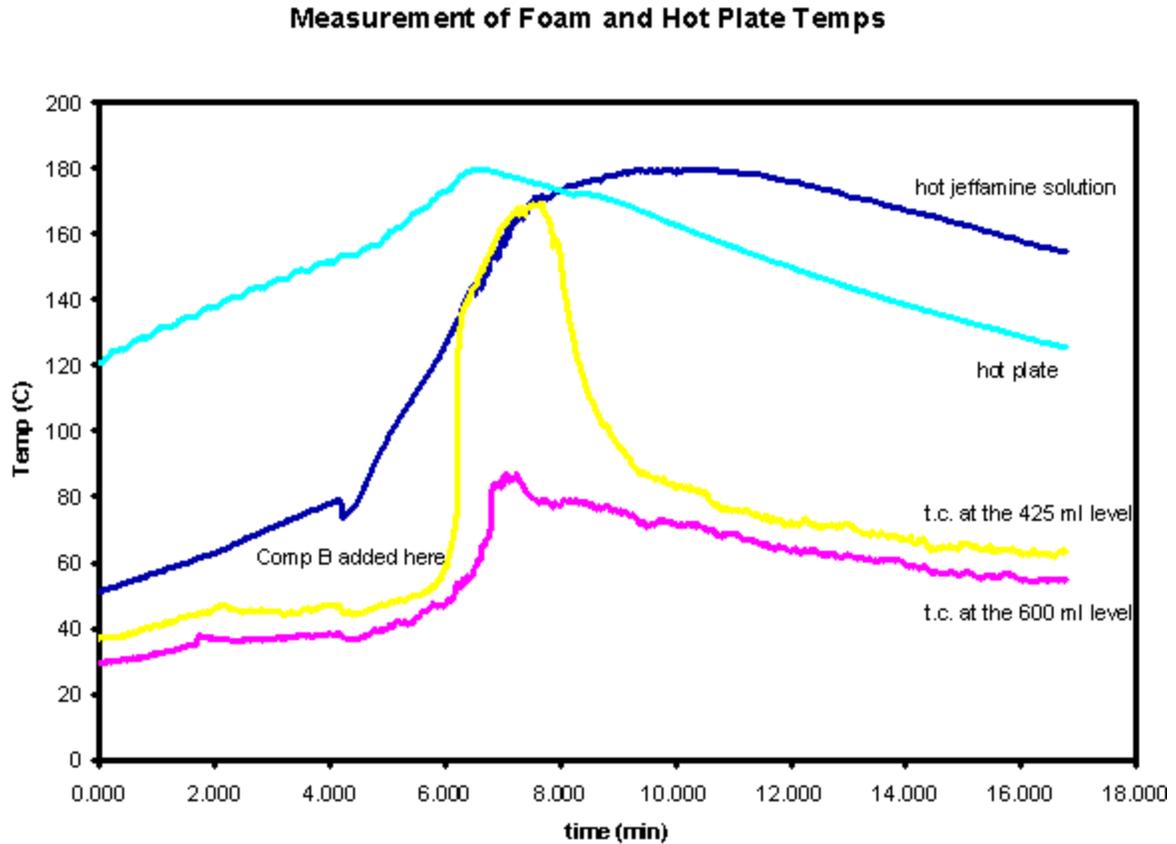


Figure 4. Thermal Histories for Reduction of Comp. B Using a Slow Heating Process

4.0 DESCRIPTION OF THE NUMERICAL CODE AND PHYSICAL MODELS

The foundation for the model is the general purpose, commercial computational fluid dynamics code, CFD-ACE, which is a transient, three-dimensional, Navier-Stokes code capable of simulating multi-species transport, heat transfer (including thermal radiation, fully coupled gas-phase and surface chemistry for conventional chemical vapor deposition (CVD) reactors. The CFD-ACE package is a very flexible code, that is coupled with preprocessing and post-processing software (CFD-GEOM and CFD-VIEW) that make it relatively straightforward to set up models for complex geometries and analyze the results.

4.1 Basic Features of CFD-ACE Code

The governing equations that are solved by CFD-ACE are:

Mass:
$$\frac{\partial \rho}{\partial t} + \nabla \cdot \rho \mathbf{u} = 0 \quad (1)$$

$$\text{Momentum:} \quad \frac{\partial \rho \mathbf{u}}{\partial t} + \nabla \cdot \rho \mathbf{u} \mathbf{u} = -\nabla p + \nabla \cdot \mathbf{t} + \rho \mathbf{g} \quad (2)$$

$$\text{Energy:} \quad \frac{\partial \rho h}{\partial t} + \nabla \cdot \rho \mathbf{u} h = \nabla \cdot \mathbf{q} + \mathbf{t} : \nabla \mathbf{u} + \frac{dp}{dt} \quad (3)$$

$$\text{Species:} \quad \frac{\partial \rho Y_i}{\partial t} + \nabla \cdot \rho \mathbf{u} Y_i = \nabla \cdot \mathbf{j}_i + \dot{w}_i \quad (4)$$

where ρ , \mathbf{u} , p , h , Y_i are density, velocity, pressure, enthalpy and species mass fraction, respectively. \dot{w}_i is species production rate due to gas-phase reaction.

$$\text{Shear Stress:} \quad \boldsymbol{\tau} = \mu (\nabla \mathbf{u} + \nabla \mathbf{u}^T) - \frac{2}{3} \mu (\nabla \cdot \mathbf{u}) \mathbf{I} \quad (5)$$

$$\text{Diffusive Energy Flux:} \quad \mathbf{q} = \lambda \nabla T + \sum_i h_i \mathbf{j}_i \quad (6)$$

$$\text{Diffusive Species Flux:} \quad \mathbf{j}_i = \mathbf{j}_i^c + \mathbf{j}_i^T \quad (7)$$

$$\text{Stefan-Maxwell Diffusion:} \quad \mathbf{j}_i^c = \rho D_i \nabla Y_i + \frac{\rho Y_i}{M} D_i \nabla M - M \sum_j D_j \nabla Y_j - \nabla M \sum_j D_j Y_j \quad (8)$$

(M is the mixture molecular weight)

$$\text{Soret Diffusion:} \quad \mathbf{j}_i^T = \frac{\rho D_i^T}{T} \nabla T - \rho Y_i \sum_j \frac{D_j^T}{T} \nabla T \quad (9)$$

4.2 Chemistry

Very complex chemistry is currently available in the single fluid module of the CFD-ACE code. This chemistry may be comprised of multi-step finite rate reactions of the form:

$$\frac{\partial}{\partial t} (\mathbf{r} Y_i) + \frac{\partial}{\partial x_j} (\mathbf{r} u_j Y_i) = \frac{\partial}{\partial x_j} J_{ij} + M_i \dot{w}_i \quad (10)$$

The diffusive flux of species i , $J_{i,j}$, includes ordinary diffusion driven by concentration gradient and, optionally, thermally induced diffusion driven by temperature gradients. The mass diffusivities of individual species do not have to be equal with this chemistry model. The reaction rate constant to calculate the reaction rate is represented in the modified Arrhenius form:

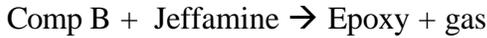
$$k = A \cdot T^n \exp(-E/RT) \quad (11)$$

where A is the pre-exponential factor, E is the activation barrier, R is the universal gas constant and n is the temperature exponent. These parameters were calibrated for the current application.

4.3 Mechanisms

It is probable that reaction between Jeffamine with RDX and TNT is a multi-step process. The initiation reaction occurs probably via a highly exothermic reaction, and the energy released from the reaction is used for initiating other reactions. Probably, RDX and TNT undergo kinetically favored reactions with low activation barriers as well as with low reaction energy. Perhaps, this prevents the reactions with higher activation barrier and higher reaction energies to occur which causes explosion.

Although the actual process is expected to be a multi-step, a one step reaction of the form



was assumed per the model to simplify the analysis.

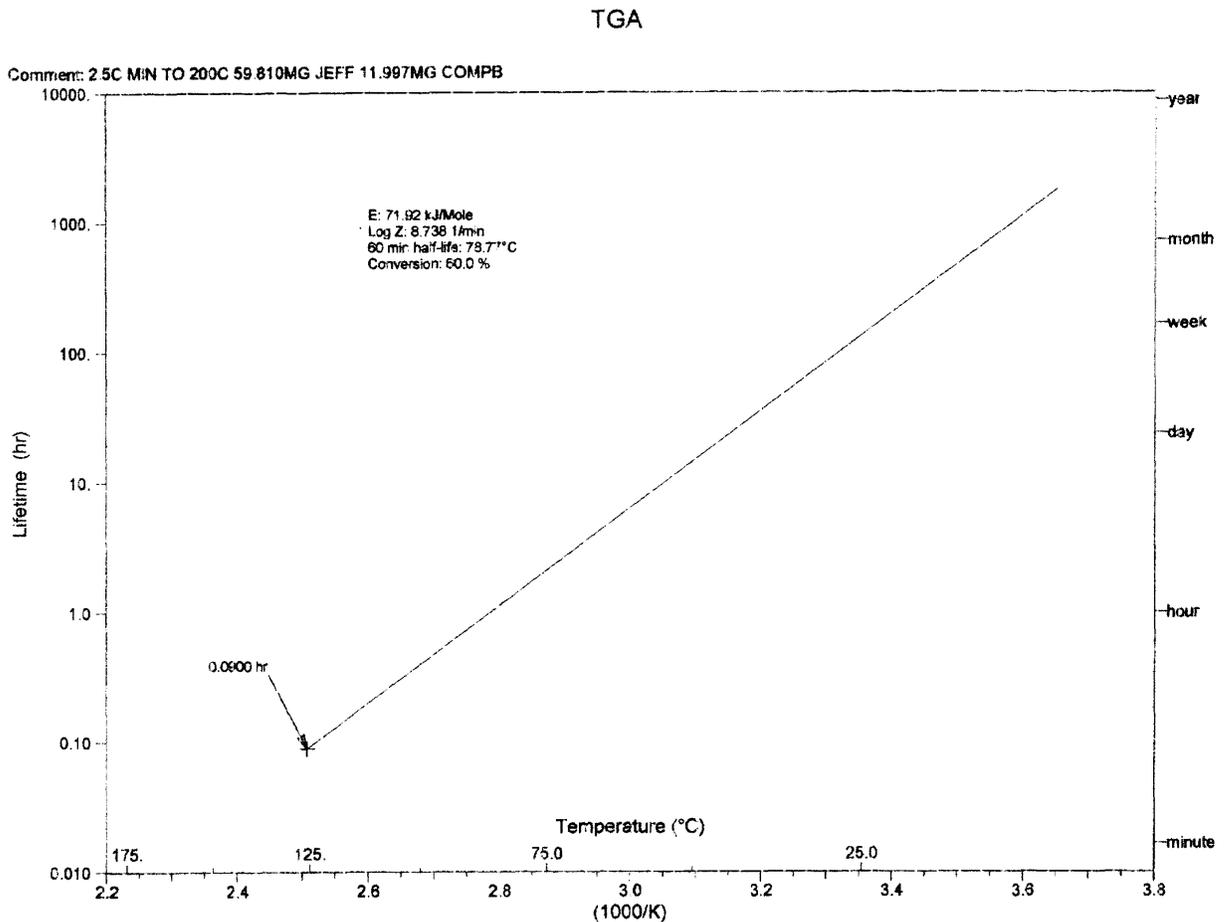


Figure 5. Conversion of Comp. B as a Function of Temperature

Figure 5 shows the temperature dependence of lifetime of Comp.B-Jeffamine mixture based on experiments conducted at Sandia National Labs. The pre-exponential factor and activation barrier have been calculated from the above plot, and their values are $9.1 \cdot 10^6 \text{ sec}^{-1}$ (with $n=0$) and 17 kcal/mol, respectively. However, the numerical simulation with the above rate constant was unable to reproduce the experimental temperature profile shown in Figure 4. This rate constant is too large to reproduce the slow temperature increase observed in experiment. The reaction rate for the above was therefore recalibrated against the empirical data shown in Figure 4. We have chosen Arrhenius type of first order rate constant expression with pre-exponential factor and activation barrier as $5 \cdot 10^{-2} \text{ sec}^{-1}$ (with $n=0$) and 2 kcal/mol respectively which are much lower than the experimental value. As will be seen later, that this rate constant is able to reproduce the correct temperature *vs.* time profile. The heat of the reaction is taken from the data provided by Sandia. This value is 468 cal/gm for Comp. B and Jeffamine reaction.

In the single fluid model, there is no mechanism for the gas to escape from the liquid. In order to model the foaming, we artificially remove the gas by introducing a pseudo reaction which partially converts gas back into a liquid. Negligible energy is involved with this contrived conversion of gas back to liquid, such that it does not affect the reaction rate or the temperature. If we did not remove this gas, the simulation would predict excessive foaming to the extent that the solution would foam out of the beaker, resulting in an unrealistic mass loss.

The rate constants of the gas \rightarrow liquid reaction dictates the degree of foaming. The rate constant for this reaction has been calibrated to match the foaming observed in the experiment. The pre-exponential factor for this reaction is chosen to be 0.1 sec^{-1} ($n=0$) with zero activation barrier. This essentially means the gas \rightarrow liquid conversion is temperature independent.

4.4 Properties

Selected properties of Jeffamine and Comp B are provided in Table 2. A more complete list of properties is provided in Appendix A. The reference enthalpy of the TNT and Epoxy in the model is adjusted to correspond to the heat of reaction as measured by Sandia.

Table 2. Material Properties (Courtesy of Sandia National Laboratories)

Material	Density gm/cc	Viscosity (cps)	Density gm/cc	Conductivity Cal/sec/cm/°C
Jeffamine	0.981	70 at 25C	0.981	$4.70 \cdot 10^{-4}$
Compound B	1.65	11200 at 25C* 25 at 130C*	1.65	$7.68 \cdot 10^{-4}$

*viscosity for mixture of Comp. B and Jeffamine

Special user-subroutines were created to compute the average density and conductivity of the fluid mixture as a function of the individual properties of the reactants and products, listed in Table 2. The formulas used are as follows:

Density:

$$\mathbf{r} = \frac{1}{\sum Y_i / \mathbf{r}_i}$$

where Y_i and \mathbf{r}_i are the mass fraction and density of the i^{th} species in the mixture.

Conductivity:

$$k = \sum k_i Y_i$$

where k_i are the thermal conductivities of the i^{th} specie in the mixture.

Since the density of the fluid is a function of the gas volume, production of gas due to reaction significantly reduces the average fluid density, causing foaming and buoyancy driven flow. This foaming action reduces the effective conductivity of the fluid, increasing the potential for overheating of the reaction. The inclusion of mixture properties in the model enables the use of the code to analyze these physical effects.

4.4 Model Assumptions

The current model has the following Assumptions:

- ❑ Single Fluid
- ❑ Simplified One-step Mechanism
- ❑ Calibrated Rates
- ❑ Pre-melted explosives

The limitation of the single fluid approach is that it cannot model the rise of bubbles through the liquid. Instead, it considers the combination of liquid and gas as foam with common velocities. The simplified one-step mechanism treats the reaction as an averaged process, when in fact, multiple reactions are occurring. Given the assumed one-step reaction mechanism, the rates of the reaction were calibrated using empirical data.

Another assumption used in the model is that the explosives have already melted prior to the onset of reactions. Clearly, this is not the case for some of the chunk experiments. However, it does represent a “worst-case” scenario, and considering that the melting temperature of Comp B is 80C, is most likely a good assumption for the powder and flake experiments.

It is recommended that these assumptions be improved upon. However, they do not invalidate the conclusion of this report.

5. WORK ACCOMPLISHED

The original tasks, as listed in the proposal are

- ❑ Link the CFD-ACE+ Two Fluid/Chemistry Modules
- ❑ Conduct Literature Search of Jeffamine -RDX /TNT Mechanisms
- ❑ Create a Model of the Sandia Test and Prototype Reactors
- ❑ Validate with Sandia experimental measurements
- ❑ Documentation

All of these tasks were completed, as planned, with the exception that task one was modified such that a single fluid model was adapted to model the chemical reaction and fluid dynamics of the process. The work accomplished under these tasks is described in detail below.

5.1 Adapt the CFD-ACE+ Single Fluid/Chemistry Modules

The Chemistry module in CFD-ACE was adapted to simulate multi-step chemistry, including the formation of a gas phase in the liquid. In this simulation, single-phase

model with chemistry has been used. Within this framework, liquid is assumed to be a incompressible gas, but the properties of the liquid have been used (such as density, thermal conductivity, molecular weight). Two user subroutines have been written in order to perform this task. They are provided in the Appendix B.

5.2 Conduct Literature Search of Jeffamine -RDX /TNT Mechanisms

No literature data were found for the reaction mechanism between RDX/TNT with Jeffamine. This includes the order of reaction, reaction rate constants of every reaction pathways as a function of temperature. We therefore decided to calibrate the rate constant assuming that the entire process happens in one step. We preferred to use one-step reaction mechanism as opposed to multi-step. Number of unknown parameters in the multi-step mechanism would be large, and is therefore difficult to calibrate. In the one-step mechanism there are two unknown parameters (pre-exponential factor and the activation barrier) to be calibrated, and therefore relatively easier.

5.3 Create a Model of the Sandia Test and Prototype Reactors

Two-dimensional models of both the laboratory beaker experiment and the full scale reactor (four times the size of the laboratory beaker) were created. Figure 6 shows the model of the beaker reactor, with sample initial conditions and boundary conditions. The boundary conditions were set up to mimic the experiments as shown in Figure 4. For example, the boundary condition of the bottom wall of the beaker was set to the measured temperature profile of the hot plate heater element. The initial temperature of the mixture solution was set to 353K, which was the Jeffamine temperature when the Comp B was added.

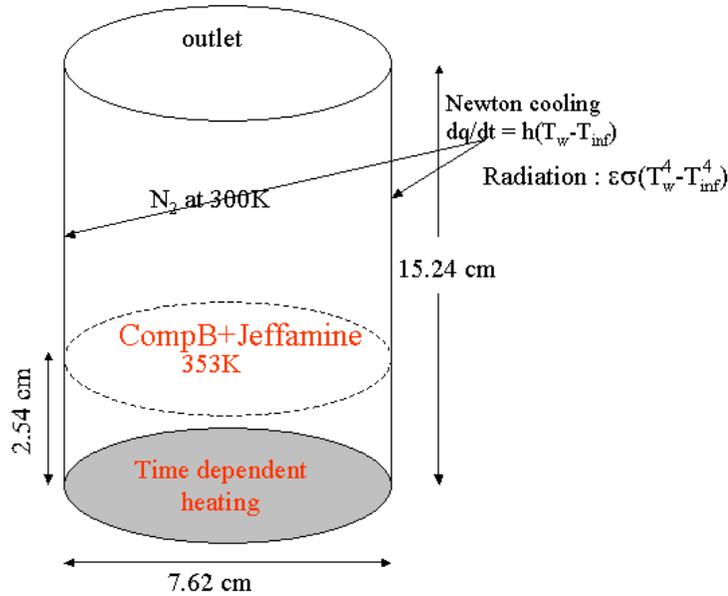


Figure 6. Numerical Model of the Beaker Experiment. The temperature of the bottom of the beaker is set according to the heating rate provided in Figure 4. External heat transfer and radiation boundary condition are applied to the sidewall of the beaker.

5.4 Validate with Sandia Experimental Measurements

The model was calibrated using the data in Figure 4. As discussed in Section 4.3. This required adjusting the pre-exponential and activation barrier of the assumed one step reaction. The numerical simulation was started at an experiment elapsed time of 270 seconds, which corresponds to the addition of Comp B powder.

Figure 7 provides a comparison of the predicted versus measured temperatures of the hot Jeffamine solution.

**Sandia Energetic Materials Neutralization
Jeffamine + Comp B Explosive Powder
(Test Date: 22 Feb 2001)**

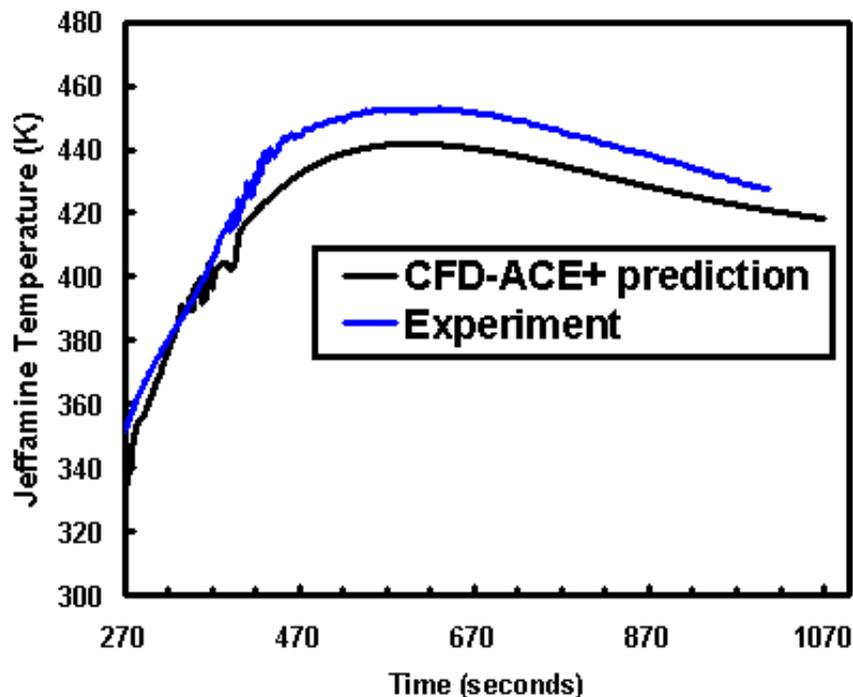


Figure 7. Comparison of Experimental Temperature Profile with the Simulation

Qualitatively the simulated temperature profile matches quite well with the experiment. This correlation includes the oscillations observed in both the experiment and the model during the rapid heat-up from approximately 320 to 420 seconds. These fluctuations are due to gravity driven convective rolls in the beaker. The model also matches the cool down phase of the solution quite well.

Quantitatively, the match between the experiment and the prediction is also reasonable, with the model predicting time of maximum temperature very well and the maximum temperature to within 10 degrees.

5.5 Parametrics

The calibrated model was used to investigate the effect of initial mixing, scale-up, and mixture ratio on the maximum temperature in during reaction.

Pre-mixing:

One concern is that the extent of melting and mixing, prior to the initiation of reaction, is expected to have a significant effect on the reaction rate. For example, large chunks, which would be expected to melt more slowly, would most likely begin reacting prior to fully melting. The existence of solid chunks would delay mixing of the explosive with the Jeffamine, and reduce both the reaction rate and the maximum temperature. On the contrary, thin flakes, which would more easily melt and mix, might result in rapid reaction and explosive temperatures. It is possible to investigate this effect in the model

by starting with different initial degrees of mixing. For the baseline, the Comp B and the Jeffamine were assumed to be fully melted and fully mixed. As a comparison, a subsequent simulation was conducted, using the same proportions of Comp B and Jeffamine, but with the Comp B initially concentrated in a melted “blob” in the middle of the beaker.

The predicted temperature for of the unmixed case is very similar to the fully mixed case, as shown in Figure 8. This is because, at the relatively slow reaction rates in the baseline case (on the order of minutes), there is sufficient time for the explosive and Jeffamine to fully mix due to natural convection. For a faster reaction, this might not be the case.

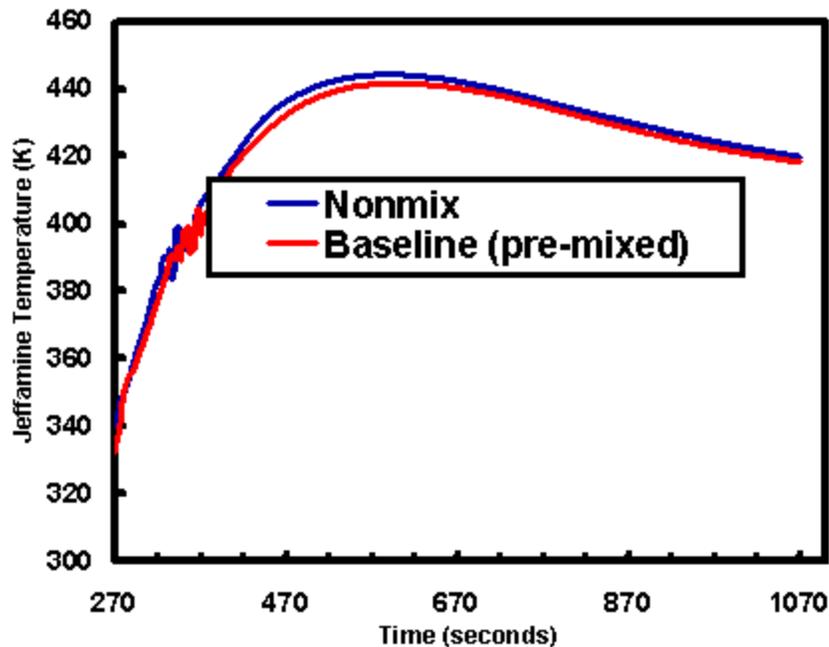


Figure 8. *Temperature Profile of Baseline Case (pre-mixed) vs. Non-Mixed Case. The maximum temperature for the mixed case is slightly higher than that of non-mixed case*

Scale-up:

The concern with scale-up is that as the reactor gets bigger, the volume of reactants gets larger by a factor of the characteristic length cubed, while the surface area available to cool the reaction only increases as a function of the square of this length. As such, hotter temperatures are expected for larger reactors, with the same relative proportion of reactants. In order to investigate this effect, a large-scale model was created. This model is 4 times larger than the laboratory scale beaker and resembles the actual full scale reactor used by Sandia (Figure 9). The model was then run using the same ratio of Comp. B to Jeffamine, as for the beaker scale reactor. The result is that the maximum temperature increases by nearly 69 degrees and occurs later in the process, as shown in Figure 10.

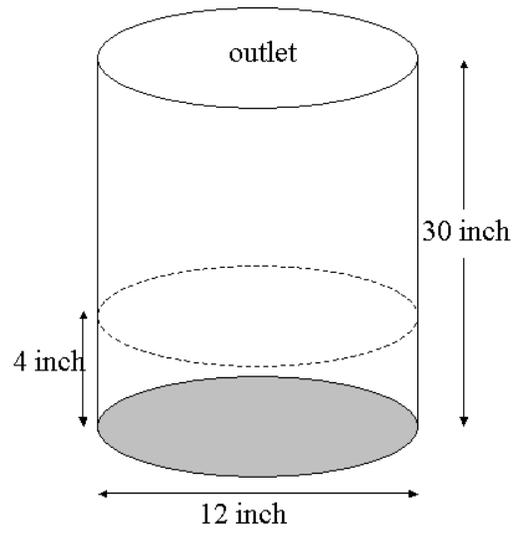


Figure 9. Geometry of the Actual Full Scale Reactor

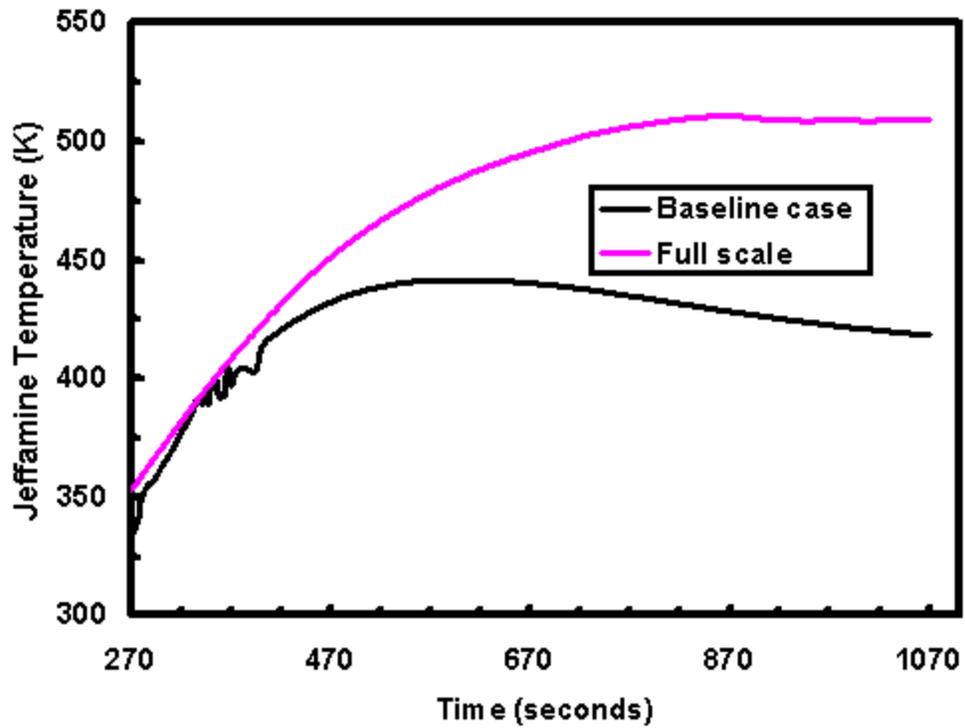


Figure 10. Comparison of Temperature Profile for the Baseline Case and to the Full Scale Reactor

Mixture ratio:

During reaction, the Jeffamine acts as a heat sink. In the experiments to date, the reaction was conducted using an excess of Jeffamine. If, instead, only the amount of Jeffamine required to react with the Comp B were used, the maximum temperature would be higher. This case was investigated by repeating the baseline case with 58 grams of Jeffamine instead of 97gms. The result was an increase in the peak temperature (see Fig. 11). These results indicate that Jeffamine is acting as a heat sink. Also, the maximum temperature is reached relatively quicker when less Jeffamine is used.

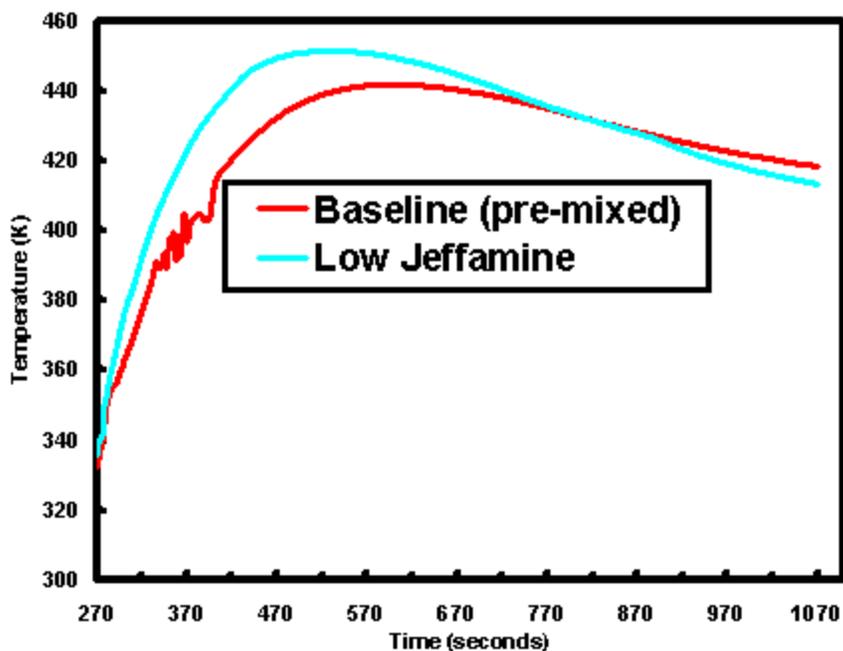


Figure 11. Effect of Maximum Temperature on the Amount of Jeffamine. Value of maximum temperature increases when less Jeffamine is used.

In summary of parametric studies, Table 3 shows the relative increase or decrease in the maximum monitoring point temperature relative to the baseline case.

Table 3. Parametric Study

	Time to Max T	Max T	Delta T
Baseline	~597 sec	442K	0
Unmixed	~592 sec	444K	2K
Decreased Jeffamine	~532 sec	451K	9K
Full Scale	~868 sec	511K	69K

Figures 12 and 13 provide two-dimensional images of the predicted reaction process. The images are split in half to present density on the left side and temperature on the right. Figure 12 shows the initial condition for the simulation (this corresponded to 270 elapsed time in the experiment). Figure 13 shows subsequent predicted temperature and density profiles at different stages of the reaction. The monitor points are indicated by the cross signs “+.” These monitor points correspond to the position of the thermocouple in the laboratory experiments. During the early stage of the reaction (approximately 370-470 seconds) there is a strong re-circulation near the bottom thermocouple. This buoyancy driven convection gives rise to the local oscillations in the measured Jeffamine temperatures evident in both the experimental data and the numerical predictions (Figures 7,8,10 and 11). Figure 13 shows the density change (or foaming) as a function of time. Based on the velocity field, the model predicts that the foam has begun to recede starting at approximately 414 seconds, even before the reaction temperature has peaked (597 seconds). Experimentally, this change in foam level is indicated by the thermal response of the upper thermocouples at the 425 and 600 ml level (figure 4). Note that the top thermal couple appears to be uncovered at 7 minutes (420 sec). Thus the predicted onset of the foam recession is very close to that indicated by the experimental data. Figure 14 provides a plot of the predicted temperature as “measured” at the numerical monitoring point corresponding to the 425 ml thermocouple. Although the thermal response at this monitoring point is temporally smeared due to the inaccuracy of the single fluid model in modeling foam formation and collapse, it indicates a qualitative rise in temperature similar to that of the real data.

One last important observation is that the position of the maximum temperature in the beaker is predicted to occur near the middle of the solution (see Figure 13 at 600 sec). This indicates that reaction is still occurring in the foam near the top of the beaker, with a corresponding temperature build-up. Furthermore, it indicates that a single thermocouple (e.g. such as the bottom thermocouple in the baseline case) located at the periphery may provide a misleading peak temperature which is significantly lower than the real peak.

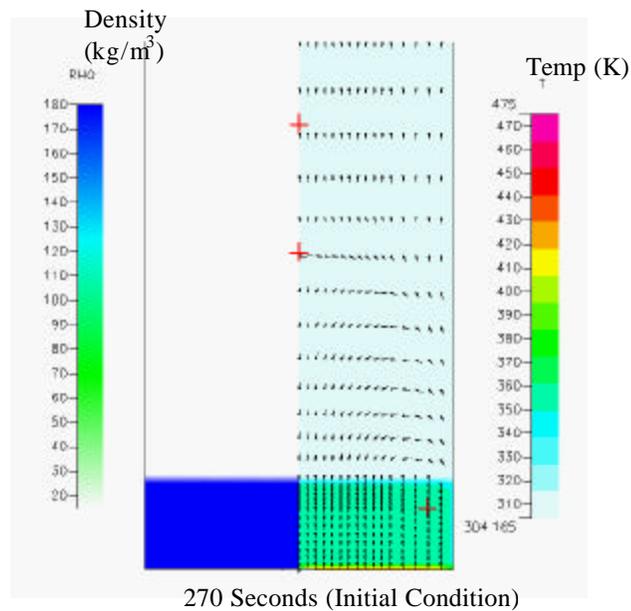


Figure 12. *Initial Conditions for the Simulation. Density and temperature are expressed in kg/m^3 and Kelvin.*

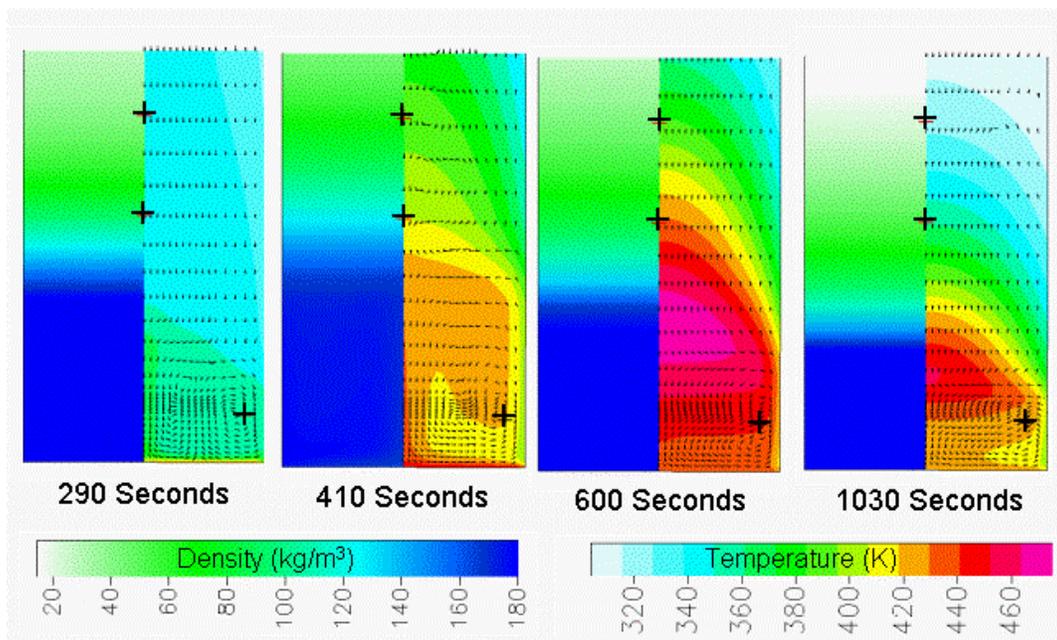


Figure 13. *Temperature and Density Profile at Different Stages of the Reaction. Temperature and density are expressed in Kelvin and kg/m^3 , respectively. The “+” signs indicate the positions of the thermocouples.*

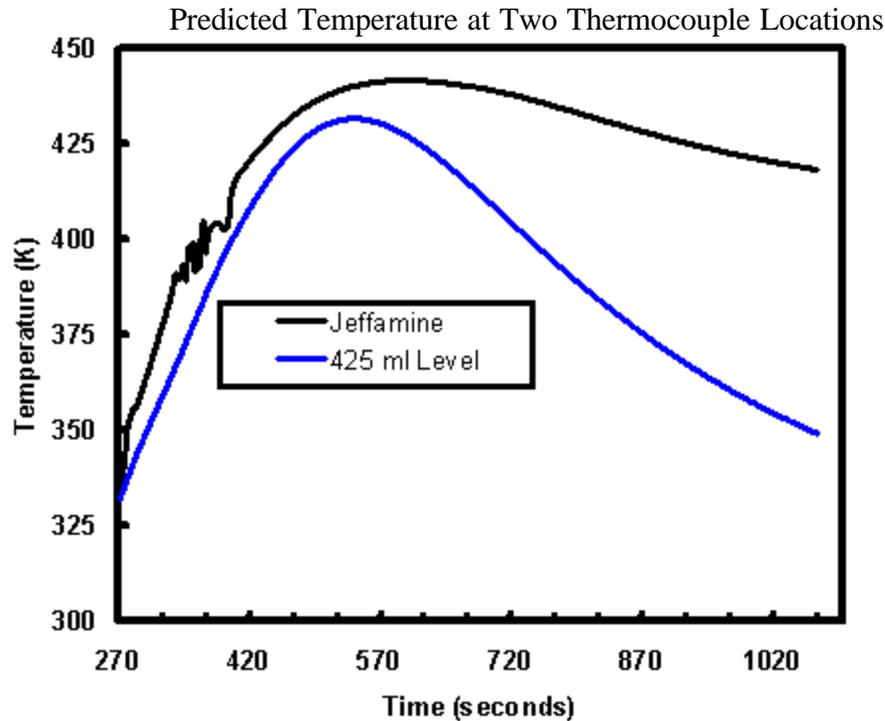


Figure 14. Temperature Profile at the 425 ml Level of the Beaker Compared to that of Jeffamine Solution

7. RECOMMENDATIONS AND FUTURE TASKS

Based on the above simulations, the following recommendations are made:

When scaling up, reduce the proportion of explosive to Jeffamine such that the increase in the quantity of explosive mass is directly proportional to the increase in surface area of the container.

Since Jeffamine acts as heat sink, a low proportion of Jeffamine may increase the temperature of the reaction. A higher proportion of Jeffamine is therefore recommended.

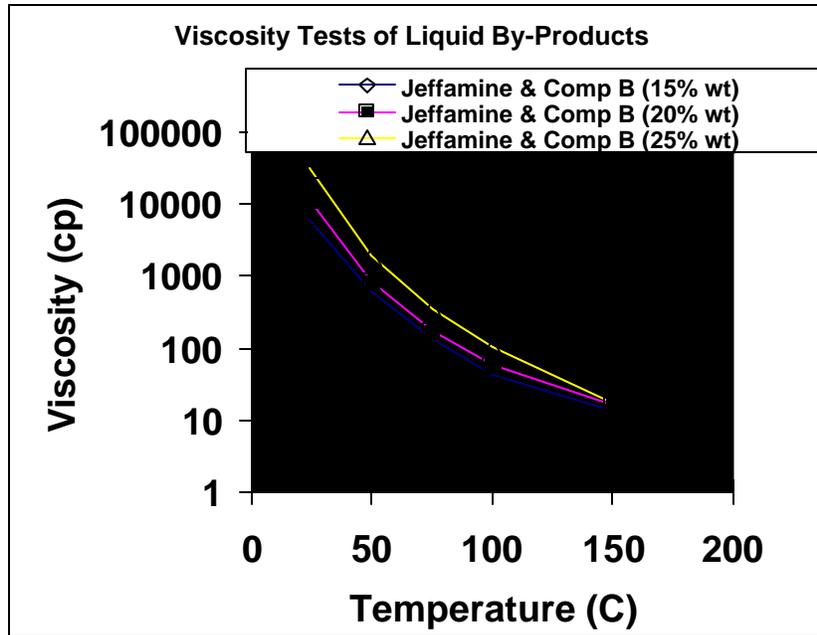
For a slow process (e.g. on the order of minutes), pre-mixing of the explosive and Jeffamine is not predicted to make much difference in the maximum temperature, since natural convection has time to mix the reactants during the reaction process. However, whether the materials are pre-mixed or not would be expected to influence the reaction time and the corresponding peak temperature for faster reaction times.

The hottest temperatures are predicted to occur in the center of the solution. Consequently, care should be exercised when adding additional reactants to the top of the reactor. Fresh material will be in contact with fluid at much higher temperatures than indicated by a thermocouple positioned near the bottom of the tank. Also, the mixer should be designed to reduce thermal stratification and the thermocouple(s) positioned to record the true maximum.

We expect the reaction occurring within the beaker is a complex, multi-step process as opposed to the simple one-step reaction assumed in the model. In order to perform simulation with experimental rate constant, the rate constants measurements of all steps should be performed. In addition, a two fluid model with chemistry would be required to more accurately predict the foaming action associated with this process.

APPENDIX A: Properties

Temperature Variation of Viscosity



Sandia Nat/l Labs							12/8/2000
Jeffamine + high explosives reactions							P. Walker
PROPERTIES OF REACTANTS AND PRODUCTS:							
	Density (g/cm³)	Melt pt. (C)	Heat of reaction (calories/gram of explosive)	Spec. heat (cal/g-°C)	Thermal conduct. (cal/sec/cm/°C)	Viscosity at 25 C (cps)	Viscosity at 130 C (cps)
Reactants:							
TNT solid	1.59	81		at 80C=0.374	8.83E-04	n/a	n/a
TNT liquid	1.47						
RDX solid	1.82	204		at 140C=0.446	6.91E-04	n/a	n/a
Comp B solid (60%RDX+40%TNT)	1.65	78-80		at 100C=0.312	7.68E-04	n/a	n/a
Jeffamine	0.981	n/a		at 130C=2.03	4.70E-04 approx.	70	
Products :							
TNT + jeff (10% by wt)		n/a				12,816	34
RDX + jeff (25% by wt)	1.03	n/a				6756	24
Comp B + jeff (20% by wt)		n/a	468			11,200	25
Jeffamine							
Temp C	Heat capacity J/g/deg C						
50	1.583						
60	1.626						
70	1.674						
80	1.724						
90	1.782						
100	1.848						
110	1.880						
120	1.988						
130	2.030						
140	2.039						
150	2.011						
160	1.962						
170	1.924						
180	1.878						
190	1.814						

APPENDIX B

User Subroutines

```
!*****
MODULE cfdrc_user
!*****
  IMPLICIT NONE

  INTEGER, PARAMETER :: int_p = SELECTED_INT_KIND(8)

  INTEGER, PARAMETER :: string_length = 80

  INTEGER, PARAMETER :: real_p = SELECTED_REAL_KIND(8)

  INTEGER, PARAMETER :: XDIR = 1, YDIR = 2, ZDIR = 3

! Utility parameters.
  REAL(real_p), PARAMETER :: zero = 0.0d0, one = 1.0d0, two = 2.0d0, &
    three = 3.d0, four = 4.0d0, &
    pi = 3.1415926535898d0

  LOGICAL:: first_time = .TRUE., error,first_time1 = .TRUE.

  INTEGER(int_p) :: ind_SANNO2=0, ind_TNT=0, ind_TNTB=0, &
    ind_N2=0, ind_JEFF=0,ind_VOL=0,ncells=0,ind_DENS=0

  REAL(real_p) :: sum_first=0.0
! Declare global variables
! USER CODE BEGIN

! USER CODE END

END MODULE cfdrc_user

SUBROUTINE ucond(iopt, vindex)
!*****
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!
! purpose : set local conductivity
!
! iopt: option for ways of specifying conductivity
!
! This routine is called on a cell-by-cell basis for each user-defined
! conductivity for each zone or volume condition where conductivity is
```

```

! specified as user defined.
!
! Use get_active_cell_index(ic,error) to get the current cell index in
! the volume condition.
!
! One may use get_value_one_cell to obtain values of various dependent
! variables such as temperature, velocity etc.
!
! Use set_value_one_cell to set the value for conductivity.
!
!-----

! Include required global variables declared in cfdrc_user module.
USE cfdrc_user

IMPLICIT NONE
REAL(real_p) , PARAMETER :: cond_SANNO2=0.0236,cond_TNT=0.37d0,  &
                        cond_JEFF=0.1974d0, cond_N2=0.0236,      &
                        cond_TNTB=0.1974d0
INTEGER(int_p), INTENT(IN) :: iopt, vcindex

REAL(real_p) :: SANNO2_mass_f, TNT_mass_f, TNTB_mass_f,N2_mass_f, &
                cond_cell, JEFF_mass_f
INTEGER(int_p) :: ind_COND

CHARACTER(len = string_length) :: var_name

INTEGER(int_p) :: ic

! Declare required local variables here.
! USER CODE BEGIN

! USER CODE END

!-----

!el@uiuc.edu Start writing code here.
! USER CODE BEGIN

IF (first_time) THEN

    first_time = .FALSE.
    CALL get_cells(ncells,error)

```

var_name = 'SANNO2'
CALL get_var_index(var_name, ind_SANNO2, error)

var_name = 'TNTB'
CALL get_var_index(var_name, ind_TNTB, error)

var_name = 'TNT'
CALL get_var_index(var_name, ind_TNT, error)

var_name = 'JEFF'
CALL get_var_index(var_name, ind_JEFF, error)

var_name = 'N2'
CALL get_var_index(var_name, ind_N2, error)

var_name = 'THERMAL_CONDUCTIVITY'
CALL get_var_index(var_name, ind_COND, error)

var_name = 'VOLUME'
CALL get_var_index(var_name, ind_VOL, error)

ENDIF

CALL get_active_cell_index(ic,error)

CALL get_value_one_cell (ind_SANNO2, ic, SANNO2_mass_f, error)

CALL get_value_one_cell (ind_TNT, ic, TNT_mass_f, error)

CALL get_value_one_cell (ind_JEFF, ic, JEFF_mass_f, error)

CALL get_value_one_cell (ind_TNTB, ic, TNTB_mass_f, error)

CALL get_value_one_cell (ind_N2, ic, N2_mass_f, error)

cond_cell = SANNO2_mass_f * cond_SANNO2 + TNT_mass_f*cond_TNT &
+ TNTB_mass_f * cond_TNTB + N2_mass_f*cond_N2 &
+JEFF_mass_f*cond_JEFF

CALL set_value_one_cell (ind_COND, ic, cond_cell, error)

! USER CODE END

RETURN
END SUBROUTINE ucond

SUBROUTINE udens(iopt, vcindex)

!*****

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!

! purpose : set local density

!

! iopt: option for ways of specifying density

!

**! This routine is called on a cell-by-cell basis for each user-defined
! density for each zone or volume condition where density is specified
! as user defined.**

!

**! Use get_active_cell_index(ic,error) to get the current cell index in
! the volume condition.**

!

**! One may use get_value_one_cell to obtain values of various dependent
! variables such as temperature, velocity etc.**

!

! Use set_value_one_cell to set the value for density.

!-----

! Include required global variables declared in cfdrc_user module.
USE cfdrc_user

IMPLICIT NONE

! Declare required local variables here.

! USER CODE BEGIN

! USER CODE END

! REAL(real_p) :: den_TNT,den_JEFF, &

! den_TNTB

REAL(real_p) , PARAMETER :: den_TNT=1650.0d0,den_JEFF=981.0d0, &

den_TNTB=981.0d0

INTEGER(int_p), INTENT(IN) :: iopt, vcindex

REAL(real_p) :: SANN02_mass_f, TNT_mass_f, TNTB_mass_f,N2_mass_f, &

den_cell, JEFF_mass_f, den_SANNO2, den_N2, wt_SANNO2, &
wt_N2, cell_T

INTEGER(int_p) :: ind_T
CHARACTER(len = string_length) :: var_name

INTEGER(int_p) :: ic

IF (first_time1) THEN

first_time1 = .FALSE.

var_name = 'SANNO2'

CALL get_var_index(var_name, ind_SANNO2, error)

CALL get_species_mol_wt(ind_SANNO2, wt_SANNO2, error)

var_name = 'TNTB'

CALL get_var_index(var_name, ind_TNTB, error)

var_name = 'TNT'

CALL get_var_index(var_name, ind_TNT, error)

var_name = 'JEFF'

CALL get_var_index(var_name, ind_JEFF, error)

var_name = 'N2'

CALL get_var_index(var_name, ind_N2, error)

CALL get_species_mol_wt(ind_N2, wt_N2, error)

var_name = 'DENSITY'

CALL get_var_index(var_name, ind_DENS, error)

var_name = 'T'

call get_var_index(var_name, ind_T, error)

ENDIF

CALL get_active_cell_index(ic, error)

CALL get_value_one_cell (ind_SANNO2, ic, SANNO2_mass_f, error)

CALL get_value_one_cell (ind_TNT, ic, TNT_mass_f, error)

CALL get_value_one_cell (ind_JEFF, ic, JEFF_mass_f, error)

CALL get_value_one_cell (ind_TNTB, ic, TNTB_mass_f, error)

CALL get_value_one_cell (ind_N2, ic, N2_mass_f, error)

CALL get_value_one_cell (ind_T,ic,cell_T,error)

den_SANNO2 = 101300.0d0 * wt_SANNO2/(8314.0d0*cell_T)

den_N2 = 101300.0d0 * wt_N2/(8314.0d0*cell_T)

den_cell = SANNO2_mass_f/den_SANNO2 + TNT_mass_f/den_TNT &
+ TNTB_mass_f/den_TNTB + N2_mass_f/den_N2 &
+JEFF_mass_f/den_JEFF

den_cell = 1.0d0/den_cell

CALL set_value_one_cell (ind_DENS, ic, den_cell, error)

RETURN

END SUBROUTINE udens

SUBROUTINE uout(iflag)

!*****

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!

! purpose : for customized user output.

!

! iflag: flag indicating calling location.

!

! This routine is called 5 times at different instances of iterative

! cycle indicated by iflag.

!

! iflag :

! 0 - At the beginning (only for dtf reading calls, At this point
! most of the other data may not be available.
! users can get variable indices, and may be
! external reading of files can be done with this
! flag = 0)

! 1 - At the beginning of RUN. (At this poin most of the boundary
! conditions, properties are set. users
! should be able to get cell or boundary
! values for different variables.)

! 2 - At the beginning of time step (only for transient problems).

! 3 - At the end of each iteration.

! 4 - At the end of each time step.(only for transient problems).

! 5 - At the end of RUN.

```

!
! One may use get_value_one_cell to get the values. To get the cell
! indexes, user has to supply the x,y,z locations and use the
! get_cell_index(vc_index,x,y,z,ic_global,error).
!-----

! Include required global variables declared in cfdrc_user module.
USE cfdrc_user

IMPLICIT NONE

REAL(real_p) :: VOL,sum,den_cell,TNT_mass_f,timet,ratio,sum_vol,sum1
INTEGER(int_p), INTENT(IN) :: iflag
INTEGER(int_p) :: i,user_iflag,time_step_no

!-----

    user_iflag = 4
    if(iflag /= user_iflag) RETURN
    sum = 0.0d0
    sum1 = 0.0d0
    CALL get_time(timet,time_step_no,error)
DO i=1,ncells
    CALL get_value_one_cell(ind_VOL,i,VOL,error)
    CALL get_value_one_cell(ind_TNT,i,TNT_mass_f,error)
    CALL get_value_one_cell(ind_DENS,i,den_cell,error)

    sum = sum+TNT_mass_f*den_cell*VOL
    sum1 = sum1 + den_cell*VOL
ENDDO
    IF(time_step_no == 1) sum_first = sum
    ratio = sum/sum_first
    write(10,*) timet, ratio,sum1

RETURN
END SUBROUTINE uout

```

Distribution

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