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ENERGETIC SALTS: DEGRADATION AND TRANSFORMATION

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ENERGETIC SALTS: DEGRADATION AND TRANSFORMATION

BY

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OF

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Abstract

The first part of this work mainly focuses on distinguishing and characterizing two white solids namely urea nitrate (UN) and nitrourea (NU) with similar melting point (~160^{o}C). Urea Nitrate is an inorganic salt. It has found use as an improvised explosive and was used in the first world trade center bombings. Nitrourea, a dehydrated product of UN, is an organic salt. In this study we reported and compared two routes to NU synthesis. We also proposed a decomposition route for UN.

The second part of the work investigates perchlorate contamination in soils following fireworks displays. A total of two hundred and twenty two soil specimens were collect before and after ten individual July 4th fireworks display events from 2007 to 2012. Soils were extracted in water and analyzed using ion chromatography by a modified EPA Method 314.0. Our study showed that soils are free of perchlorates before and four months after fireworks, but the soil samples collected within 24 hrs of fireworks showed perchlorate contamination from below the detection limit up to hundreds or thousands of nanograms per gram of soil. Through this study we also suggest that poor adsorption of perchlorates by soil matrices results in ground water contamination.

The third part of the manuscript explores the methodologies used to prevent solid phase changes in ammonium nitrate (AN) for expanding its usage in applications. These solid phase changes occur because of absorption of moisture from the atmosphere. AN was thoroughly dried to stop these phase changes and then attempts were made to maintain dryness of AN by coating with polymers. Dried AN and polymer coated AN performance was tested using differential scanning

calorimetry (DSC). We have succeeded in drying and encapsulating AN. Many questions are unanswered at this moment, such as the amount of polymerization, the uniformity of coating, the amount of absorption of moisture and if there are any more methodologies or other polymers which would improve the performance. This study is underway.

Acknowledgements

I would like to thank Dr. Jimmie C. Oxley and Dr. James L. Smith for their excellent mentorship, advises and suggestions during my research, and valuable time. I would like to thank to Dr. Louis J. Kirschenbaum, who has counseled me in both my research and career matters and for agreeing to be a part of my thesis committee. I owe Dr. Joel Dain for all the Friday afternoon coffee hours where we spent time lauging and discussing not only science related but also various other topics in general that enlightened my knowledge. I would like to thank him for the advises, suggestions he has provided me and also for being a part of my thesis committee. I would like to thank Dr. Aftab Ahmed for helping me with ICP-MS and also for serving in my thesis committee. I sincerely thank Dr. Lenore Martin for her time and being a member in my thesis committee.

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Thank Maria Donelly for helping me with sample collections. I would like to thank Hari Kateplli for helping me with FESEM. I would like to thank my undergraduates Elizibeth Hanke and Katelyn Dash for the help they have provided me.

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DEDICATED TO MY PARENTS

Preface

The following dissertation is written in manuscript format in accordance with guidelines provided by graduate school of University of Rhode Island. The first manuscript is entitled "Synthesis and Characterization of Urea nitrate and Nitrourea". In this study we distinguished Urea Nitrate and Nitrourea with various analytical techniques and proposed a decomposition pathway for Urea Nitrate. It has published in *Propellants Explosives and Pyrotechnics,* 2013, 38(3), 335-344.

In the second manuscript, "Fate of Perchlorates in Soils after Fireworks Displays", we have analyzed for perchlorates in soil samples collected before and after July 4th firework displays. This study gave us a scope to understand and confirm the poor adsorption of perchlorate salts by soil and ultimate contamination of ground water. This manuscript is under preparation for submission in *Journal of Environmental Management.*

The third manuscript is "Encapsulate Ammonium Nitrate". We have made attempts to dry ammonium nitrate and coat it with different polymers to prevent its phase changes that occur at atmospheric pressure i.e. IV-III and III-II. By preventing these phase changes in ammonium nitrate its use in applications like solid rocket propellants will be enhanced. We have made several attempts to dry and coat AN. Via this work we were able to lay down steps to answer many unanswered questions and explore more methodologies to improvise AN applications. This part of the work is in progress.

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Manuscript 1

Synthesis and Characterization of Urea Nitrate and Nitrourea

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Abstract

Although urea nitrate (UN) has not found use as a legitimate explosive, it has been popular as an improvised explosive. In this paper the dehydration product of UN, nitrourea (NU), is characterized for the purpose of distinguishing the two white solids. Although they both melt around 160°C, all other properties differ markedly as might be expected from an inorganic salt (UN) and an organic molecular compound (NU). Two reported routes to the NU product are compared and a decomposition route of UN proposed.

Keywords: Urea Nitrate, Nitrourea, Characterization, Mass Spectrometry, Infrared Spectrometry, Raman Spectroscopy, Differential Scanning Calorimetry, Thermal Gravimetric Analysis, Nuclear Magnetic Resonance, Solubility, Melting Point, Thermal Decomposition, Synthesis

1 Introduction

Dehydration of ammonium nitrate (AN) salts yields nitramine. Nitramine (eq. 1) is relatively unstable compared to nitroguanidine (eq. 2) and nitrourea (eq. 3). The difficulty in the synthesis of nitrourea (NU, CAS 556-89-8) from urea nitrate (UN, CAS 124-47-0) is providing adequate proof of product. Structures of NU and UN are shown in Figure 1. Both NU and UN are white solids with few physical properties available in the literature. Literature melting points are nearly the same, 158-160°C (UN) and 158°C dec (NU)[1]. Herein we report an extensive physical characterization of NU and contrast it with UN. In addition the two reported routes to the NU product are compared and a decomposition routes of UN proposed.

$$NH_4NO_3 \leftrightarrows H_2NNO_2 + H_2O \tag{1}$$

$$[HN{=}C(NH_2)NH_3]^+ NO_3^- \leftrightarrows HN{=}C(NH_2)NHNO_2 + H_2O \tag{2}$$

$$[NH_2CONH_3]^+NO_3^- \leftrightarrows NH_2CONHNO_2 + H_2O \tag{3}$$

2 Experimental Section

2.1 Synthesis

NU was synthesized using two different methods, both based on dehydration of UN. In each, the scale of the reaction was designed to make about 1 g of NU. The UN starting material was synthesized by the reaction of nitric acid and urea (U), as previously reported [2].

2.1.1 Method 1: Using UN and sulfuric acid

Sulfuric acid (7.54g, 0.0769 mol) was poured into a round bottom flask equipped with a football stirrer and cooled to -3.0ºC in a salt/ice bath. UN (1.17g, 0.0096 mol) was slowly added, maintaining the temperature between 0 and -3.0ºC. The mixture was allowed to stir for 30 minutes keeping the temperature below +3.0 ºC; then it was poured over ~10g of ice. The white precipitate that formed (NU) was collected on filter paper by vacuum filtration. The product was rinsed with three aliquots of cold water, and dried under gentle flow of air. The NU was re-crystallized from glacial acetic acid [1]. Re-crystallized yield was 125 mg, 1.19 mmol, 13%.

2.1.2 Method 2: Using UN, acetic anhydride and acetic acid

Acetic anhydride and glacial acetic acid were purchased from Fisher Scientific. Acetic anhydride (1.40g, 0.0137 mol) was placed in a round bottom flask with a football stirrer and acetic acid (14.0g, 0.233 mol) was added. The mixture was heated to 60ºC, and UN (1.40g, 0.0113 mol) was slowly added. The mixture was stirred at 60ºC for 15 minutes before removal of heat source. The mixture was allowed to quiescently cool to room temperature. NU was collected on filter paper by vacuum filtration, rinsed with three aliquots of benzene, and oven dried at 40ºC. The NU was re-crystallized from glacial acetic acid to yield 670 mg, 6.45 mmol, 67.2% NU [3].

2.2 Densities, Solubility and Melting Points of UN and NU

Ten density determinations for UN and NU products were obtained using a Micromeritics AccuPyc 1340 gas pycnometer. For each determination a sample cup (1.0 mL) was filled to about 75% capacity, weighed, capped, and inserted into the pycnometer. For each sample, ten helium purges and measurements were taken in succession. Arithmetic means and standard deviations of the UN and NU sets were calculated (Table 1).

The solubility of UN and NU in water, ethanol, methanol and acetone are reported in Table 1. Samples of 10-20 mg were weighed into two 10 mL glass vials and capped. Approximate solubility was determined by adding 1.0 mL and 2.0 mL aliquots to the first and second vial, respectively, and followed by sonication for 5 minutes. Samples were removed and visually inspected for presence of solid. If solid was still present, an aliquot of 2.0 mL was added to each vial and the process repeated until dissolved or 10.0 mL of solvent had been added. If the analyte was still not dissolved it was classified “insoluble.” Once approximate solubility was obtained, the process was repeated for new samples near the estimated solubility with small aliquots of solvent ranging from 0.05 mL – 0.75 mL using 100 µL and 1.0 mL syringes. Arithmetic means and standard deviations (5 replicates) were calculated for the UN and NU sets. Melting points of UN and NU are given in Table 1. Small amounts (~0.5-1.0 mg) of UN or NU were loaded into melting point glass capillaries and positioned into a MelTemp melting point apparatus. At a setting of 4, samples were observed as they heated. Temperature was recorded to the nearest degree as crystals of UN started to melt (range about 3-4^{o}C). The melting temperature was taken as the mid-point of the melt range. For NU, decomposition without melting was observed. No solid residue was observed after completion of this procedure. The decomposition temperature was recorded to the nearest degree. Arithmetic means and standard deviations (10 replicates) were calculated for the UN and NU sets.

2.3 Infrared (IR), Raman and Nuclear Magnetic Resonance (NMR) Spectroscopy

Fourier Transform Infrared (FTIR) spectra were obtained with Nicolet 6700 FTIR Spectrometer employing DTGS TEC detector and KBr beam splitter. Spectral range was 650 to 4000 cm^{-1} at resolution of 4.0 cm^{-1}. For attenuated total reflectance (ATR) of solids 22 scans was sufficient. An IR gas cell (pathlength 10 cm), with MCT/A detector, was used to monitor decomposition gases at 290˚C from a transfer line (250˚C) connected to a TA Instruments Q5000 thermogravimetric analyzer (TGA).

Raman spectra were obtained on a Bruker Sentera Raman Microscope. The microscope module was a Olympus BX51. Excitation source was a 785 nm diode laser. A Bruker Advance III nuclear magnetic resonance spectrometer (NMR) was used to collect both proton and carbon NMR spectra (^{1}H at 300 MHz and ^{13}C NMR at 75 MHz). In the proton mode 16 scans were collected; carbon mode was run proton decoupled and 512 scans were collected.

2.4 Gas Chromatography Mass Spectrometry (GC/MS)

Gas chromatograph (Agilent model 6890) coupled with mass selective detector (Agilent model 5793) (GC/MS) was used to characterize the samples. The GC/MS inlet was operated in splitless mode with inlet temperature of 125°C and a flow of 11.2mL/min (helium carrier gas). A 15 meter VF200MS column (J&W) with a 0.25mm inner diameter and a 0.25µm film thickness was operated under a constant flow condition of 1.5mL/min. The oven program had an initial temperature of 40°C with a 5 min hold followed by a 20°C/min ramp to 250°C and a post-run at 310°C for 1 min. The transfer line temperature was 250°C and the mass selective detector source and quadrupole temperatures were 230°C and 150°C, respectively. Chemical ionization (positive mode) was used with methane as the reagent gas.

2.5 Liquid Chromatography High-Resolution Mass Spectrometry (LCMS)

Both UN and NU were analyzed using liquid chromatography/high-resolution mass spectrometry (LCMS). The mass spectrometer was operated in both negative and positive ion mode under multiple ionization conditions coupled with the HPLC or direct injection into the atmospheric pressure chemical ionization (APCI) source via syringe pump. The vaporizer temperature was set at 150°C, and capillary was set to 125°C. The discharge current ranged from 5-10 μA, and the sheath gas and auxiliary gas were operated at 25 and 10 arbitrary units, respectively, for negative mode, and 20 and 0 for positive mode. When directly injected into the ionization source via syringe pump, sample flow rate was ~10 μL/min, and the material was dissolved in a 50:50 methanol-water solution. If adduct formation was desired, 0.25wt% carbon tetrachloride or 0.23wt% aqueous ammonium acetate was added to the methanol-water mixture. MS resolution was set to high (50,000 at 2 Hz), and the maximum injection time was 250 ms.

2.6 Differential Scanning Calorimeter (DSC)

Analyses were performed using a TA Instruments model Q-100 DSC. Samples were run under nitrogen flow (50mL/min), and the system was calibrated against indium (m.p. 156.60ºC, H_f 28.71 J/g). Sample amounts ranged from 0.2 to 0.5mg and were sealed in glass micro-ampoules (1.5mm O.D., 0.28mm wall thickness, and 8mm length) [4]. Samples were run in triplicate.

2.7 Thermal Gravimetric Analyzers (TGA)

The TGA (TA Instruments Q5000) used nitrogen purge gas to constantly sweep the balance (10 mL/min) and furnace (25 mL/min). Samples (10 mg) were held in open platinum pans (110 uL). Runs were performed in duplicate or triplicate, ramping the temperature at 20 ^{o}C/minute from 40°C to 400°C. For some samples decomposition gases were transferred via a heated (250^{o}C) transfer line to a Nicolet 6700 FTIR spectrometer.

3 Results

3.1 Infrared Spectroscopy

Figures 2 show the IR spectra of UN and NU, respectively. There were no significant changes in spectra of NU prepared using sulfuric acid or acetic anhydride. Both UN and NU had bands around 1700 cm^{-1} (CO) and in the high and low end of 1300 cm^{-1} (NO), but UN is clearly distinguished by the broad band around 2400 cm^{-1}. NU differs from UN between 3400 cm^{-1} and 2765 cm^{-1} where at least five bands are resolved. Both the Israeli Police Laboratory [5] and a Canadian government laboratory [6] have reported IR of UN. The Canadian facility assigned bands at 3402 cm^{-1} (NH_2 asymmetric stretch), 3354 cm^{-1} (NH stretch), 3198 cm^{-1} (NH_2 symmetric stretch), 1704 cm^{-1} (CO stretch), 1568 cm^{-1} (N–H), 1426 cm^{-1} (C–N), 1298 cm^{-1} (NO_3–). They suggested the peak at 2410 cm^{-1} in UN was OH symmetric stretching from hydrogen bonding of adjacent UN molecules, C=O--H-ONO_2. This is consistent with our comparison of IR spectra for UN and NU (Figures 2) where we found this band only in UN.

3.2 Raman Spectroscopy

Raman spectra of UN, NU, U and AN are given in Figure 3. Literature assignments are available for the prominent 1043 cm^{-1} and 1057 cm^{-1} lines in AN and UN, respectively. They are due to internal symmetric stretching of the NO_3^- anion [7,8]. The 715 cm^{-1} in AN and the 537 cm^{-1} in UN may also be due to internal covalent stretches of NO_3^- anion. A C-N symmetric stretching mode has been assigned to the 1011 cm^{-1} line in urea and is likely responsible for the 1020 cm^{-1} line in UN and possibly the 989 cm^{-1} line in NU. The weak lines in urea at 1625 and 1649 cm^{-1} have been assigned to NH_2 deformations. A similar assignment is possible in UN and NU. The 1540 cm^{-1} line in urea has been assigned to C-O stretching. Raman lines at 1583 cm^{-1} (NU) and 1574 cm^{-1} (UN) may also result from C-O stretches.

3.3 ^1H and ^{13}C NMR Spectroscopy

Proton NMR spectra of NU in d^6-acetone showed 2 broad peaks--one around 12 ppm, assigned to the proton adjacent to nitro group, and one around 7 ppm, assigned to the proton attached to the amino group. In contrast, UN showed a single peak at about 8 ppm; indicating that the hydronium ion exchanges with amino protons and cannot be observed by proton NMR. Proton decoupled ^{13}C NMR in d^6 acetone yielded a single peak-at 151 ppm for nitrourea and at 163 ppm for UN. The latter is higher due to proton-bonding on the oxygen site of the carbonyl group.

3.4 Gas Chromatography Mass Spectrometry (GC/MS)

No attempt was made to obtain GC/MS of UN. NU in acetonitrile solution was analyzed by chemical ionization GC/MS. NU, made by methods 1 and 2, as well as crude and recrystallized NU, were examined. The chromatographic peak of NU was broad and asymmetric with mass fragments: 44 (medium), 63 (large), 91 (small), 106 (small, $NU+H^+$).

3.5 Liquid Chromatography High-Resolution Mass Spectrometry (LCMS)

Mass spectra for UN and NU (HPLC and direct injection) are given in Figures 4 and 5. The solvent system was equal portions water and methanol spiked with 0.25 wt% carbon tetrachloride (CCl_4) for adduct formation. Most of the major peaks remained the same for NU spectrum whether the sample was introduced via HPLC or direct injection. The negative ion spectrum with CCl_4 (Figure 4) provided the best comparison of UN and NU. In the negative mode, the principle anionic fragments from NU were NU + Cl^- (139.986), NU - H^+ (104.010) and nitrate (61.987), and for UN, urea + Cl^- (95.002), 2 urea + Cl^- (155.034), nitrate (61.987), and nitric acid + NO_3^- (124.983), the latter two being observed with direct injection. In positive mode (Figure 5) the major fragment for both NU and UN was about m/z 61.040. For UN, in addition to 61.040 fragments, m/z 121.072 and 181.104 values suggest that the 61.040 m/z fragment be assigned as urea + H^+; and the other two fragments as 2x urea + H^+, and 3x urea + H^+ (Tables 2 & 3). The NU spectra did not have m/z 121.072 and 181.104 peaks leading to the assignment of the 61.040 fragment as cyanic acid complexed with ammonium ion.

Direct injection spectra of NU and UN in equal amounts of methanol/water with and without 0.23% ammonium acetate for adduct formation. With the ammonium acetate the negative ion spectrum of NU has 3 major m/z values (61.003, 61.987, 104.009). Tentative assignments are nitramide - H^+, nitrate, NU - H^+ (See Tables 2 & 3). The corresponding negative ion spectrum of UN produced only a nitrate peak at 61.987 m/z. The ammonium acetate positive ion spectra for NU and UN, both have a prominent m/z at 61.040 believed to be cyanic acid + NH_4^+ in NU and urea + H^+ in UN (for the same reasons as the positive CCl_4 spectra). The direct injections in methanol/water without adduct former for both NU and UN did not provide useful information.

Mass spectrum of nitrourea changed as the solution aged. In a freshly made methanol/water solution, NU - H^+ (104.010) was the largest peak in the negative mode of the MS fragmentation pattern. However, when a methanol/water solution of NU is allowed to sit one week under ambient conditions all evidence of the NU - H^+ fragment disappears and essentially only dicyanic acid - H^+ (85.044) becomes the major peak. This corresponds to the decomposition of NU previously reported [9].

3.6 Differential Scanning Calorimeter (DSC)

Figure 6 shows thermograms of UN and NU. The thermogram of UN showed a melt near 162°C and a sharp exotherm immediately thereafter at 167°C. A second broader exotherm was observed around 380°C (Table 4). At the completion of each DSC run samples were re-weighed to ensure there had been no leaks from the sealed capillaries. A small amount of white residue was observed in all UN samples. A sharp exotherm for NU was observed at about 162°C. While the DSC of UN showed a melt, the NU did not. The NU energy released, according to DSC, was about double the energy of UN (1100 vs. 480 J/g). For NU samples a trace amount of black residue remained.

3.7 Thermal Gravimetric Analyzer

A DSC trace of NU is shown is Figure 7. There was no discernable difference between the TGA traces of the crude and re-crystallized NU or between the NU made by the first or second synthesis methods. The TGA traces of UN (Figure 8, bottom) and NU (Figures 7) were distinctly different. Weight-loss of both UN and NU started at ~140^{o}C; NU exhibited a single weight-loss event, while UN experienced three thermal events. The TGA trace of urea (Figure 8, top) also exhibited three thermal events before being completely consumed. FT-IR spectra of the gases from decomposition of NU, UN and urea are compared in a stack plot (Figure 9) that also includes a mixture of CO_2 and N_2O gas (second spectrum from top). Overlapping spectra of neat CO_2 and N_2O gases and a mixture of the two, shown in Figure 10, distinguish peaks associated with these two gases. Comparison of the IR spectral region between 2100 cm^{-1} and 2400 cm^{-1} (Figure 11) for UN, NU, U and CO_2/N_2O mixture suggest that UN decomposition produced significant amounts of CO_2 while NU and urea decomposition did not. Further, N_2O gas appeared to be present in UN, NU and urea as demonstrated by prominent peak at 2240 cm^{-1} and an isolated doublet centered at 1288 cm^{-1} (Figure 10). The 1355 cm^{-1} peak in Figure 10, adjacent to the doublet and only appearing in UN was not assigned. Closer inspection of all three materials (Figure 11) reveals another peak centered between the N_2O peak (2240 cm^{-1}) and CO_2 peak (2360 cm^{-1}). This peak (2283 cm^{-1}) is assigned to gas phase isocyanic acid, literature value 2269 cm^{-1}[10]. Since NU was completely consumed, a suggested mechanism is as shown by eqs. 4 and 5. Isocyanic acid (HN=C=O) was also observed in the mass spectrum fragmentation pattern of NU and UN (Table 3). The other product nitramide (H_2NNO_2) is believed to decompose via eq. 5.

$$H_2N\text{-}C(O)\text{-}NH\text{-}NO_2 \rightarrow HN{=}C{=}O + H_2NNO_2 \qquad (4)$$

$$H_2NNO_2 \rightarrow H_2O + NNO \qquad (5)$$

The formation and subsequent hydrolysis of isocyanic acid to ammonia and carbon dioxide has been demonstrated[9]. This hydrolysis had been observed by mass spectrometry in the aging of aqueous methanol solutions of NU via eq. 6.

$$HN{=}C{=}O \text{ -- } H_2O \rightarrow NH_3 + CO_2 \qquad (6)$$

The first weight-loss event for UN (~140^{o}C) only consumed about 40% of the sample (Figure 8). The weight-loss events for NU and UN do not appear to proceed via the same mechanism as their decomposition products are notably different. The decomposition gases of UN exhibit peaks at 2400 and 1350 cm^{-1} not observed in the spectra of the NU off gases. Formation of urea from UN (eq. 7) and the subsequent reactions of urea (eqs. 8-13) to form melamine, cyanourea, biuret and cyanuric acid results in species which are likely to survive at high temperatures [10].

$$[NH_2C(OH)NH_2]^+NO_3^- \Leftrightarrow O{=}C(NH_2)_2 + HNO_3 \qquad (7)$$

$$O{=}C(NH_2)_2 \rightarrow NH_{\underline{3}} + HCNO \qquad (8)$$

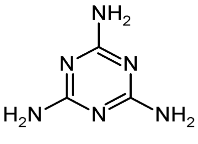
$$NH_3 + HCNO \rightarrow NH_4CNO \qquad (9)$$

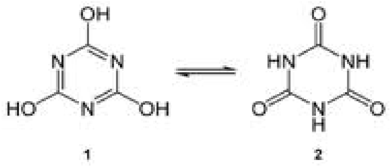
$$O{=}C(NH_2)_2 \xrightarrow{-H_2O} NH_2CN \rightarrow N_3(CNH_2)_3 \quad \text{melamine } (C_3H_6N_6) \qquad (10)$$

$$O{=}C(NH_2)_2 + HNCO \rightarrow O{=}C(NH_2)(NH\text{-}NC) + H_2O \quad \text{cyanourea } (C_2H_3N_3O) \qquad (11)$$

$$O{=}C(NH_2)_2 + HNCO \rightarrow NH_2CONHCONH_2 \quad \text{biuret } (C_2H_5N_3O_2) \qquad (12)$$

$$3\ HNCO \rightarrow O_3C_3(NH)_3 \quad \text{cyanuric acid } (C_3H_3N_3O_3) \qquad (13)$$





melamine cyanuric acid

The IR spectrum corresponding with the weight loss in the NU thermogram is shown in Figure 9. The location of the single weight-loss event for NU and the IR spectrum of its decomposition gases match those observed for urea (also Figure 9). The IR spectrum of urea decomposition gases match those predicted in eq. 5. The remaining solid residue was likely one of the products in eqs. 8-13. Not only is the TGA thermogram of UN more complex than that of NU, but the IR spectra of its decomposition gases also differed. Thus, urea nitrate decomposes via urea (eq. 7) and the decomposition route of urea (eqs. 8-13), while nitrourea decomposes via isocyanic acid and nitramide (eq. 4).

4 Conclusion

UN and NU can be distinguished by a number of their physical properties (Table 1). As expected UN behaves like an ionic compound and decomposes to urea and nitric acid. A difficulty in differentiating between UN and NU has been that they are both white solids with similar melting points.

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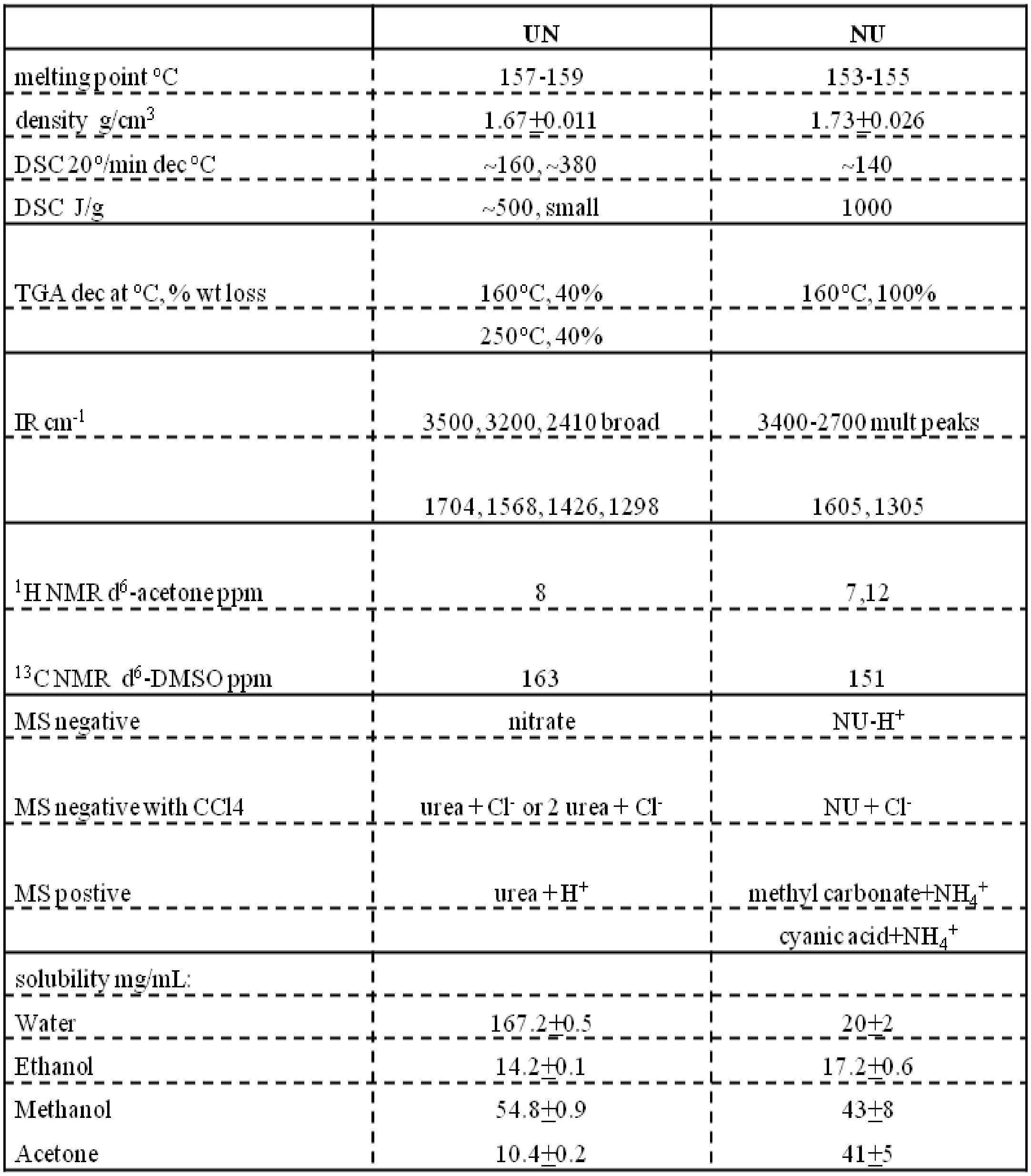
TABLE 1.



	UN	NU
melting point °C	157-159	153-155
density g/cm^3	1.67±0.011	1.73±0.026
DSC 20°/min dec °C	~160, ~380	~140
DSC J/g	~500, small	1000
TGA dec at °C, % wt loss	160°C, 40%	160°C, 100%
	250°C, 40%	
IR cm^{-1}	3500, 3200, 2410 broad	3400-2700 mult peaks
	1704, 1568, 1426, 1298	1605, 1305
^{1}H NMR d^6-acetone ppm	8	7,12
^{13}C NMR d^6-DMSO ppm	163	151
MS negative	nitrate	NU-H$^+$
MS negative with CCl4	urea + Cl$^-$ or 2 urea + Cl$^-$	NU + Cl$^-$
MS postive	urea + H$^+$	methyl carbonate+NH$_4^+$
		cyanic acid+NH$_4^+$
solubility mg/mL:		
Water	167.2±0.5	20±2
Ethanol	14.2±0.1	17.2±0.6
Methanol	54.8±0.9	43±8
Acetone	10.4±0.2	41±5

Table 1. Comparison of UN and NU Physical Properties

TABLE 2.

		Nitrourea		Urea Nitrate	
Solvent & Additive	Size	negative	positive	negative	positive
Liquid Chromatography					
methanol/water CCl_4	large	NU-H^+	isocyanic acid+NH_4^+	urea+Cl^-	urea+H^+ 2(urea)+H^+
	M-S	NU+Cl^- dicyanic acid-H^+ nitramide+Cl^-	methyl carbamate+NH_4^+ methyl carbamate+H^+	2(urea)+Cl^- biuret+H^+ methylol urea+Cl^-	3(urea)+H^+ methylol urea+H^+ urea+NH_4^+
methanol CCl_4	large	NU-H^+	isocyanic acid+NH_4^+	urea+Cl^-	urea+H^+ 2(urea)+H^+
	M-S	NU+Cl^- dicyanic acid-H^+ nitramide+Cl^-	methyl carbamate+NH_4^+	2(urea)+Cl^- biuret+H^+ methylol urea+Cl^-	3(urea)+H^+ methylol urea+H^+ urea+NH_4^+
Direct Inject					
methanol/water CCl_4	large	NU-H^+	N/A	NO_3^-	2(urea)+H^+
	M-S	NU+Cl^- nitramide+Cl^- NO_3^-		HNO_3+NO_3^-	urea+H^+ 3(urea)+H^+ methylol urea+H^+
methanol/water NH_4 acetate	large	NO_3^- NU-H^+	isocyanic acid+NH_4^+	NO_3^-	urea+H^+
	M-S	nitramide-H^+			
no additive	large	urea-H^+	isocyanic acid+NH_4^+	NO_3^- urea-H^+	N/A
	M-S	dicyanic acid-H^+ NO_3^-	urea+NH_4^+ methyl carbamate+NH_4^+	Biuret-H^+	

Table 2. Summary of HRMS fragmentation

TABLE 3.

			Negative Mode							
			Nitrourea				Urea Nitrate			
Additive	Mode	Solvent	Obs. Mass	Assignment	Calc. Mass	Size	Obs. Mass	Assignment	Calc. Mass	Size
CCl_4	LC	Fresh 50-50 MeOH-H_2O	85.0050	[Dicyanic acid - H^+]$^-$	85.0044	S	95.0008	[Urea + Cl^-]$^-$	95.0018	L
			96.9799	[Nitramide + Cl^-]$^-$	96.9810	T	96.9978	[Urea + $^{37}Cl^-$]$^-$	96.9988	M
			104.0090	[Nitrourea - H^+]$^-$	104.0102	L	102.0299	[Biuret - H+]-	102.0309	T
			139.9858	[Nitrourea + Cl^-]$^-$	139.9868	M	127.0271	[Ammelide - H^+]$^-$	127.0262	S
							155.0334	[2xUrea + Cl^-]$^-$	155.0341	S
		One Week Old 50-50 MeOH-H_2O	85.0050	[Dicyanic acid - H^+]$^-$	85.0044	L	Urea nitrate was not run with aged samples			
			96.9858	[Nitramide + Cl^-]$^-$	96.9810	S				
	Direct Inject	50-50 MeOH-H_2O	61.9871	[$Nitrate^-$]$^-$	61.9884	S	61.9878	[$Nitrate^-$]$^-$	61.9884	L
			96.9799	[Nitramide + Cl^-]$^-$	96.9810	S	124.9829	[Nitric acid + NO_3^-]$^-$	124.9840	T
			104.0090	[Nitrourea - H^+]$^-$	104.0102	L				
			139.9859	[Nitrourea + Cl^-]$^-$	139.9868	M				
NH_4^+ Acetate	Direct Inject	50-50 MeOH-H_2O	61.0032	[Nitramide - H^+]$^-$	61.0044	S	61.9872	[$Nitrate^-$]$^-$	61.9884	L
			61.9871	[$Nitrate^-$]$^-$	61.9884	L				
			104.0090	[Nitrourea - H^+]$^-$	104.0102	L				

			Positive Mode							
			Nitrourea				Urea Nitrate			
Additive	Mode	Solvent	Obs. Mass	Assignment	Calc. Mass	Size	Obs. Mass	Assignment	Calc. Mass	Size
CCl_4	LC	Fresh 50-50 MeOH-H_2O	61.0401	[Isocyanic acid + NH_4^+]$^+$	61.0396	L	61.0401	[Urea + H^+]$^+$	61.0396	L
			76.0395	[Methylcarbamate + H^+]$^+$	76.0393	S	78.0665	[Urea + NH_4^+]$^+$	78.0662	T
			93.0659	[Methylcarbamate + NH_4^+]$^+$	93.0659	M	93.0660	[Methylol urea + H^+]$^+$	93.0659	S
							121.0721	[2xUrea + H^+]$^+$	121.0720	L
							181.1045	[3xUrea + H^+]$^+$	181.1044	T
		One Week Old 50-50 MeOH-H_2O	61.0401	[Isocyanic acid + NH_4^+]$^+$	61.0396	L	Urea nitrate was not run with aged samples			
			93.0658	[Methylcarbamate + NH_4^+]$^+$	93.0659	M				
	Direct Inject	50-50 MeOH-H_2O	N/A				61.0394	[Urea + H^+]$^+$	61.0396	M
							121.0724	[2xUrea + H^+]$^+$	121.0720	L
							130.0652	[Cyanuric acid + H^+]$^+$	130.0253	S
							181.1049	[3xUrea + H^+]$^+$	181.1044	S
NH_4^+ Acetate	Direct Inject	50-50 MeOH-H_2O	61.0401	[Isocyanic acid + NH_4^+]$^+$	61.0396	L	61.0408	[Urea + H^+]$^+$	61.0396	M
							62.0435	[Nitromethane + H^+]$^+$	62.0237	M
							93.0666	[Methylol urea + H^+]$^+$	93.0659	M

Table 3. Fragmentation patterns of NU and UN. Assignments with Cl^- adduct were supported by additional mass peaks corresponding to the $^{37}Cl^-$ adduct.

TABLE 4

UN Ramp Rate (°C/min)	MP (°C)	Max. (°C)	Heat (J/g)	NU Ramp Rate (°C/min)	Max. (°C)	Heat (J/g)
20	163.74	175.79	304.5	20	163.11	1143
20	163.77	174.27	627.3	20	164.15	1077
20	161.15	174.26	415.3	20	161.92	1099
10	159.18	166.7	477.6	20	163.69	887.1
10	159.42	167.12	477.4	20	154.21	1054
10	160.73	167.09	424.9	20	158.71	1113
10	159.51	167.13	399.14	10	152.68	1105
10	158.75	166.55	433.5	10	148.74	1140
				10	148.19	1089
				10	143.67	1045

Table 4. DSC Summary of Urea Nitrate & Nitrourea

FIGURE 1

Nitrourea (NU)

Urea Nitrate (UN)

Figure 1. Chemical Structures of Nitrourea (NU) and Urea Nitrate (UN)

FIGURE 2

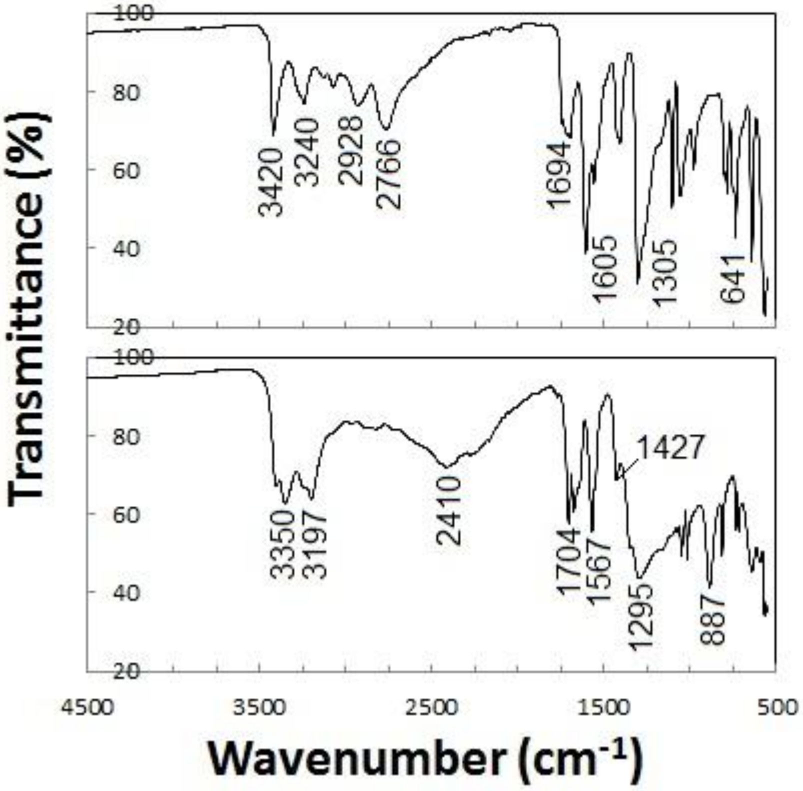


Figure 2. Stacked transmission mode IR spectra of recrystallized Nitrourea (Top) and Urea Nitrate (Bottom)

Figure 3

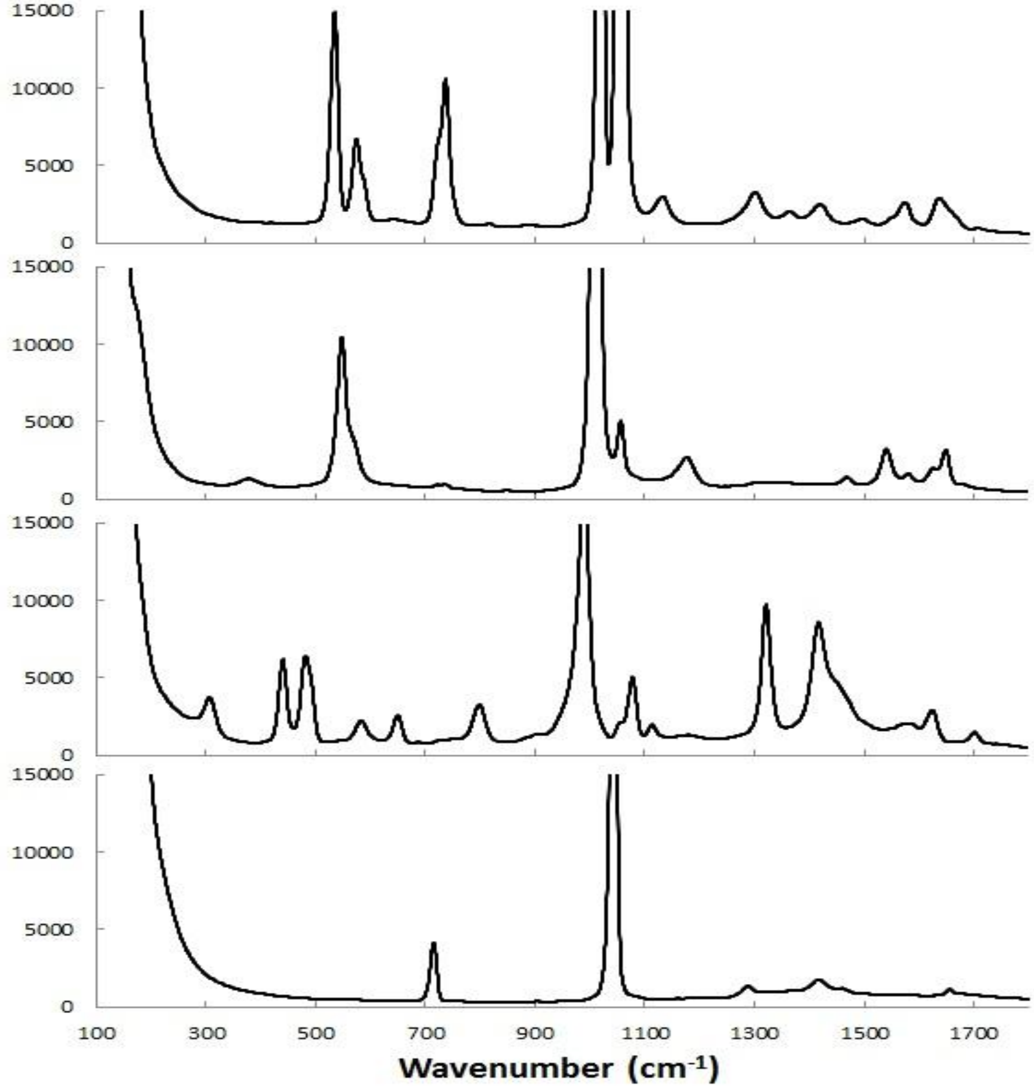


Figure 3. Raman Spectrum, from top, of UN, Urea, NU, Ammonium Nitrate, respectively. Ammonium nitrate exhibited additional small peak at ~2900cm^{1-}.

FIGURE 4

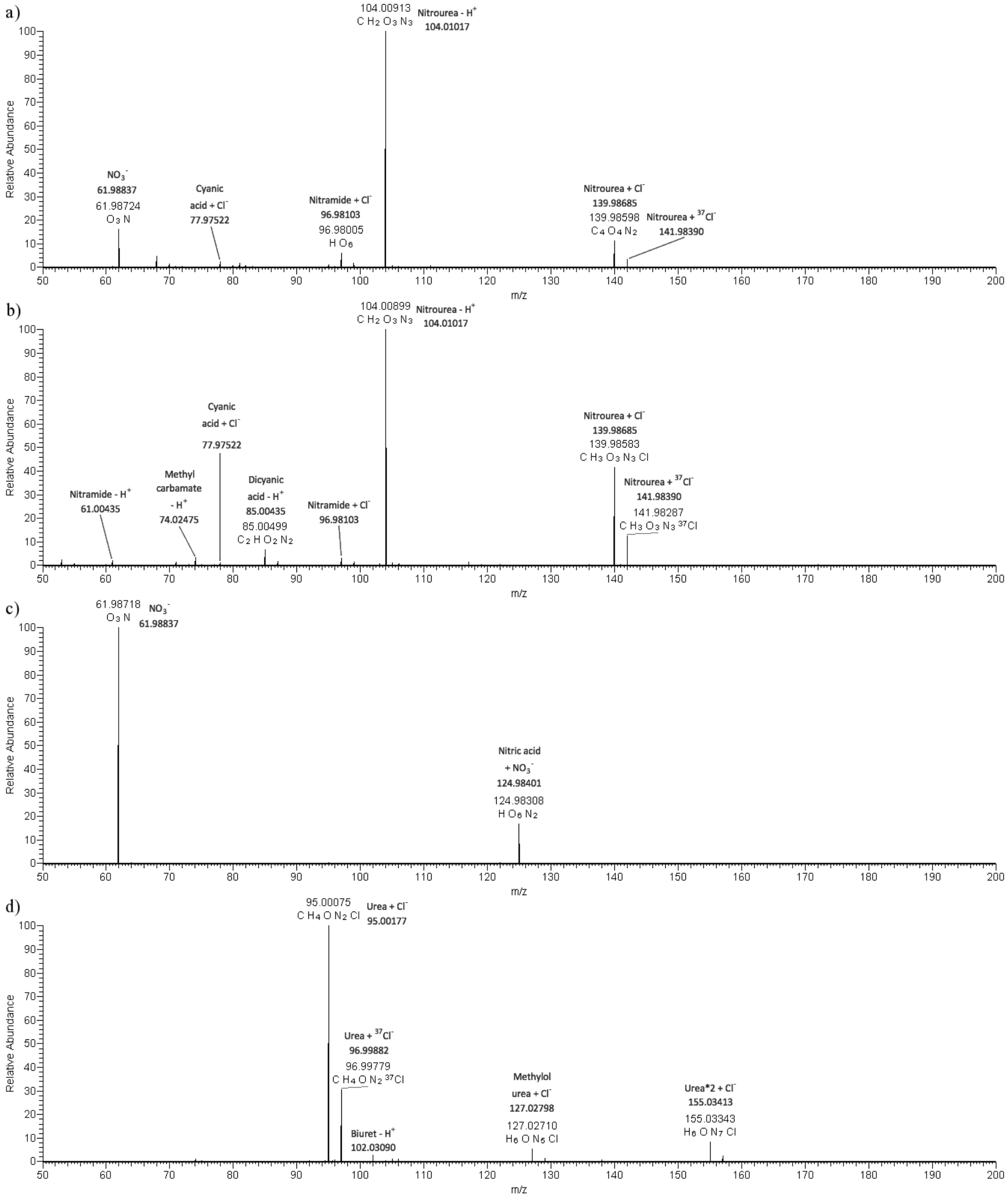


Figure 4. Negative mode mass spectra of NU and UN in 50-50 MeOH-H_2O with CCl_4. a) direct inject NU, b) LC NU, c) direct inject UN, d) LC UN.

FIGURE 5

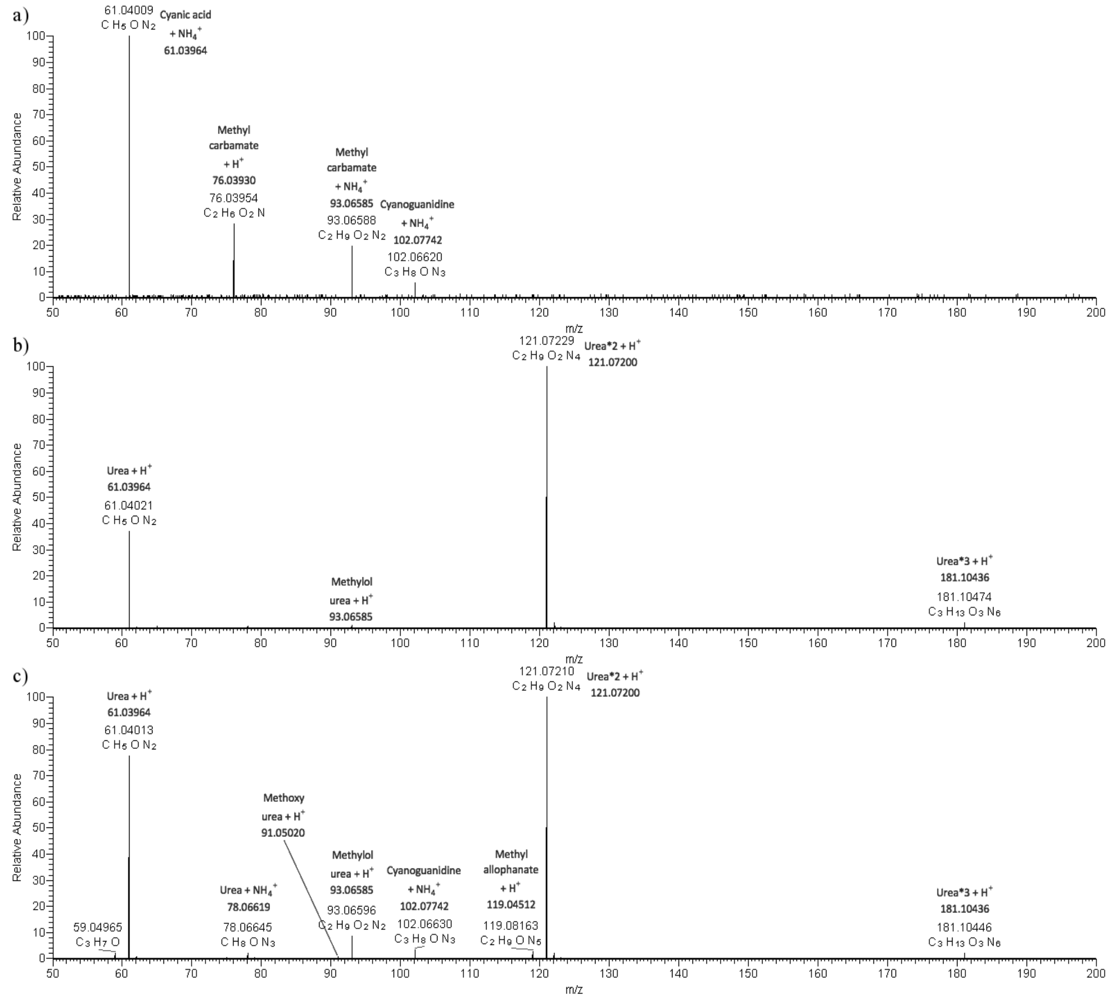


Figure 5. Positive mode mass spectra of NU and UN in 50-50 MeOH-H_2O with CCl_4. a) LC NU, b) direct inject UN, c) LC UN.

FIGURE 6

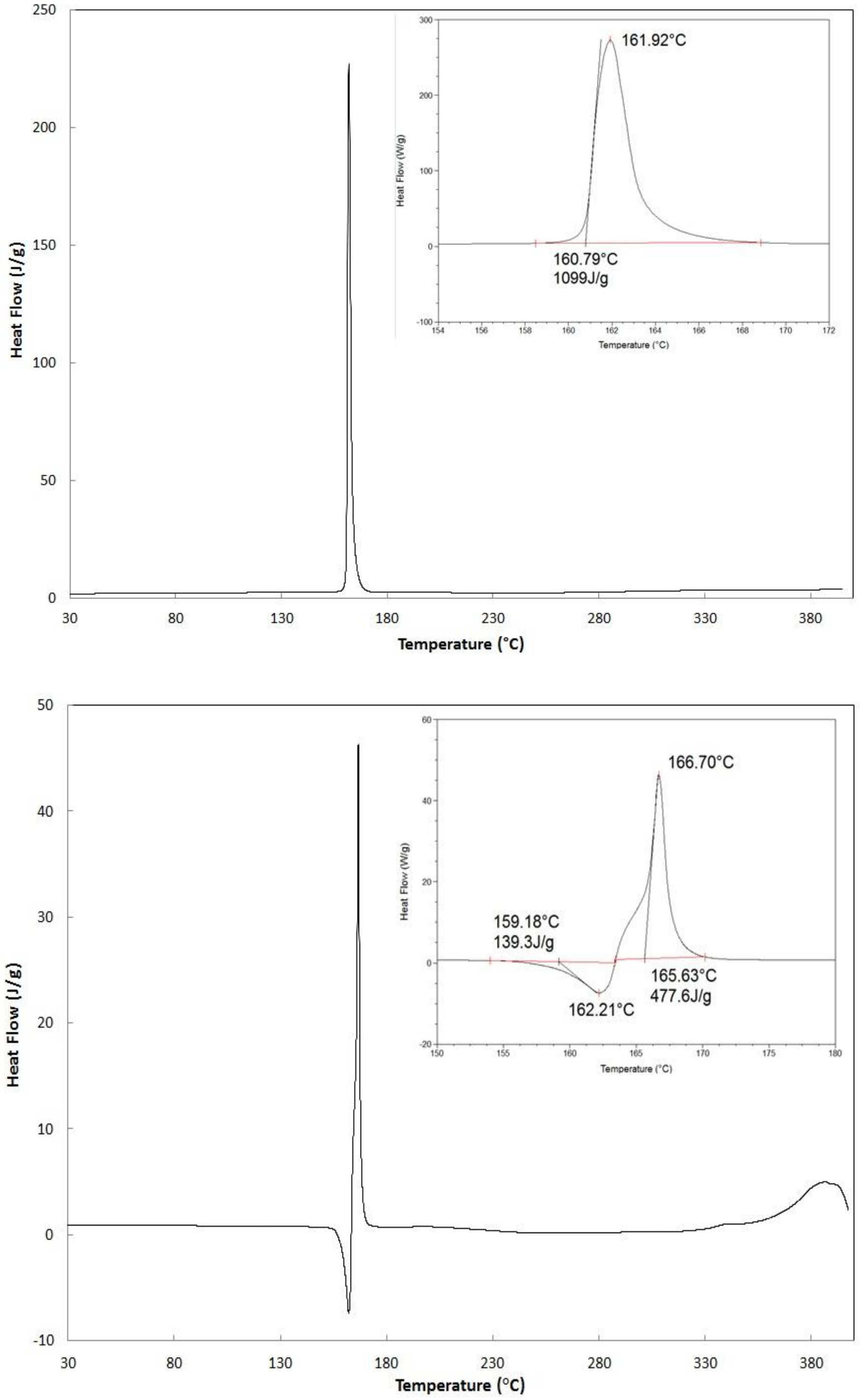


Figure 6. DSC thermograms of nitrourea (top) & urea nitrate (bottom) scanned at 10 °C/minute

Figure 7

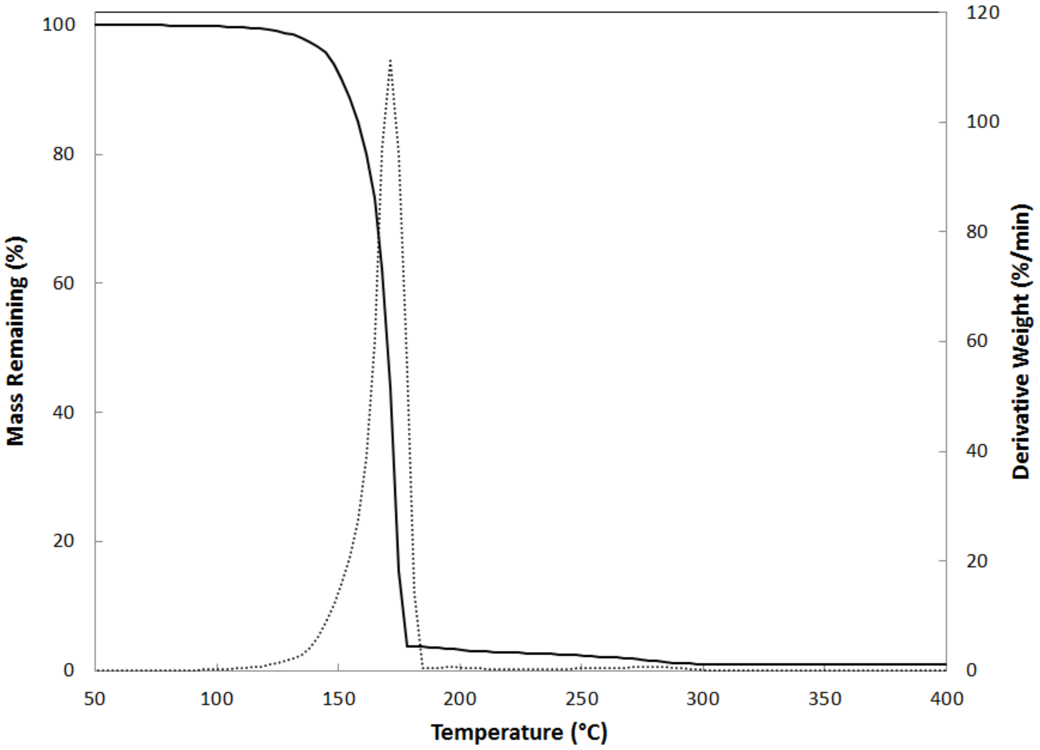


Figure 7. TGA trace of nitrourea

FIGURE 8

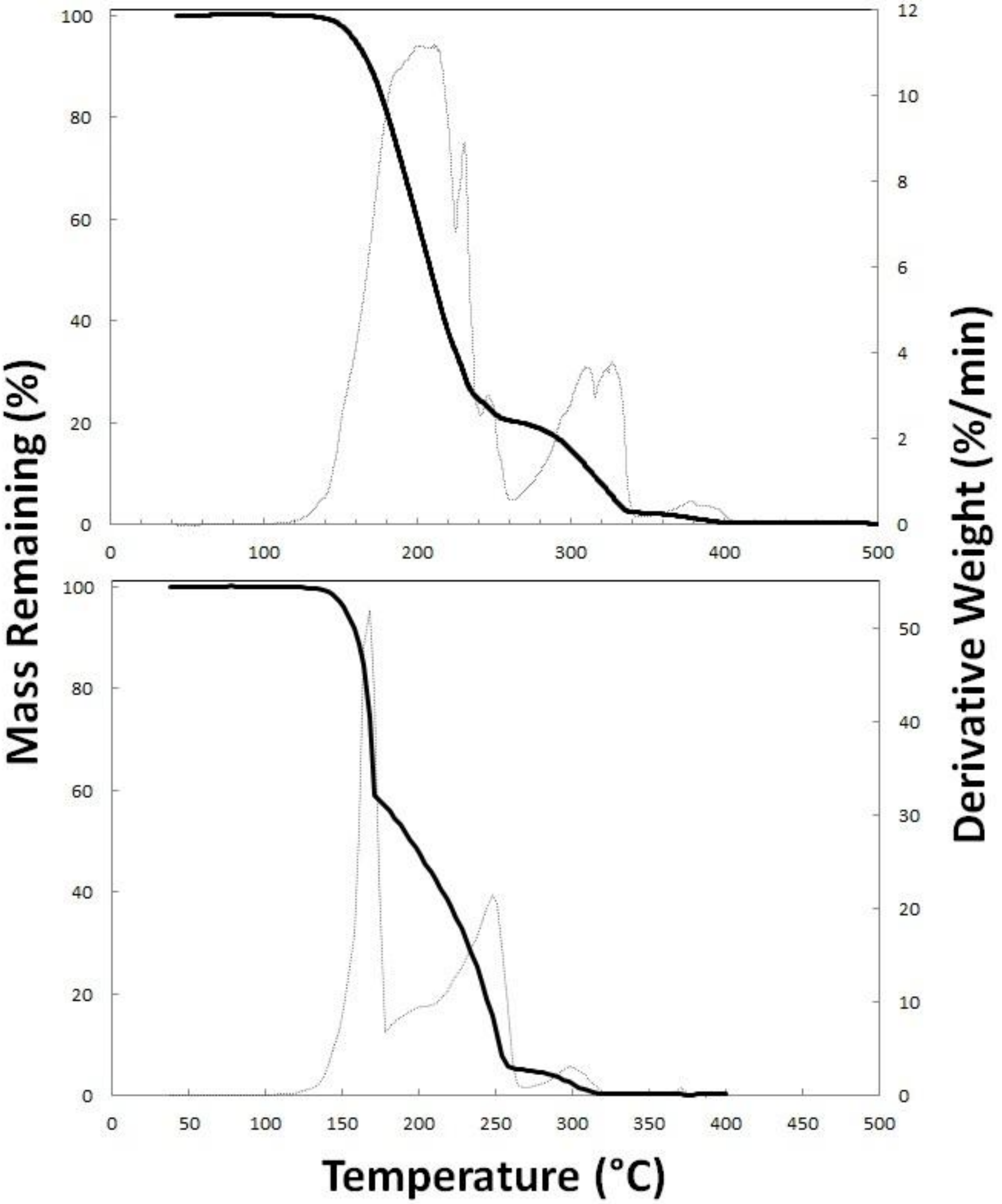


Figure 8. Stacked TGA Trace of urea (top) and recrystallized Urea Nitrate (bottom)

Figure 9

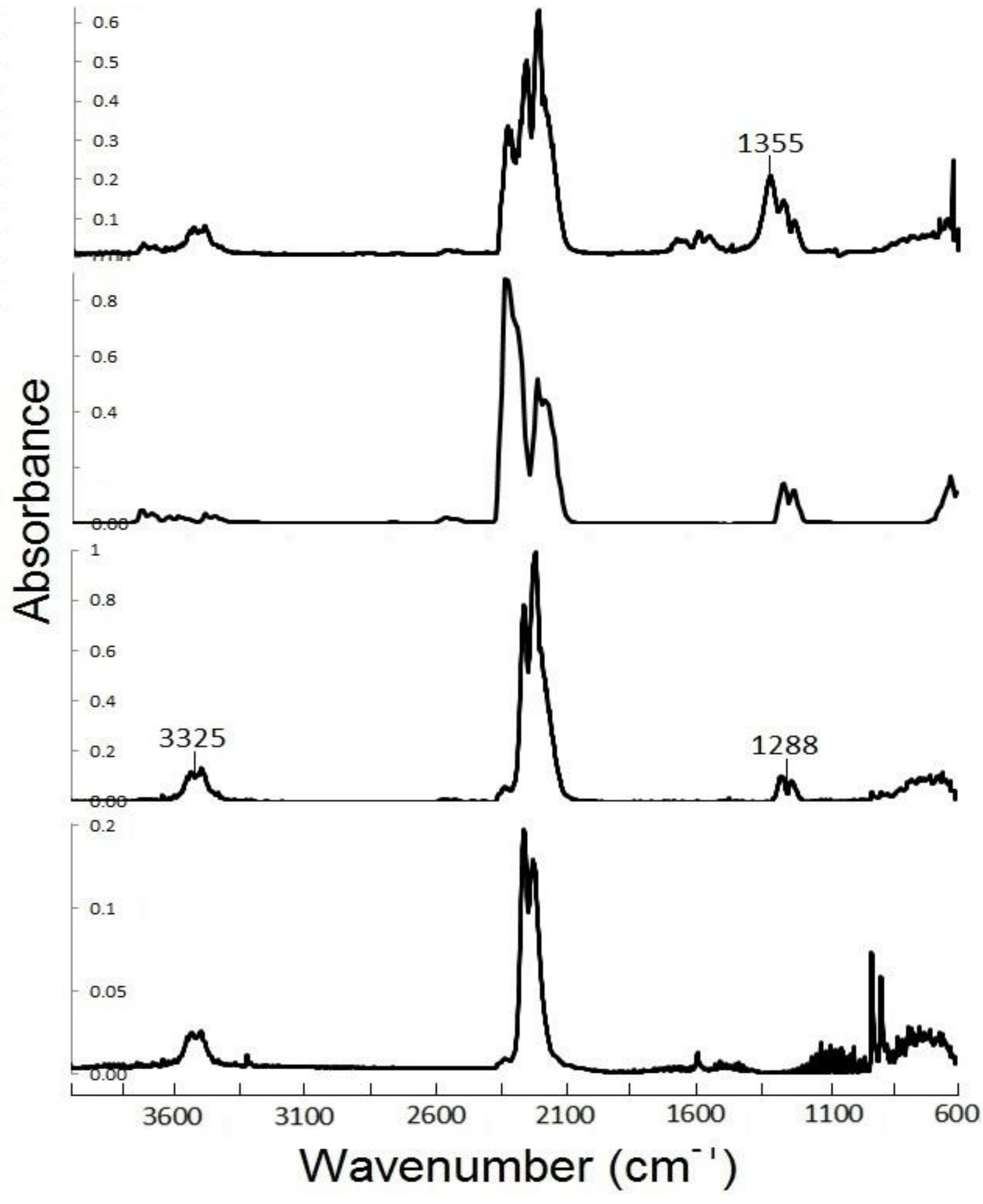


Figure 9. Stacked IR spectra of urea nitrate, CO_2 and N_2O mixture, nitrourea, and urea from top to bottom, respectively. Selected wavenumbers are shown.

FIGURE 10

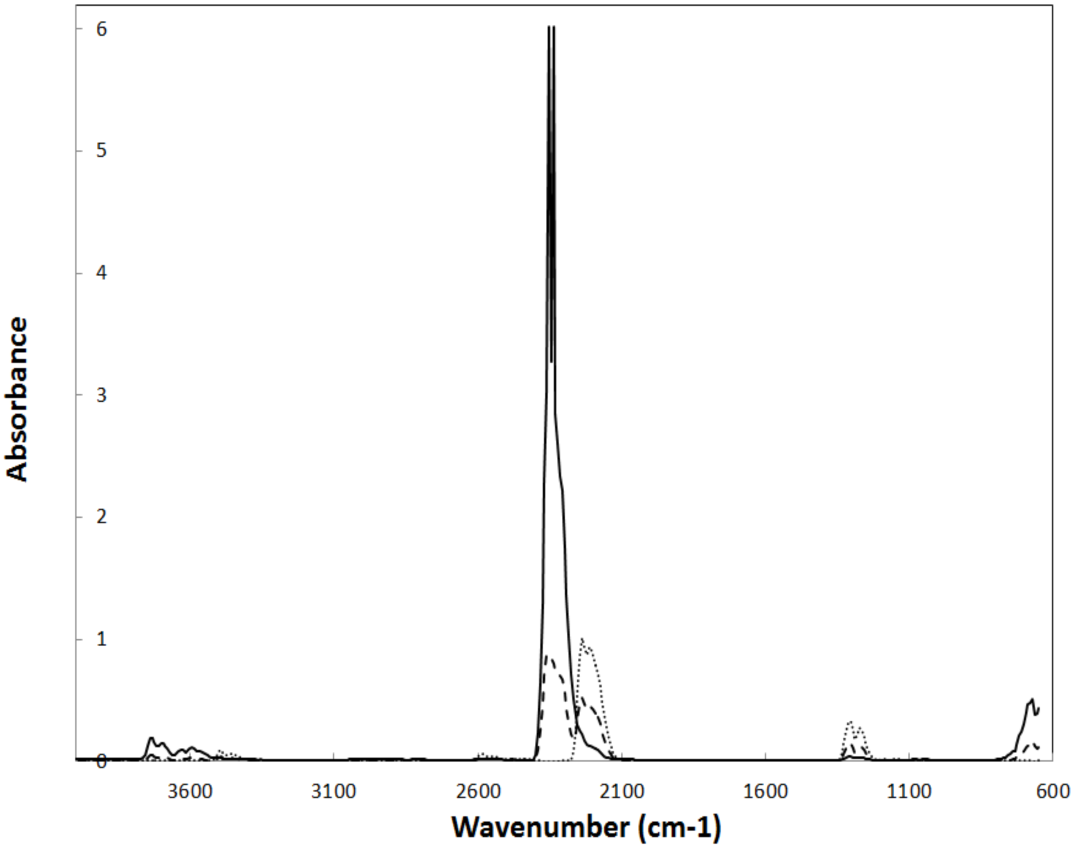


Figure 10. Overlap spectra of CO_2 (—), N_2O (···), and a mixture of both (---).

FIGURE 11

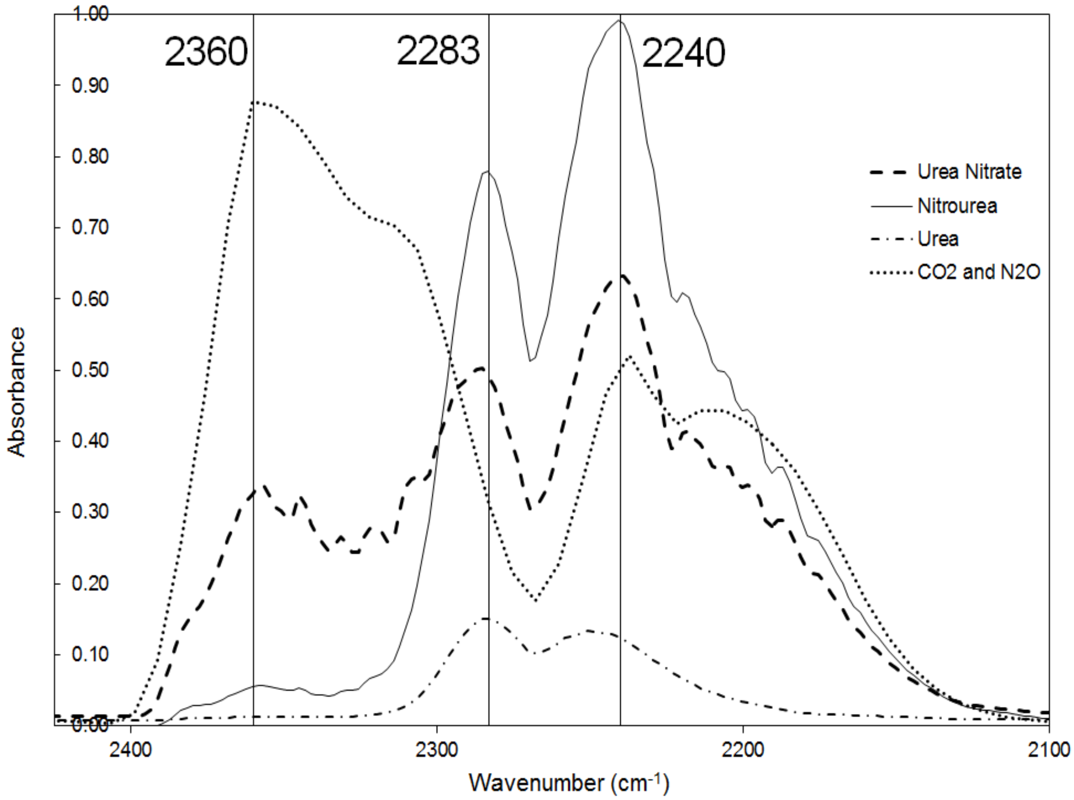


Figure 11. Overlap magnified IR spectra of urea nitrate, nitrourea, urea, and a mixture of CO_2 and N_2O.

Manuscript 2

Fate of Perchlorates in Soils after Fireworks Displays

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Abstract:

Perchlorate salts are used as oxidizing agents in solid rocket propellants, road flares, and fireworks. This study investigates the perchlorate contamination in a total of 222 soil samples collected before and after 10 individual July 4th fireworks events from 2007-2012. Aqueous extracts of soils were analyzed using ion chromatography by a modified EPA Method 314.0. Prior to fireworks displays, the concentrations of perchlorates in the soil were below the detection limit (0.5 ng). Afterwards, perchlorate concentrations ranged from below detection limits to hundreds or thousands of ng/g of soil. The levels of perchlorates dropped to below detection limits in soil samples collected 4 months after the event. Our study also suggested that poor sorption of perchlorates by the soil matrix, is likely to result in groundwater contamination.

Keywords: Perchlorates, Fireworks, Ion Chromatography, Soils

1. Introduction

Urbansky.et.al., 2001 reported homogeneous distributions of about 0.5-2 mg perchlorate anions per gram sodium nitrate fertilizer obtained from Chilean caliche. This high enrichment was attributed to natural sources. It is now evident that trace amounts of perchlorate ions appear to be widespread in areas around the world not usually associated with anthropogenic activity. In Arctic snow, having no known anthropogenic sources, concentrations ranged from about 1 to18 pg per g of snow (Furdui.et.al., 2010). Arid areas, where evaporation of moisture (i.e. from rain or snow) leaves dry deposition, tend to have elevated amounts of perchlorate in soil. Studies in unsaturated zones of semi-arid and arid regions of New Mexico, Nevada, Texas, Utah and Arizona indicated amounts ranging from 1-13 ng of perchlorate ions per gram of soil (subsurface/sediment samples)(Rao.et.al., 2007). Current theories suggest atmospheric reactions of chlorine compounds with ozone and other reactants result in formation of perchlorates. (Simonaitis-Heicklen., 1975, Prasad-Lee., 1994, Dasgupta.et.al., 2005, Gu.et.al., 2006) The authors of the Arctic snow study related ice depth to seasonal variation in perchlorate ions and suggested perchlorate formation was maximal during Arctic summer months. They concluded that peak production of perchlorate probably resulted from multiple mechanisms but the major contributor likely involved sodium chloride aerosols in the presence of electrical discharges. These authors point out that there are heightened baseline perchlorate levels at latitudes near the Gulf of Mexico where frequency of lightning flashes are highest in contrast with the Arctic where lightning activity is minimal and perchlorate concentrations are relatively low. They also concluded that perchlorate formation does not contribute significantly to chlorine removal from the atmosphere. Proliferation of perchlorates is almost entirely the result of activities considered essential in the civilized world. Significant anthropogenic sources include rocket fuels, road flares, munitions, blasting agents and pyrotechnics (fireworks) (Oxley. et. al., 2009). Detection of perchlorate from specific sources is elusive because perchlorate salts are mobilized when in contact with water and ultimately move into the water table. Some monitoring studies of soils, ground water, tap water and bottled water from industrialized countries are available in the literature (Kosaka. et. al., 2007, Kannan. et. al., 2009, Wu. et. al., 2010, Her. et. al., 2011). Values range from tenths of ng/g to about 10 ng/g. There are a few studies monitoring soils and ground water located near fireworks manufacturing facilities and active fireworks displays. The occurrence of perchlorate ions at these sites are as high as 7700 ng/g in contaminated ground water surrounding a fireworks manufacturing facility in India (Isobe et.al., 2012), 15 ng/g from soil samples immediately following a fireworks display in Germany (Scheytt. Et. al., 2011), 44 ng/g following a display in Oklahoma (Wilkin. et. al., 2007), 34000 ng/g (with extensive fireworks debris included) following a Massachusetts display (Mass. DEP, 2006). One study on Long Island, New York collected wet/dry atmospheric deposition in surrounding areas following a fireworks display (Munster. et. al., 2008). Average perchlorate concentrations were 0.21 ng/g with a maximum value of about 3 ng/g. In general for areas not involved in fireworks displays perchlorate concentrations were below the drinking water limit set by Massachusetts (i.e. 2.0 ng/g) (Daley, 2006). A study of large surface water reservoirs in the Great Lakes Basin and proximal to highly industrialized communities detected perchlorates near detection limits (0.2 ng/g) in only 8 out of 55 collection locations (Backus et. al., 2005).

The EPA has debated setting drinking water limits but to date have not arrived at a consensus. They currently listed perchlorate on a third level contamination candidate list (USEPA, 2011). Concern over the extent of perchlorate contamination in the environment relates from research suggesting harmful health effects. The physiological basis of adverse health effects is competitive inhibition of iodide uptake into the thyroid gland. Inadequate iodide levels in the thyroid result in decreased production of thyroid hormones T3 and T4, which play a role in regulating normal functioning at all stages of human life (Sherwood, 4th edition). Impact on the vital stages for growth and development of the central nervous system suggest that the fetus and the nursing child are particularly vulnerable. A National Academy of Science Committee and the EPA have suggested limits of 15ng/g water based on established health effects and current levels of perchlorate (Kucharzyk. et. al., 2009).

In this study we investigated the amounts of perchlorate recovered from soils at four sites conducting July 4th fireworks celebrations. A total of 222 soil samples collected from ten individual fireworks displays from 2007 to 2012 were analyzed. The purpose of this study was to evaluate perchlorate concentrations before and after such events. In most cases selected sites had been used for fireworks displays in previous years. With one exception perchlorate contamination, prior to the specific event, was not observed. Perchlorate content in measured masses of soils was evaluated from water extracts by ion chromatography according to a modified EPA Method 314.

2. Materials and methods

2.1. Sampling

Soil samples were collected before and after July 4th firework displays from 2007, 2009-2012 (5 years). Grass and other plant growth was removed from the top layer of the soil and discarded. Approximately 1-2 lbs of the soil was collected into Ziploc bags and stored at 4˚C until analysis.

2.2. Sample Preparation

Collected soil specimens (i.e. 1-2 lb each) were homogeneously mixed and air dried overnight, then sieved (mesh # 500µm) to remove small stones and other organic debris (MacMillan. et. al., 2007). Triplicate samples of soil (about 5.0 grams) were extracted in 18.0MΩ cm Milli Q water (10.0mL). Samples were agitated overnight in a shaker bath at 250 rpm and ambient temperature. The resulting slurries were centrifuged to collect the supernatant layer (2500rpm, 30min, and 25˚C). The resulting supernatant layer was centrifuged (4000rpm, 15min, and 25˚C) to remove fine particles and filtered through a 0.45-µm PTFE syringe filter and analyzed for perchlorates via EPA Method 314.0.

2.3. Sample Analysis

A Dionex ICS-2100 Reagent Free Ion Chromatograph was used for analysis of the supernatant layer for perchlorates, using a 100 μL sample loop, an IonPac AG16 guard column (4 X 50 mm I.D.), an IonPac AS16 analytical column (4 X 250 mm I.D.); 50.0mM potassium hydroxide mobile phase, flow rate of 1.50 mL/min and ASRS (4 mm). The heated conductivity cell suppression current was 190 mA. Samples were run in triplicates. Detection limit for perchlorates was about 5 μg/L (0.50 ng). Samples containing excess perchlorate were diluted accordingly. An external calibration method was used. Calibration standards were prepared from dilutions of a certified standard solutions (999mg/ml, VHGLabs, Cerilliant) with very low conductivity water (18.0MΩ·cm) obtained from a Milli Q Water System. Water blanks and quality assurance samples were introduced following every 6-9 authentic samples.

2.4. Recovery Studies

A protocol analogous to that for authentic samples (Section 2.3) was used to evaluate perchlorate recoveries in uncontaminated soil specimens obtained near sampling locations. Approximately 5.0 g homogenized soils were weighed into 50.0 mL falcon tubes. These samples were spiked with standard perchlorate solutions in the range of 100-5000ng/mL and extracted with 10.0 mL of water after the soils were air dried overnight. They were analyzed in triplicate. Reference samples were prepared by spiking empty 50.0 mL falcon tubes with comparable standard solutions and air dried and extracted with 10.0 mL water (18.0MΩ cm Milli Q). Perchlorate peak areas of spiked samples, with and without soil, were compared to assess recoveries. In all cases recoveries from soils was close to 100%.

3. Results

A total of 10 fireworks events were evaluated over a period of six years. The sites with geographical locations are summarized in Table 1. Sites 1 and 3 were municipal parks. Site 2 an academic campus, and site 4 was a public beach. Soils at the Samples were not tested to identify the soil type. By visual inspection, we have predicted Site 1 samples were different at from at sampling locations. Most of the samples looked like sandy clay soils with organic content in them and few other soil samples looked like sandy clay. Site 2 and 3 soil samples were more like sandy clay soils and Site 4 samples were sandy. Soil samples were collected prior to fireworks display and within

24 hours after the event (usually 10-18 hrs). Site 1 samples were collected from the surroundings as described above for five July 4th events. There was no rainfall prior to collection of specimens. Distances from the specific firing site and results of perchlorate analyses, including averages, are given in Table 2. They ranged from below detection limit (BDL) to a few thousand ng/g (i.e. about 2000 ng/g) of soil. With the exception of one sample (July 2007) perchlorates were not detected in any samples before the fireworks event. The data for the first two years were similar but year 3 showed a substantial rise in quantities of perchlorate. At this time we decided to extend the study to other locations having fireworks displays. For years 4 and 5, at Site 1, there was a decline in perchlorate back to about previous levels. Soil samples collected from Site 2 were from fireworks displays at a different location. These sampling locations contained substantial evidence of the previous day's event. There was gray-brown residue covering the soil, paper debris and pieces of wires. The results for perchlorates at Site 2 are shown in Table 3. Perchorate contamination ranged from BDL to about 2700 ng/g of soil. Results form Site 3 and 4 are given in Tables 4 and 5, respectively. Perchlorate contamination ranged from BDL to 25000 ng/g and 3000 ng/g, respectively.

4. Discussion

Strong oxidants, ammonium and postssium perchlorate, are major components of almost all pyrotechnic including fireworks. The high water solubility of perchlorate anions results in rapid transport to the ground water when rainfall is extensive. Under these conditions residence times for perchlorates within soils are likely to be short.

Under arid or semi-arid conditions plants and microbes associated with soils are capable of phytoaccumulation and phytodegradation of perchlorate (Schneider. R. L. and Yifru. D. D., 2009). Perchlorates accumulated in plants are likely returned to the food chain or returned to the plants local environment. Rhizodegradation is a relatively fast process involving nitrate reductase bacteria associated with plant roots. Under anaerobic conditions perchlorates sequentially convert to chlorate (ClO_3^-) then chlorite (ClO_2^-) then chloride (Cl^-). Bacteria like *Staphylococcus epidermidis* are capable of reducing perchlorates in the absence of nitrate reductase, (Schilt, 1979). Cell free extracts of nitrate adapted *Bacillus cereus* is capable of reducing perchlorates, (Urbansky, E.T. 1988), *Vibrio dechloraticans* was patented by Korenkov et al. in 1976 as perchlorate reductase. Ethanol and acetate have been used as a source of nutrients to these bacteria (Rikken et al; 1996). *Wolinella succinogens*, strain HAP-1 was first isolated from a municipal anaerobic digestor and has been shown to metabolize perchlorate and chlorate. It has been used at AFRL (U.S. air Force 1994, Wallace and Attaway 1994). They have demonstrated that perchlorate concentration of 3000 μg/mL can be reduced to less than 0.5 μg/mL. In the present study we monitored the occurrence of perchlorate anion following fireworks displays.

Prior to the July 4th events, except for one isolated sample, perchlorates were not detected. To our knowledge the only reason for the perchlorate contamination at these sites were the fireworks displays. After the fireworks displays the amounts of perchlorates ranged BDL to a maximum of 24,585ng/g at Site 3. To further test our assumption that fireworks were the exclusive source of perchlorates, soil samples were collected and analyzed about four months following the event. Perchlorates were not observed at the detection limits of this study. Our results are consistent with a MassDEP study of soils collected following a fireworks display in 2004 (Mass DEP, 2006). Prior to the event perchlorates were not observed. Following the event they reported samples with as much as 560 ng/g in soil.

5. Conclusion

Fireworks are a source of perchlorate contamination. Increase in the concentration of perchlorates in soils has been noted after fireworks displays. Figure 1 summarizes the results of this study as average values for all sampled locations at a given site. Site 3 which was monitored for two years showed the greatest overall contamination following fireworks displays (4065 and 1894 ng/g soil). Least contamination was at Site 1 where overall average values ranged from 118 to 472 ng/g soil. These amounts are higher than the set EPA interim limits in drinking water (15ng/g water) (USEPA, 2008). The fact that perchlorates were not detected at sites repeatedly used for fireworks displays over the years suggested they are highly mobile in soil due to their poor adhesion to the soil matrix facilitating seepage into ground water.

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Table 1

Location	Geographical Description (Lat. & Long.)		Years
Site 1	Municipal Park	41°26'47.30"N; 71°29'12.62"W	2007, 2009-2012
Site 2	Academic Campus	41°55'29.93"N; 71°32'26.63"W	2011-2012
Site 3	Municipal Park	41°29'20.72"N; 71°23'2.74"W	2011-2012
Site 4	Public Beach	41°57'59.00"N; 71°26'28.39"W	2011

Table 1: Locations with geographical description and years specimens collected

Table 2

Location	Distance from firing site (ft)	(ngClO4-/g soil)				
		2007	2009	2010	2011	2012
O 1	76.5	136	260	129	224	X
O 2	59.8	175	243	112	1054	X
O 3	67.3	115	X	164	X	89
O 4	88.6	145	116	1244	138	70
O 5	118.5	X	X	109	X	X
O 6	86.8	X	218	235	149	X
O 7	100.3	151	X	1951	X	X
O 8	121.3	X	190	X	144	X
O 9	239.4	X	147	205	198	X
O 10	264.1	149	X	X	X	196
O 11	508.9	X	X	101	X	X
O 12	478.8	148	X	X	X	X
O 13	525.7	X	XX	XX	XX	XX
O 14	576.8	100	XX	XX	XX	XX
Average		139	196	472	318	118

Table 2: Site 1 distance from firing site and amounts of perchlorates recovered.

*X= Below Detection Limit

**XX= Samples were not collected at the site

Table 3

Location	**Distance from firing site (ft)**		**(ngClO4-/g soil)**	
	2011	**2012**	**2011**	**2012**
B 1	87.6	45.5	28	196
B 2	107.5	61.9	46	730
B 3	31	216.9	2689	89
B 4	36.8	103.9	1371	1093
B 5	91.6	185	22	202
B 6	110.4	290.9	100	112
B 7	95.6	330.5	XX	123
B 8	148.1	350.9	XX	179
Average			709	341

Table 3: Site 2 distance from firing site and amounts of perchlorates recovered

**XX= Samples were not collected at the site

Table 4

Location	Distance from firing site (ft)	(ngClO4-/g soil)	
		2011	**2012**
M 1	50.4	514	8,151
M 2	47.4	647	81
M 3	68.8	4,852	X
M 4	74.8	313	1,043
M 5	78.3	24,585	1,448
M 6	137	268	X
M 7	151	431	519
M 8	136	913	125
Average		4,065	1,894

Table 4: Site 3 distance from firing site and amounts of perchlorates recovered

*X= Below Detection Limit

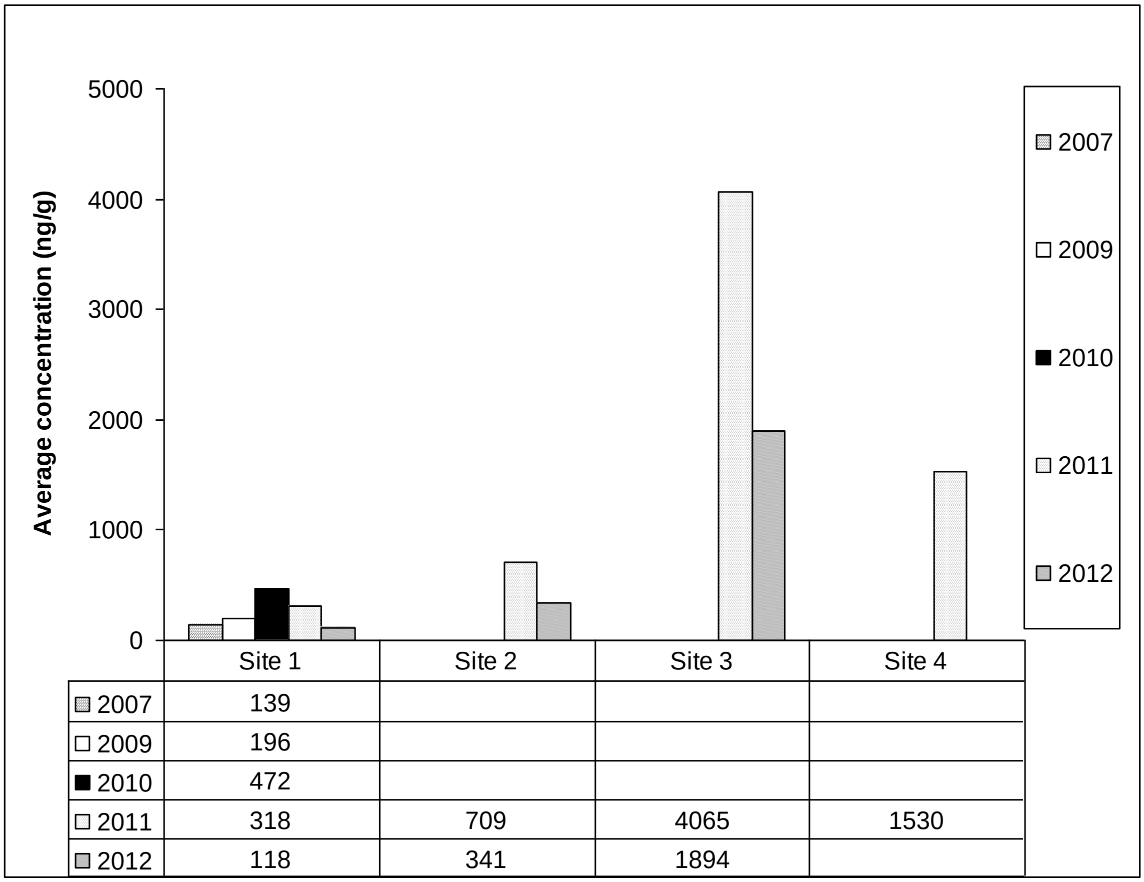
Table 5

Location	Distance from firing site (ft)	(ngClO4-/g soil)
		2011
J 1	111	X
J 2	93.7	2869
J 3	195	916
J 4	307	X
J 5	439	804
J 6	532	X
J 7	650	X
Average		1530

Table 5: Site 4 distance from firing site and amounts of perchlorates recovered

*X= Below Detection Limit

Figure 1



	Site 1	Site 2	Site 3	Site 4
▨ 2007	139			
☐ 2009	196			
■ 2010	472			
☐ 2011	318	709	4065	1530
▩ 2012	118	341	1894	

Figure 1: Average perchlorate concentration (ng/g of soil) recovered per site per year.

Manuscript 3

Encapsulation of Ammonium Nitrate

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Abstract:

The goal was to make ammonium nitrate more useable in applications where volume changes cannot be tolerated, e.g. solid rocket propellant. To accomplish this, a way was sought to eliminate solid phase changes which resulted in volumetric changes. In particular, elimination of the IV – III AN phase change was targeted. Elimination of this was thought to be possible through extreme drying; vacuum drying with heat was used. To maintain dry AN coating methodologies were explored. Polystyrene or polyacrylonitrile were applied using precipitation polymerization method. The performance of the dried and the coated ammonium nitrate was analyzed by differential scanning calorimetry (DSC).

Keywords: Ammonium Nitrate, Solid phase changes, Polymer, Precipitation Polymerization, Encapsulation, Differential Scanning Calorimetry, Thermal Gravimetric Analysis, Field Emission Scanning Electron Microscope.

1.0. Introduction:

Ammonium nitrate (AN) was discovered by Glauber in 1659 and used as an ingredient in explosive formulations as early as the 1860.[1] Though widely used with trinitrotoluene in both World War I and II, it was not widely used as a fertilizer until after World War II. Today worldwide production of pure AN is around 39 million metric tons.[2] Over half this production goes to the fertilizer market, the other half into commercial explosives. AN finds only minor use in military systems despite the fact it would be inexpensive and environmentally friendly. The barrier to the use of AN in military systems is its multiple solid-state phase changes and their accompanying volume changes.

Figure1 taken from reference 3

The phase change near room temperature (32 to 55°C) III → IV results in a volume change slightly more than 3.5% (Fig. 1)[3]. The phase transitions of AN are believed to be facilitated through thermally induced vibronic couplings.[4] This is problematic in AN systems which cannot tolerate cracking. While this problem prevents military use, the fertilizer industry, which employs AN as prills, can afford to be more tolerant. The fertilizer industry is concerned about powdering and creation of AN fines. To reduce the III/IV phase change various "phase stabilizers" are added--potassium, magnesium, or metal oxides like copper, zinc or nickel.[5-21] These can be added while the AN is aqueous or when it is a hot melt, or they can be introduced by chemical reaction. [9, 10, 19-21] The additives generally serve one of two functions; they fit into the AN crystal structure or they act as internal desiccants. Potassium nitrate is an example of the former; and magnesium nitrate, an example of the latter.[5-10] Although a number of potential solutions to the III/IV problem have been fielded, [10-21] none have been fully successful. The transition III/IV temperature changes as a function of water content. In fully dry AN, state IV changes directly to state II around 51°C (Table 1).

In a comprehensive study of the properties of AN, Kiiski of Yara, notes that phase III AN can be avoided; the change can be II to IV: "if there is no water, phase III will never exist…."[22] As water content is increased from 0.01 to 0.35% it is reported that the temperature of the IV → III transition temperature decreased, [23] and an increase in water content also increases the rate of the IV → III phase change. One way to reduce water content is temperature cycling across the III/IV transition.[24, 25] The above discussion suggests that producing AN, which does not have a phase change at room temperature, is possible, if it is dry. Our goal, therefore, is to “encase” the AN in such a manner that it remains dry for its lifetime. We believe the way to do that is with a coating or encapsulating species.

Generally, immediately after prilling, AN prills are coated with a thin layer (1 to 2 microns) of chemicals to reduce hygroscopicity, caking and cracking and dust formation. Coatings may be clay or diatomaceous earth or anionic alkylarylsulfonates or cationic long chain fatty amines which are applied as melts or oils on the order of a few kilograms per ton. Common commercial coatings include Galoryl alkyl-aryl sulphonates, anionic and nonionic surfactants, and fatty amines. Coatings/encapsulating agents will not only provide a moisture barrier, critical to suppressing the phase change, but may also contribute as a plasticizer to the total propellant formulation.

AN was first coated by the treating AN granules with oleum followed by NH_3 or MgO leading to an acid-base reaction which produced the coating on the surface of the AN. This approach was patented by Goodale et al. in 1969 (U. S. Patent 3,419,379).[26] Coated AN granules resisted caking; the AN was slow released upon contact with moisture. Following this invention attempts have been made to coat AN with various polymers for various applications. Table 1 provides a list of references and polymers used for coating. Polymers used for coating include potassium salt of polyacrylate (APSP)[27], polyvinyl butyral (PVB)[28], polystyrene (PS)[29], acrylonitrile (AcrN)[30], ehthyl cellulose (EC)[31], polyurethane (PU)[32,33], poly (lactic-co-glycolic acid) (PLGA)[34], poly methyl methacrylate (PMMA);[35] polyethylenime (PEI);[36] poly (diallyldimethylammonium chloride) (PDA);[36] poly (sodium4-styrenesulfonate) (PSS),[36,37] Polyallylaminehydrochloride (PAH);[36,37] polydiallyldimethylammonium chloride (PDADMA)[38], polymethacrylate (PMA).[38]

Our approach to making AN useable for applications where volume changes could not be tolerated was to create dry AN and then shield it from moisture by encapsulation. For that reason a literature search of encapsulation techniques was undertaken. Table 1 provides a summary, and particularly promising methods are discussed below.

Using a Wurster-type, fluidized bed apparatus the Fernandez-Perez group at University of Almeria coated fertilizer-grade granulated AN with either 10wt% or 20wt% ethyl cellulose (EC) using two different plasticizers [dibutyl sebacate (DBS) and dibutyl phthalate (DBP)].[31] Fluidized bed was operated at 60 to 70˚C. Typically, the average granule size was 2 mm in diameter with mean coating thickness of 50-90 um. Goodness of coated AN granules were evaluated by microscopic examination using SEM and by the rate of AN release in water or in soil. Application appears suitable for control release in soil systems.

The French team of Saihi and Bourbigot illustrated an interfacial polymerization technique for applying a polyurethane shell to di-ammonium hydrogen phosphate (DAHP).[32] Polyoxyethylene dioleate (POEDO) and Span 85 surfactants in toluene were used to form an emulsion with aqueous DAHP. Addition of diphenyl methylene diisocyanate (MDI) a monomer and dibutyl tin dilaureate (DBDL) as catalyst and stirring for 4 hrs at 63˚C resulted in formation of microcapsules. Microcapsule size was on average 15 um. IR and NMR were used to prove the presence of the DAHP. TGA showed increased thermal stability of encapsulated DAHP. Thus, better performance as intumescent flame retardant for textile use was predicted.

The addition of 2% or greater APSP prevented the IV→III transition and raised the III→II transition to 110°C.[27] As a crystal phase stabilizer, APSP has two effects; the potassium ion replaces the NH_4^+ ion and provides a polymer coating for the surface of AN. The latter effect was thought to prevent/reduce water sorption to ammonium nitrate. When liquid phase separation techniques were used to coat ammonium nitrate with PVB, absorptivity and caking were greatly reduced.[28] It also was responsible for the shift to higher temperature and eventual disappearance of the III→II crystal transition. Under certain conditions hygroscopicity declined 88.8% in comparison with uncoated ammonium nitrate when a precipitation polymerization method involving polystyrene (PS) in chloroform solution was used to coat ammonium nitrate.[29] Reduction in hygroscopicity has also been observed using precipitation polymerization of acrylonitrile (AcrN) in cyclohexane to ammonium nitrate.[30]

2.0. Experimental Procedure:

Raw materials:

Ammonium nitrate (Cerified ACS grade), cyclohexane (Certified ACS grade), n-hexane (95% Optima, Meets ACS Specifications), chloroform (Spectranalyzed, meets ACS specifications) were purchased from Fisher Scientific. Benzoylperoxide, 70% max. Active water wet (BPO) was purchased from PolySciences. Polystyrene, MW 250,000 (PS) and Acrylonitrile, 99^{+}% (AcrN) were purchased from Acros Organics. 2,2'-Azobis(2-methyl propionitrile), 98% (AIBN)was purchased from Sigma Aldrich.

2.1. Synthesis:

2.1.1 Drying AN

Ammonium nitrate (AN) was ground in a motor and pestle. Drying was either by holding the AN overnight at 110˚C in a vacuum oven or at 100˚C in a conventional oven. Dried AN was stored in a desiccator until use.

2.1.2. Coating AN Method 1

To a 250 mL round-bottomed flask, equipped with a football stirrer, and reflux condenser, chloroform (5.0 mL), PS (1.00 g, 9.52×10^{-5} mol) and BPO (100 mg, 9.83×10^{-3} mol) were added. The mixture was heated to 60ºC in silicon oil bath and stirred until the entire polymer is dissolved. AN (4.00g, 1.19 mol) was added to the mixture and stirred four hours to allow the reaction to go to completion. Precipitation of the coated AN was facilitated by addition of cyclohexane (5.0 mL). The coated AN was collected on filter paper by vacuum filtration. The product was rinsed with three 2 mL aliquots of cyclohexane, and dried in a desiccator.

2.1.2. Coating AN Method 2

Cyclohexane (5.0 mL) was poured into a 250 mL round-bottomed flask equipped with a football stirrer and reflux condenser. AcrN (1.00 mL, 0.322 mol) and AIBN (100 mg, 10.32 mol) were added and heated to 60ºC in silicon oil bath. AN (4.00g, 0.847 mol]) was added to the mixture and stirred ten hours to allow the reaction to go to completion. Hexane (5.0 mL) was added and the mixture was stirred for 10 minutes to facilitate precipitation. The AcrN-coated AN with was collected on filter paper by vacuum filtration, rinsed with three 2 mL aliquots of hexane, and dried in a desiccator.

2.2. Differential Scanning Calorimeter (DSC)

Thermal analyses were performed using a TA Instruments model Q-100 DSC. Samples were run under nitrogen flow (50mL/min), and the system was calibrated against indium (m.p. 156.60ºC, H_f 28.71 J/g). Sample of about 0.5mg and were sealed in glass micro-ampoules (1.5mm O.D., 0.28mm wall thickness, and 8mm length).[39] Samples were run in triplicate. Samples were run in triplicate at a scan rate of 20°C/minute from -10 to 225°C if only the endotherms were to be examined or up to 500°C if the complete thermal decomposition of AN was to be observed.

2.3. Field Emission Scanning Electron Microscope (FESEM)

The surface morphology of the coated AN was examined using a ZEISS Sigma-VP Field Emission Scanning Electron Microscope (FESEM).

2.4. Infrared Spectroscopy (IR)

Attenuated total reflectance (ATR) spectra of coated and uncoated AN were obtained with Nicolet 6700 FTIR Spectrometer using 32 scans, 650 to 4000 cm^{-1} spectral range and at resolution of 4.0 cm^{-1}.

2.5. Thermal Gravimetric Analyzers (TGA)

TGA thermograms were obtained using a TA Q5000 TGA using nitrogen purge gas to constantly sweep the balance (10 mL/min) and furnace (25 mL/min). Coated and uncoated AN (10-15 mg) were held in open platinum pans (100 µL). Runs were performed in triplicates, ramping the samples at 5 °C/min from 40 °C to 325°C.

3.0. Results

3.1. Differential Scanning Calorimeter (DSC)

The solid-state phase changes of ammonium nitrate are often written as simply as the diagram at the top of Table 2, but the lower half of that Table shows a much more complex story.[41-51] In the temperature region between 32°C and 84°C the AN transitions are particularly sensitive to the moisture content and thermal history.

These solid state phase changes involve large structural changes in the AN crystal (Fig. 1); thus they can be observed by thermal analysis[43-51] For that reason

DSC was used to assess the effectiveness of the AN drying protocol as well as the state of the AN. Figure 2 shows the entire DSC thermogram of AN as received. Generally, endotherms were visible before the AN decomposition exotherm at 316^{o}C (which released 1000 J/g on average). An additional endotherm was observed immediately after the exotherm. This has been shown to be the phase change of water formed during the ammonium nitrate decomposition.[41]

$$NH_4NO_3 \rightarrow 2\ H_2O\ +\ N_2O$$

Occasionally (4 out of 27 samples), five endotherms were visible before the exotherm. Figure 3 expands this region for two of the anomalous “as received” AN samples. In one two endotherms were observe—one at 39^{o}C and one at 52^{o}C—and the other shows only one endotherm but it is at 41^{o}C. There was a fair amount of variation among samples; therefore Table 3 tabulates the position the results for 28 “as received” samples. The first endotherm, the IV to III phase transition, was not observed at 32^{o}C where it is often cited in the literature;[40, 52] and is pictured in the top of Table 2. Instead it was observed as low as 41^{o}C and as high as 56^{o}C (Table 3). The variability in the temperature at which the phase changes between 32^{o}C and 84^{o}C occur has been previously reported. It has been suggested that this endotherm around 50^{o}C may actually be two endotherms: the IV to III phase transition of dry AN and the IV to II transition.[22, 23, 43] This may also explain the two endotherms near 50^{o}C visible in Figure 3.

Figure 4 shows the DSC trace of AN after drying, and Table 4 summarizes the data for 34 of these dry AN samples. The ~50^{o}C endotherm is approximately in the same location, but possibly the small increase in heat absorbed ~4 J/g indicates more of the sample undergoes this transition. In most of the dried AN samples (25 out of 34), the ~90^oC endotherm, indicative of the III to II transition, disappeared entirely. This change suggests that AN is no longer transiting through phase state III. AN moved from state IV to II (54^oC) to I (129^oC) and melt (170^oC). [49-53]

Since the DSC traces suggested AN was successfully dried, encapsulation techniques were sought to act as a long-term moisture barrier. Polystyrene[29] and acrylonitrile.[30] were used since the methods previously applied match the resources we had at hand. DSC scans of the coated AN were collected. Figure 5 and Table 5 record the DSC data from samples of AN coated with polystyrene; 138 out of 187 samples evidenced no endotherm at ~90^oC. Figure 6 and Table 6 record the same data for AN coated with acrylonitrile. In this case 12 out of 18 samples lacked the ~90^oC endotherm. These results show the level of moisture present in the uncoated AN (Fig. 3) can be maintained throughout the encapsulation protocol. It is also noticeable that more heat is released during the exotherm ~1500 J/g versus 1000 J/g due to the fact fuel is present.

3.2. Field Emission Scanning Electron Microscope (FESEM)

Figures 7 and 8 show the FESEM images of the uncoated (Fig. 7) and polystyrene (PS) coated AN (Fig. 8).The samples were observed at a same scale. The uncoated AN presents a smooth, almost amorphous surface compared to a AN coated with PS. The image of the coated AN is rather difficult to read, but it appears that the PS coating may be around 2 mm thick.

3.3. Water absorption Data

To determine how effectively the "encapsulated" AN was protected from moisture sorption, samples (~0.5 g each) of the polystryene (PS) and polyacrylonitrile (ACrN) coated AN as well as uncoated AN were sealed in a container along with an open dish of water. The weights of the AN samples were monitored every half hour for about 5 hrs for 24 hours. In the first 5 hours of observation there was no visible difference in the coated AN samples, whereas uncoated AN became visibly "wet." After 15 hours in the humidity chamber, the coated AN samples had water droplets, appeared as sweat, on the surface. Even though there was a visual difference, the coated AN gained as much weight as the uncoated AN within the first 5 hours in the chamber. This suggested the AN was not sufficiently or uniformly coated. The results are shown in Table 7.

Table 8 shows the weight gain of the AN and the PS-coated AN during initial exposure to a moist atmosphere. The coated sample showed significant resistance to water absorption to the first five hours.

3.4. Infrared (IR)

The infrared (IR) spectra of AN, neat polystyrene (PS) and PS-coated AN are shown together in Figure 9. AN exhibits NH_4^+ stretching, symmetric and asymmetric modes, near 3234 cm,$^{-1}$ 3058 cm,$^{-1}$ and 3025cm.$^{-1}$ Total stretching and in-plane and out-of-plane deformation modes of NO_3^- were observed around 2500 cm.$^{-1}$ In the region 1300-1500 NH_4^+ and NO_3^- asymmetric stretching and deformations have been reported by Chan.[52] Polystyrene shows aromatic C−H stretching at 2900 cm^{-1} and aromatic C=C stretching around 1600 cm.$^{-1}$ The latter was observed in PS-coated AN although the majority of resonances are due to AN. Acrylonitrile has a charecteristic band around 2200cm^{-1} corresponding to C≡N stretching.[53] This was also observed in AN coated with acrylonitrile as shown in Figure 10.

3.5. Thermal Gravimetric Analyzers (TGA)

In an attempt to determine the amount of polymer coating present on the ammonium nitrate, TGA was performed. TGA of uncoated AN is shown in Figure 11. AN weight loss began at about 170°C, its melting point, and resulted in complete loss by 250°C. Figure 12 is the TGA trace of polystryrene-coated AN. Weight loss begins about the same temperature as in the uncoated sample, but reaches a maximum about 20 degrees later (270°C). Figure 13 overlays the TGA traces of neat polystyrene (which shows little weight loss up to 320°C) to that of uncoated AN (maximum weight loss 250°C) and PS-coated AN (maximum weight loss 270°C). Figure 14 is the TGA trace of polyacrylonitrile-coated AN alone, and Figure 15 compares neat AN to polyacrylonitrile and polyacrylonitrile-coated AN. Again the polymer coating extends the time to maximum weight loss about 20 degrees.

Each thermogram showed only a single-step weight loss. While we had expected to see the polymer-coated AN evidence a two-step weight loss—first loss of polymer and then loss of AN, apparently AN is thermolyzed more readily than the polymer. Thus, the polymer coating delays the release of AN. Apparently, the polymer coating must be breached before AN is lost.

4.0. Conclusions

We have succeeded in drying and encapsulating AN. TGA experiments showed that the polymer coating acted as a protective layer delaying the volatilization of the AN. However, the moisture barrier was only effective for a few hours in a moisture saturated environment. A number of question remain to be answered-the thickness of the polymer film and its uniformity being two of the most important. Nevertheless, this initial work provides a foundation for future research. It is possible that a layer-by –layer approach would provide a better moisture barrier while maintaining a relatively low level of organic additive. Different coating techniques or different polymers may provide better protection to the AN. Many possibilities remain to be explored.

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TABLE 1

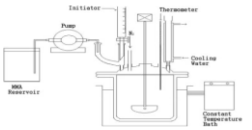
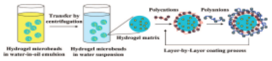
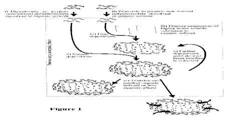
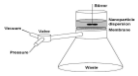
Author	Reference	Polymer	Method	Analysis	Purpose
	COATINGS				
Visagic, Pille	US2009/0301618 AN Granules	AN with alkyl naphthalene sulfonate (Galoryl) & Na sulfonate SKFert	fluidized bed	det velocity	for ANFO-coating of granules so smooth, hard & don't breakdown
Zhenhua, Hua	Chinese J of Explosives & Propellants, 33, 2, 2010, 19-22	Potassium polyacrylate	both dissolved in H2O	DSC, XRD, SEM, XPS, EDS	prevent caking
Fernandez-perez. M; Perez-Garcia; Villafranca-Sanchez; Gonzalez-	Ind.Eng.Chem.Res. 2007,46, 3304-3311	AN in Ethyl cellulose with dibutyl sebacate & dibutylphthalate	Wurster-type fluidized bed	water release, soil release kinetics were monitored	fertilizer
Zhang.J, Yang.R	Academic Journal of Fire & Explosives (CHINA), 2001, 1, 41-3	AN with Polyvinyl butaryl (PVB)	PVB in chloroform add AN heat at 60 C for 4 h, add hexane	DSC, anticaking, XPS	solid rocket propellents
Yue.J	Advances in fine petrochemical engineering, (CHINA) 2008,vol 9, 12, 35-37	AN with Acrylonitrile	acrylonitrile in chloroform, add AN , AIBN heat at 60C for 10hrs add hexane	DSC, anti caking, XPS	
Zhang .J, Wang.X	energetic materials, 2004, 12, 82-85	AN with Styrene	Styene in chloroform, add AN, BPO heat at 60C for 4 hrs add cyclo hexane	DSC, anti caking, XPS	
Saihi	Reactive & Functional polymers, 64, 2005, 127-138	Ammonium phosphate with polyurethane	coacervation technique	CP-DD-MAS NMR 13C , DTG, FTIR,	intumescent flame retardant system
Saihi	Reactive & Functional polymers, 66, 2006, 1118-1125	Ammonium phosphate with polyurethane shell	interfacial polymerization	MAS NMR 31P, DTG	intumescent flame retardant system
Shekunov	J Pharmaceutical Sci, 95,3, 667-79	AN with Poly (lactic-co-glycolic acid) (PLGA)	Supercritical fluid extraction of O/W emulsions	SEM	controlrelease of drugs
Kim. Y. H	J Polymer Sci, part A: Polymer Chem. 42, 4063-73, 2004	CaCO3 with Poly (methyl methacrylate) (PMMA)	reactor where CaCO3 is dried & coated with MMA and APS 4 times for polymerization 	IR, DSC, TGA, SEM	industrial applications like fillers, plastic ,adhesives, rubber
Trau.D;Mark. W. C.	Chem.Mater, 2008, 20, 5475-5484	Poly electrolytre coating with Poly ethylenime (PEI), Poly (diallyldimethylammonium chloride) (PDA), poly (sodium4-styrenesulfonate) (PSS),Polyallylaminehydrochloride (PAH).	agarose gel in tris buffer at 40C; analyte in tris buffer.BSA -FTIC.added to molten agarosegel span 80 was added. All mixed to form microbeads. 	florence microscope & thermal stability	biological materials like e.coli,proteins
Trau.D	WO 2008/091228 A2 Reverse Phase Layer-by-Layer Encapsulation of Highly Water Soluble Materials	polydiallyldimethylammonium chloride (PDADMA), polymethacrylate (PMA) & non-ionized PMA (niPMA)	reverse layer by layer method:non ionized polyelectrolyte:PMA in HCl, dialyze & vac dry.dissolve in EtOH (niPMA);PDADMA in NaOH overnight at 55C , dialyze & vac dry. Dissolve in EtOH (nimPDADMA). bovine serum albumin (BSA)-FTIC powder + EtOH centriguge, discard supernatant, repeat; save superatant layerand discard ppt. Layer by layer deposition niPMA & nimPDADMA. 	Floroscence microscopy	Patented is a way to encapsulate water soluble low molecular materials, e.g. NaCl
Hirsjarvi.S	collioids and surfaceB: biointerfaces,2006,49, 93-99	Polyelectrolyte coating with PAH and PSS	Nano precipitation method, polylactic acid (PLA) in DCM & ethanolic solution, slow evaporation, collect nanoparticles disperse them in polyelectrolytes with 0.02M NaCl. LBL done with vaccum filteration. Particles exposed to polyelectrolyte for 5min after 2 cycles of washing & coating continued til all oppositely charged PEs added. new membrane used before each addition. 	SEM, zeta potential, Photon correlation spectroscopy, DSC	PLA nanoparticles

Table 1: Summary of Literature Reviewed on Encapsulation.

TABLE 2

$$\mathrm{V} \xleftrightarrow{-17^\circ\mathrm{C}} \mathrm{IV} \xleftrightarrow{32^\circ\mathrm{C}} \mathrm{III} \xleftrightarrow{84^\circ\mathrm{C}} \mathrm{II} \xleftrightarrow{126^\circ\mathrm{C}} \mathrm{I} \xleftrightarrow{169^\circ\mathrm{C}} \text{melt}$$

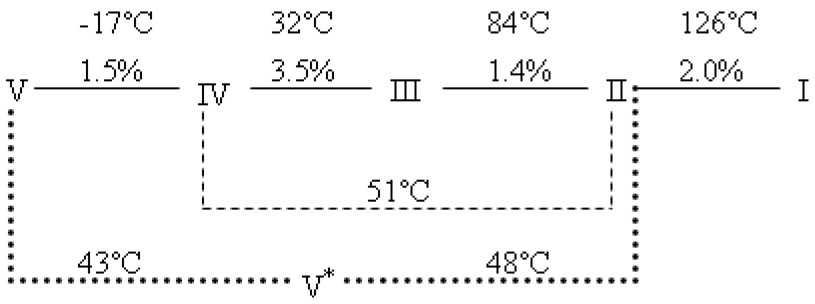


Table 2: Phase changes of Ammonium Nitrate & Percent Volume Change

TABLE 3

		Endotherms										Exotherm	
Sample	mg	1st (30-50˚C)				2nd (80-90˚C)		3rd (120-		4th (160-170˚C)		(300˚C)	
		˚C	˚C	J/g	J/g	˚C	J/g	˚C	J/g	˚C	J/g	˚C	J/g
AN	0.485		53		20	92	19	127	66	169	89	312	325
AN	0.490		53		29	92	5	126	64	168	91	308	639
AN	0.484		53		28	90	19	126	68	168	93	299	888
AN	0.482		56		21	95	5	130	45	171	55	317	998
AN	0.509		55		14	94	17	131	49	171	45	318	1103
AN	0.494		56		12	96	14	131	39	171	45	314	1232
AN	0.485		56		15	93	16	132	53	173	75	317	1319
AN	0.508		56		29	92	9	133	57	174	76	315	1405
AN	0.519		53		14	93	8	132	42	172	48	310	1331
AN	0.313		49		14	95	19	131	51	171	63	326	1254
AN	0.560		57		28	94	15	131	45	173	56	328	1252
AN	0.439		56		11	94	13	131	40	170	43	320	1457
AN	0.410		48		9	87	12	129	30	170	31	319	825
AN	0.446		55		10	90	12	130	41	172	57	323	414
AN	0.498		53		18	96	2	128	35	162	27	NR	NR
AN	0.489		54		16	90	3	129	26	161	22	NR	NR
AN	0.511		54		15			128	29			NR	NR
AN	0.517		52		27			126	56	168	63	NR	NR
AN	0.497	39	52	15	5	90	17	128	54	169	62	NR	NR
AN	0.481	41		18		90	18	128	51	170	58	NR	NR
AN	0.496	43	53	14	3	91	17	128	49	169	56	NR	NR
AN	0.505	45	52	13	2	91	19	128	55	169	62	NR	NR
AN	0.506	44	52	12	4	91	17	128	53	168	57	NR	NR
AN	0.497		52		5	90	15	128	55	169	60	NR	NR
AN	0.506		52		4	91	17	128	53	168	57	NR	NR
AN	0.505		52		2	91	18	128	54	169	61	NR	NR
AN	0.496		53		3	91	17	128	49	169	56	NR	NR
	average	42	53	14	14	92	14	129	48	169	58	316	1032

Table 3: DSC Results for AN “as received” (NR-not record, run terminated early)

TABLE 4

		Endotherms										Exotherm	
Sample	mg	1st (30-50˚C)				2nd (80-90˚C)		3rd (120-130˚C)		4th (160-170˚C)		(300˚C)	
		˚C	˚C	J/g	J/g	˚C	J/g	˚C	J/g	˚C	J/g	˚C	J/g
AN	0.534		49		14	94	21	130	60	172	82	307	1276
AN	0.343		51		17	91	22	128	66	169	90	332	1251
AN	0.541		52		16	92	20	130	60	172	78	339	1277
AN	0.506		52		4	90	17	129	50	169.1	62	NR	NR
AN	0.501	44		11		91	13	130	35	173	42	NR	NR
AN	0.488	44		19		90	19	128	54	168	55	NR	NR
AN	0.481	41		17		90	16	128	49	170	57	NR	NR
AN	0.502		53		15	91	18	128	51	170	62	NR	NR
AN	0.509		57		13	96	15	132	41	173	47	NR	NR
AN	0.504		56		22			131	52	172	61	319	NR
AN	0.512		52		27			127	59	168	76	282	1680
AN	0.486		52		26			127	54	169	67	282	1554
AN	0.500		54		21			129	44	170	56	288	1316
AN	0.505		53		21			128	43	169	50	294	1331
AN	0.507		54		19			128	40	168	50	296	730
AN	0.501		53		24			129	48	170	62	299	1373
AN	0.510		53		26			128	54	170	70	300	1322
AN	0.498		53		18			128	38	169	51	301	962
AN	0.483		53		30			126	69	168	93	304	761
AN	0.488		53		27			127	65	169	88	305	884
AN	0.519		53		28			126	65	168	89	307	696
AN	0.515		57		20			131	45	172	50	314	929
AN	0.500		55		26			130	59	172	78	315	1270
AN	0.517		56		24			131	52	172	69	322	1254
AN	0.484		53		22			129	43	168	47	NR	NR
AN	0.517		52		27			126	56	168	63	NR	NR
AN	0.502		54		23			129	45	172	52	NR	NR
AN	0.513		54		19			127	39	170	48	NR	NR
AN	0.502		54		17			129	33	167	31	NR	NR
AN	0.498		53		20			128	44	168	54	NR	NR
AN	0.506		54		23			128	48	169	60	NR	NR
AN	0.493		55		18			130	37	171	41	NR	NR
AN	0.496		55		20			128	41	170	48	NR	NR
AN	0.508		53		22			128	45	168	42	NR	NR
AN	0.515		55		17			129	31	165	26	NR	NR
	average	43	54	16	21	92	18	129	49	170	60	306	1169

Table 4: DSC Data for AN “Dried” Vacuum Dried 110^{o}C (NR-not record, run terminated early)

TABLE 5

		Endotherms								Exotherm	
Sample	mg	1st (30-50˚C)		2nd (80-90˚C)		3rd (120-130˚C)		4th (160-170˚C)		(300˚C)	
		˚C	J/g	˚C	J/g	˚C	J/g	˚C	J/g	˚C	J/g
AN/PS	0.392	49	11	95	15	128	50	164	49	241	2136
AN/PS	0.330	54	12	90	14	128	51	166	53	245	1714
AN/PS	0.557	57	25			131	58	170	80	287	570
AN/PS	0.518	55	32			130	72	171	104	294	511
AN/PS	0.600	55	25			131	57	167	49	302	2187
AN/PS	0.533	55	29			130	66	169	60	304	2139
AN/PS	0.542	56	23			131	57	171	71	304	1767
AN/PS	0.498	55	16	90	7	130	59	172	62	314	1842
AN/PS	0.543	57	23			131	52	172	69	318	2128
AN/PS	0.462	55	29			130	69	171	86	318	1360
AN/PS	0.494	56	22			131	51	173	65	321	1540
AN/PS	0.448	55	32			130	77	169	93	321	1626
AN/PS	0.483	56	26			132	53	173	74	321	1739
AN/PS	0.432	56	18			131	41	172	54	321	999
AN/PS	0.507	56	16			131	35	172	47	321	997
AN/PS	0.426	56	13	95	15	131	54	172	82	322	1655
AN/PS	0.462	55	31			131	69	171	94	325	1677
AN/PS	0.574	56	26			131	57	172	82	325	1331
AN/PS	0.499	54	26			131	56	170	63	326	1548
AN/PS	0.563	55	28			131	64	171	77	328	1427
AN/PS	0.529	55	28			130	65	171	87	328	1446
AN/PS	0.531	56	19			131	51	169	42	328	1483
AN/PS	0.479	55	24			130	55	170	78	330	1278
AN/PS	0.365	54	14	91	16	128	49	167	65	NR	NR
AN/PS	3.351	55	25	92	8	129	58	171	82	NR	NR
AN/PS	4.618	56	23	92	11	131	58	174	80	NR	NR
AN/PS	4.890	56	26	92	8	130	60	173	84	NR	NR

Table 5: DSC AN vacuum dried at 110^{o}C & Coating with Polystyrene (NR-not record)

TABLE 5 (Cont'd)

		Endotherms								Exotherm	
Sample	mg	1st (30-50˚C)		2nd (80-90˚C)		3rd (120-130˚C)		4th (160-170˚C)		(300˚C)	
		˚C	J/g	˚C	J/g	˚C	J/g	˚C	J/g	˚C	J/g
AN/PS	2.607	55	23	92	12	128	59	171	84	NR	NR
AN/PS	7.367	56	23	92	13	130	60	174	86	NR	NR
AN/PS	0.509	54	17	125	51					NR	NR
AN/PS	0.520	54	12	102	24					NR	NR
AN/PS	0.480	54	11	107	24					NR	NR
AN/PS	0.525	54	11	105	20					NR	NR
AN/PS	0.507	55	13	89	12	130	37	170	49	NR	NR
AN/PS	0.502	53	16	93	10	128	46	168	56	NR	NR
AN/PS	0.519	54	21	88	7	128	44	167	49	NR	NR
AN/PS	0.514	53	20	87	12	127	54	167	67	NR	NR
AN/PS	0.482	54	21	98	2	128	44	169	55	NR	NR
AN/PS	0.485	49	16	90	14	129	42	170	58	NR	NR
AN/PS	0.484	49	16	90	8	128	50	168	64	NR	NR
AN/PS	0.501	51	15	91	16	129	43	169	52	NR	NR
AN/PS	0.501	54	12	116	26					NR	NR
AN/PS	0.495	53	19	90	7	128	45	169	54	NR	NR
AN/PS	0.513	55	18	90	4	130	36	172	45	NR	NR
AN/PS	0.487	55	18	91	7	128	46	168	62	NR	NR
AN/PS	0.520	55	9	106	11					NR	NR
AN/PS	0.490	54	20	92	2	129	42	170	51	NR	NR
AN/PS	0.487	54	12	92	9	128	43	168	53	NR	NR
AN/PS	0.485	53	20	92	9	128	58	170	77	NR	NR
AN/PS	0.489	55	18	92	2	128	39	169	44	NR	NR
AN/PS	0.490	52	16	115	52					NR	NR
AN/PS	0.499	54	16	92	12	129	42	170	55	NR	NR
AN/PS	0.760	54	17	93	7	129	41	169	51	NR	NR
AN/PS	0.487	53	14	93	16	129	39	163	32	NR	NR
AN/PS	0.523	53	24	93	4	128	50	169	64	NR	NR
AN/PS	0.518	49	15	93	15	129	34	160	25	NR	NR
AN/PS	0.512	54	20	95	9	129	47	169	60	NR	NR
AN/PS	0.478	54	22	93	6	128	50	169	62	NR	NR
AN/PS	0.498	55	11	121	27					NR	NR
AN/PS	0.481	46	19	94	15	129	45	167	45	NR	NR
AN/PS	0.503	53	15	94	10	128	31	159	23	NR	NR
AN/PS	0.482	54	18	96	17	129	44	165	37	NR	NR
AN/PS	0.476	53	19	95	13	128	54	168	72	NR	NR
AN/PS	0.482	56	14	96	5	130	30	171	38	NR	NR
AN/PS	0.487	54	21	96	2	128	45	169	61	NR	NR
AN/PS	0.512	53	23	96	2	128	48	168	61	NR	NR
AN/PS	0.523	54	16	120	48					NR	NR
AN/PS	0.484	55	15	99	4	129	30			NR	NR
AN/PS	0.497	56	20	100	3	131	37	170	38	NR	NR
AN/PS	0.525	54	19			128	39	170	46	NR	NR
AN/PS	0.503	55	18			130	34	172	41	NR	NR
AN/PS	0.482	55	21			129	44	169	53	NR	NR
AN/PS	0.496	53	24			128	52	170	64	NR	NR
AN/PS	0.517	54	20			129	4095	167	46	NR	NR
AN/PS	0.512	54	21			129	42	167	48	NR	NR
AN/PS	0.484	54	18			129	36	169	36	NR	NR
AN/PS	0.514	53	21			128	42	168	44	NR	NR
AN/PS	0.520	53	25			129	52	167	58	NR	NR
AN/PS	0.499	53	20			128	39	166	38	NR	NR
AN/PS	0.487	54	15			129	28	165	25	NR	NR
AN/PS	0.523	55	19			130	35	170	36	NR	NR
AN/PS	0.511	54	20			129	37	162	27	NR	NR

Table 5: DSC data of AN vacuum dried at 110^{o}C and Coating with Polystyrene (cont)

TABLE 5 (Cont'd)

		Endotherms								Exotherm	
Sample	mg	1st (30-50˚C)		2nd (80-90˚C)		3rd (120-130˚C)		4th (160-170˚C)		(300˚C)	
		˚C	J/g	˚C	J/g	˚C	J/g	˚C	J/g	˚C	J/g
AN/PS	0.501	53	21			128	40	165	38	NR	NR
AN/PS	0.475	54	21			127	32	150	14	NR	NR
AN/PS	0.477	53	18			128	38	165	44	NR	NR
AN/PS	0.491	55	20			128	38	162	31	NR	NR
AN/PS	0.531	54	20			129	37	166	33	NR	NR
AN/PS	0.504	55	16			129	23	153	10	NR	NR
AN/PS	0.482	55	18			129	28	158	15	NR	NR
AN/PS	0.483	54	13			128	37			NR	NR
AN/PS	0.499	55	18			127	20	142	3	NR	NR
AN/PS	0.505	54	18			128	30	158	20	NR	NR
AN/PS	0.480	53	18			128	28	152	15	NR	NR
AN/PS	0.488	54	19			128	35	160	31	NR	NR
AN/PS	0.492	53	17			128	43			NR	NR
AN/PS	0.513	55	16			121	32			NR	NR
AN/PS	0.489	54	15			126	37			NR	NR
AN/PS	0.503	53	18			127	51			NR	NR
AN/PS	0.486	55	20			128	34	170	41	NR	NR
AN/PS	0.508	51	15			126	17	144	3	NR	NR
AN/PS	0.501	54	16			129	21	149	8	NR	NR
AN/PS	0.480	56	9			130	14	172	14	NR	NR
AN/PS	0.520	56	14			131	20	157	10	NR	NR
AN/PS	0.491	55	15			130	21	150	6	NR	NR
AN/PS	0.506	56	13			131	22			NR	NR
AN/PS	0.494	57	10			132	23			NR	NR
AN/PS	0.503	56	20			129	44	170	60	NR	NR
AN/PS	0.505	53	20			128	26	146	8	NR	NR
AN/PS	0.480	53	16			128	41			NR	NR
AN/PS	0.488	55	12			130	18	167	13	NR	NR
AN/PS	0.521	55	15			130	26	166	22	NR	NR
AN/PS	0.490	55	15							NR	NR
AN/PS	0.500	55	14			130	19	152	7	NR	NR
AN/PS	0.520	56	12			131	15	149	5	NR	NR
AN/PS	0.519	55	12			130	28			NR	NR
AN/PS	0.480	56	14			131	28	171	35	NR	NR
AN/PS	0.513	56	15			130	29	173	36	NR	NR
AN/PS	0.506	57	15			132	29	173	36	NR	NR
AN/PS	0.508	56	16			130	32	171	41	NR	NR
AN/PS	0.482	55	20			130	40	164	42	NR	NR
AN/PS	0.522	55	17			130	33	171	36	NR	NR
AN/PS	0.498	55	17			130	34	170	36	NR	NR
AN/PS	0.482	55	17			129	36	170	48	NR	NR
AN/PS	0.481	55	22			128	43	170	50	NR	NR
AN/PS	0.491	55	20			130	41	170	130	NR	NR
AN/PS	0.523	55	18			130	37	171	48	NR	NR
AN/PS	0.513	55	17			130	34	170	44	NR	NR
AN/PS	0.499	55	18			130	38	171	50	NR	NR
AN/PS	0.495	57	16			131	30	172	37	NR	NR
AN/PS	0.499	54	18			130	33	169	34	NR	NR
AN/PS	0.508	55	18			128	34	170	40	NR	NR
AN/PS	0.506	53	21			128	42	168	46	NR	NR
AN/PS	0.486	54	19			129	39	168	48	NR	NR

Table 5: DSC data of AN vacuum dried at 110^{o}C and Coating with Polystyrene (cont)

TABLE 5 (Cont'd)

		Endotherms								Exotherm	
Sample	mg	1st (30-50˚C)		2nd (80-90˚C)		3rd (120-130˚C)		4th (160-170˚C)		(300˚C)	
		˚C	J/g	˚C	J/g	˚C	J/g	˚C	J/g	˚C	J/g
AN/PS	0.502	55	18			129	34	167	29	NR	NR
AN/PS	0.480	54	23			129	46	164	54	NR	NR
AN/PS	0.501	55	19			130	38	171	42	NR	NR
AN/PS	0.482	55	17			130	33	170	40	NR	NR
AN/PS	0.483	53	14			128	8	159	3	NR	NR
AN/PS	0.525	55	16			131	80	168	29	NR	NR
AN/PS	0.496	54	22			130	45	171	61	NR	NR
AN/PS	0.502	53	22			129	47	169	64	NR	NR
AN/PS	0.487	54	20			130	39	167	40	NR	NR
AN/PS	0.486	53	24			128	49	166	59	NR	NR
AN/PS	0.501	54	18			130	36	172	44	NR	NR
AN/PS	0.503	55	17			129	28	156	17	NR	NR
AN/PS	0.502	54	19			129	38	169	43	NR	NR
AN/PS	0.504	55	17			130	33	169	36	NR	NR
AN/PS	0.497	54	23			129	47	170	62	NR	NR
AN/PS	0.475	54	20			128	38	169	46	NR	NR
AN/PS	0.518	53	23			128	49	168	57	NR	NR
AN/PS	0.510	54	19			129	39	169	46	NR	NR
AN/PS	0.489	54	20			129	40	166	36	NR	NR
AN/PS	0.504	54	21			128	42	166	44	NR	NR
AN/PS	0.498	53	25			128	52	168	66	NR	NR
AN/PS	0.517	53	24			128	49	170	60	NR	NR
AN/PS	0.495	53	21			128	44	168	56	NR	NR
AN/PS	0.480	54	22			128	46	169	51	NR	NR
AN/PS	0.533	53	24			128	50	164	57	NR	NR
AN/PS	0.486	54	22			129	44	170	57	NR	NR
AN/PS	0.503	53	24			128	48	169	55	NR	NR
AN/PS	0.518	54	22			128	48	168	59	NR	NR
AN/PS	0.495	54	24			129	47	168	66	NR	NR
AN/PS	0.525	55	18			130	33	171	42	NR	NR
AN/PS	0.480	53	23			128	49	166	60	NR	NR
AN/PS	0.480	53	22			128	47	168	60	NR	NR
AN/PS	0.492	53	23			128	48	166	80	NR	NR
AN/PS	0.487	53	24			129	52	167	64	NR	NR
AN/PS	0.507	54	16			127	35	170	43	NR	NR
AN/PS	0.518	52	20			127	27	167	27	NR	NR
AN/PS	0.485	53	21			128	25	139	12	NR	NR
AN/PS	0.480	54	18			129	19	152	19	NR	NR
AN/PS	0.481	53	17			128	17	161	12	NR	NR
AN/PS	0.488	54	16			128	49			NR	NR
AN/PS	0.491	54	19			128	71			NR	NR
AN/PS	0.517	53	20			127	70			NR	NR
AN/PS	0.509	53	20			127	74			NR	NR
AN/PS	0.525	53	20			127	74			NR	NR
AN/PS	0.502	53	18			121	50			NR	NR
AN/PS	0.525	53	18			128	65			NR	NR
AN/PS	0.487	53	23			128	43	164	39	NR	NR
AN/PS	0.493	54	19			129	22	151	12	NR	NR
AN/PS	0.504	54	17			129	56			NR	NR
AN/PS	0.486	54	16			128	18	148	9	NR	NR
AN/PS	0.517	54	17			128	56			NR	NR
AN/PS	0.506	53	22			127	28	149	14	NR	NR
AN/PS	0.521	54	20			129	20	147	10	NR	NR
AN/PS	0.481	53	17			128	12	143	4	NR	NR
AN/PS	0.498	54	16			128	50			NR	NR
AN/PS	0.488	53	18			119	50	159	12	NR	NR
	average	54	19	96	13	129	64	166	47	311	1526

Table 5: DSC data of AN vacuum dried at 110^{o}C and Coating with Polystyrene (cont)

TABLE 6

		Endotherms								Exotherm	
Sample	mg	1st (30-50˚C)		2nd (80-90˚C)		3rd (120-130˚C)		4th (160-170˚C)		(300˚C)	
		˚C	J/g	˚C	J/g	˚C	J/g	˚C	J/g	˚C	J/g
AN/AcrN	0.569	56	17			131	58	168	52	300	1605
AN/AcrN	0.478	56	38			130	56	171	88	304	1565
AN/AcrN	0.473	55	30			130	69	171	96	306	1701
AN/AcrN	0.491	56	24			131	54	171	60	306	1909
AN/AcrN	0.572	55	23			130	52	171	65	308	1328
AN/AcrN	0.537	56	35			131	83	172	120	318	1640
AN/AcrN	0.405	57	25			131	58	171	69	321	1457
AN/AcrN	0.461	55	24			129	58	171	68	321	1469
AN/AcrN	0.571	55	24			130	56	169	65	324	1098
AN/AcrN	0.494	54	13	87	2	116	29			NR	NR
AN/AcrN	0.513	55	10	90	20			149	6	NR	NR
AN/AcrN	0.525	54	12	89	13	130	26	158	10	NR	NR
AN/AcrN	0.491	54	13	92	14	128	33	162	22	NR	NR
AN/AcrN	0.508	55	7	90	6	124	17			NR	NR
AN/AcrN	0.492	45	11	90	9	131	11			NR	NR
AN/AcrN	0.525	52	18			128	24	153	14	NR	NR
AN/AcrN	0.485	55	20			130	23	153	11	NR	NR
AN/AcrN	0.488	55	8							NR	NR
	average	54	20	90	11	129	44	165	53	312	1530

Table 6: DSC Data of “dried” AN coated @ Polyacrylonitrile (NR-not record, run terminated)

TABLE 7

Time	Total weight (g) of samples			Weight (g) gained by samples (AN_{f}-AN_{0})		
	AN/PS	AN/ACrN	Neat AN	AN/PS	AN/ACrN	Neat AN
0 min(A_0 weight)	0.500	0.501	0.501	0.000	0.000	0.000
30 min	0.505	0.505	0.505	0.005	0.000	0.005
60 min	0.507	0.507	0.507	0.006	0.005	0.007
90 min	0.509	0.509	0.508	0.008	0.006	0.008
120 min	0.511	0.510	0.510	0.011	0.008	0.009
150 min	0.510	0.511	0.511	0.010	0.011	0.011
180 min	0.511	0.512	0.511	0.011	0.010	0.011
210 min	0.512	0.512	0.512	0.012	0.011	0.012
240 min	0.513	0.514	0.513	0.012	0.012	0.012
270 min	0.512	0.515	0.513	0.012	0.012	0.013
300 min	0.513	0.515	0.514	0.013	0.012	0.013
15hrs	0.556	0.557	0.557	0.056	0.013	0.057
20hrs	0.562	0.564	0.562	0.062	0.056	0.062
24hrs (A_f weight)	0.568	0.571	0.569	0.068	0.062	0.069
Empty vial weight	9.077	9.079	9.252			
$\|AN_f$-$AN_0\|$				0.068	0.062	0.069
RH%=(|ANf-AN0|/AN_0)*100				13.6	12.4	13.8

Table 7 Water Sorption of AN, Polystyrene(PS) or Polyacrylonitrile (ACrN)Coated AN

TABLE 8

Time	**Total weight (g) of samples**		**Weight (g) gained by samples (AN_f-AN_0)**	
	AN/PS	**Control AN**	**AN/PS**	**Control AN**
0 min	0.4997	0.5000		
30 min	0.5024	0.5029	0.0027	0.0032
60 min	0.5034	0.5041	0.0037	0.0044
90 min	0.5037	0.5040	0.0040	0.0043
120 min	0.4958	0.5041	0.0039	0.0044
150 min	0.4961	0.5047	0.0036	0.0050
180 min	0.4967	0.5047	0.0030	0.0050
210 min	0.4970	0.5049	0.0027	0.0052
240 min	0.4971	0.5052	0.0026	0.0055
270 min	0.4975	0.5056	0.0022	0.0059
300 min (A_f weight)	0.4974	0.5057	0.0023	0.0060
A_0 weight	0.4997	0.5000	0.4997	0.5000
Empty vial weight	9.0633	9.0510	9.0633	9.0510
$\|(A_f-A_0)\|$			0.0023	0.0060
RH%=($\|A_f-A_0\|/A_0$)*100			**0.5**	**1.2**

Table 8: Weight Gain of AN vs Polystyrene-Coated AN during Water Exposure

FIGURE 1

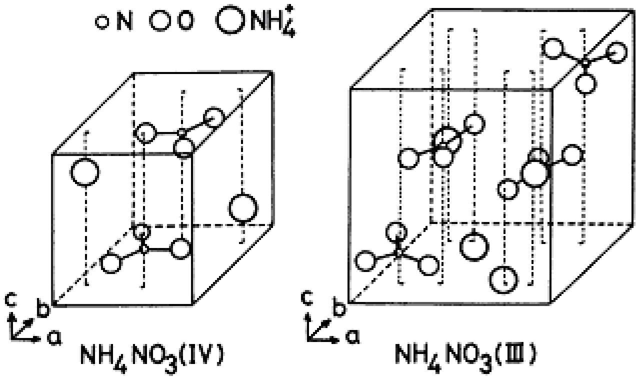


Figure 1: Structures of NH_4NO_3 (IV) and (III) Crystals

FIGURE 2

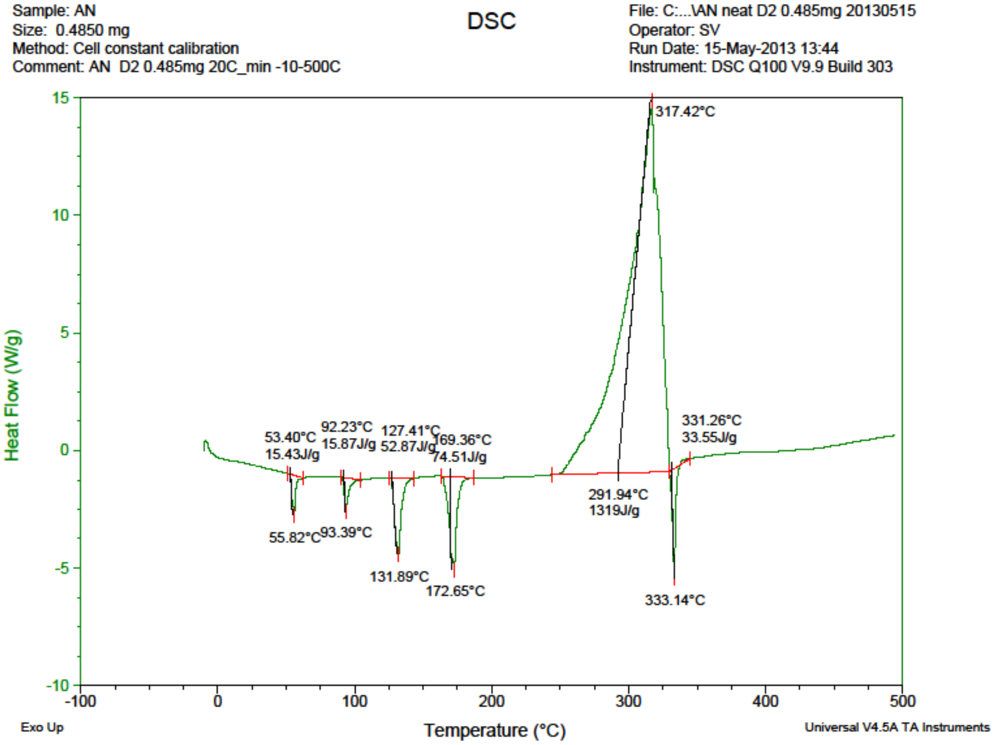


Figure 2: DSC Thermogram of Ammonium Nitrate “as received”

FIGURE 3

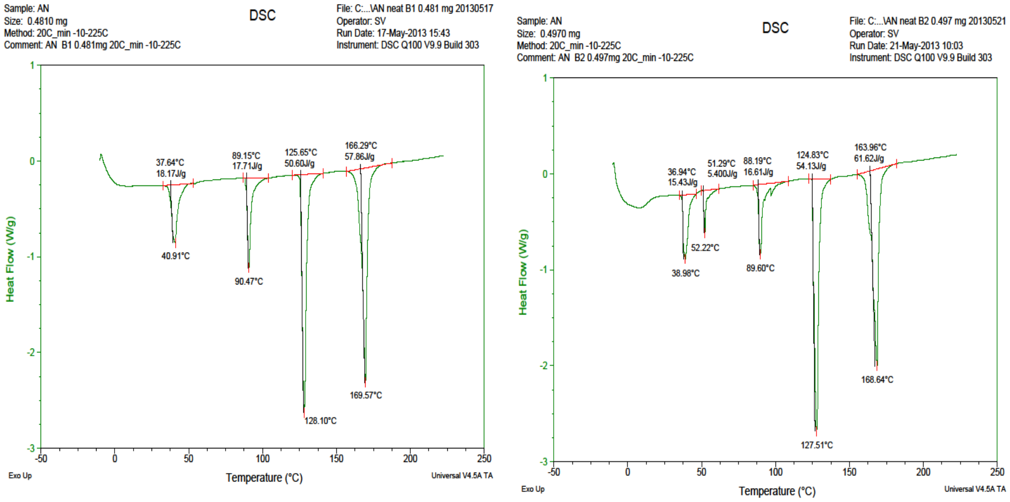


Figure 3: Expanded AN “as received” endotherms only

FIGURE 4

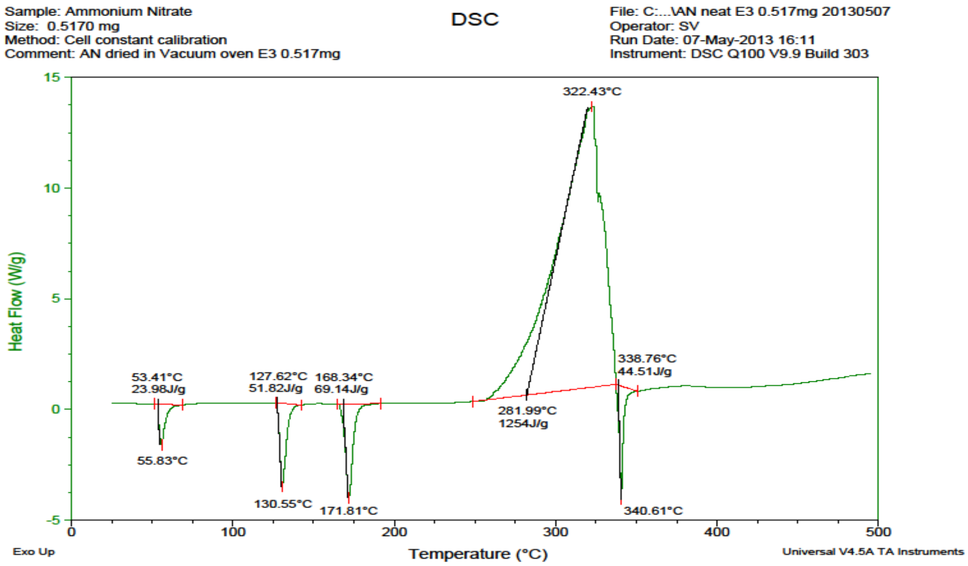


Figure 4: DSC Thermogram of Dried Ammonium Nitrate.

FIGURE 5

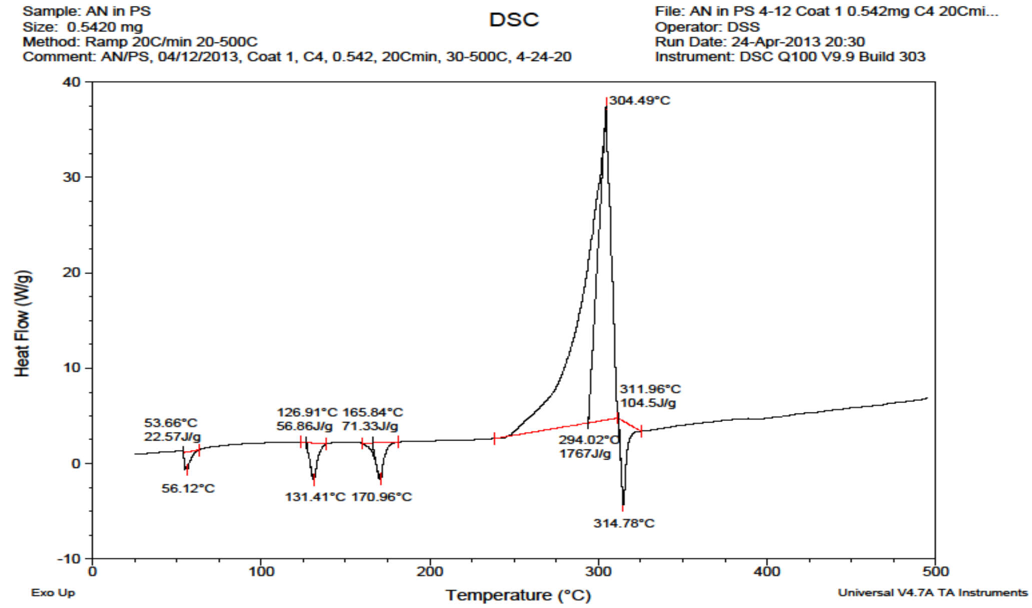


Figure 5: DSC Thermogram of Ammonium Nitrate Coated with Polystyrene

FIGURE 6

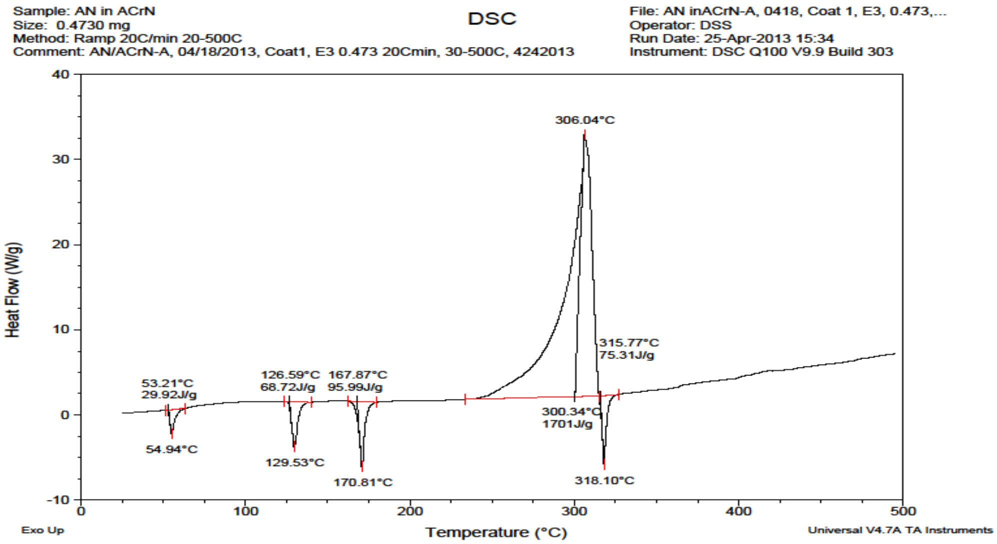


Figure 6: DSC Thermogram of Ammonium Nitrate Coated with Acrylonitrile.

FIGURE 7

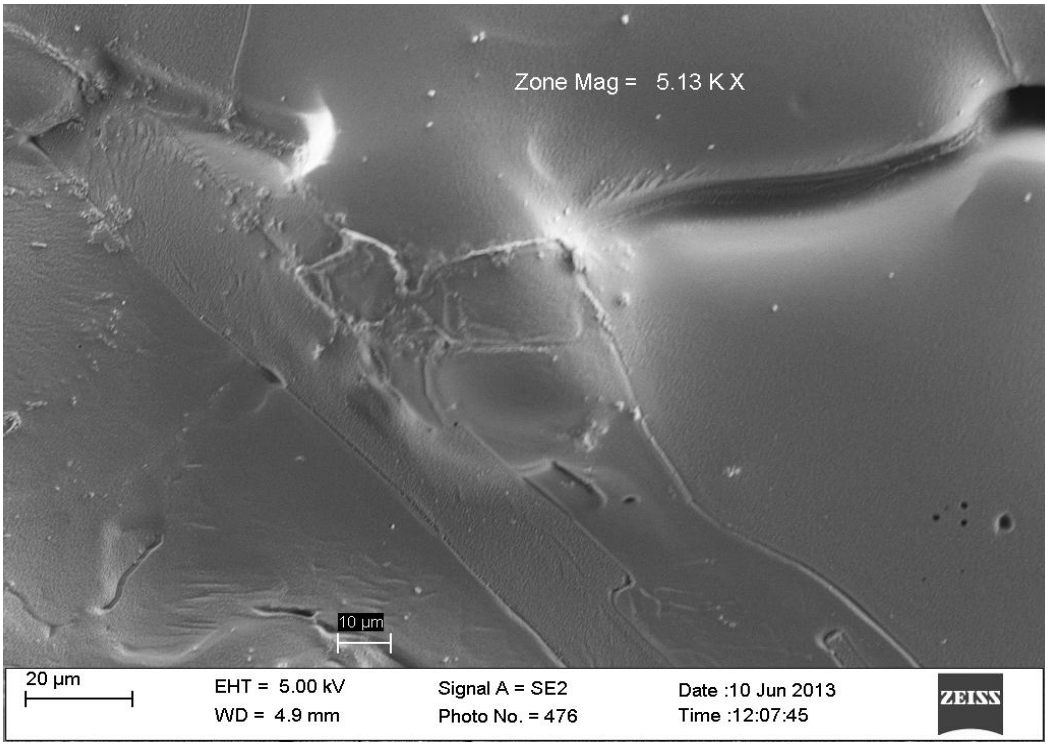


Figure 7: FESEM Image of uncoated AN

FIGURE 8

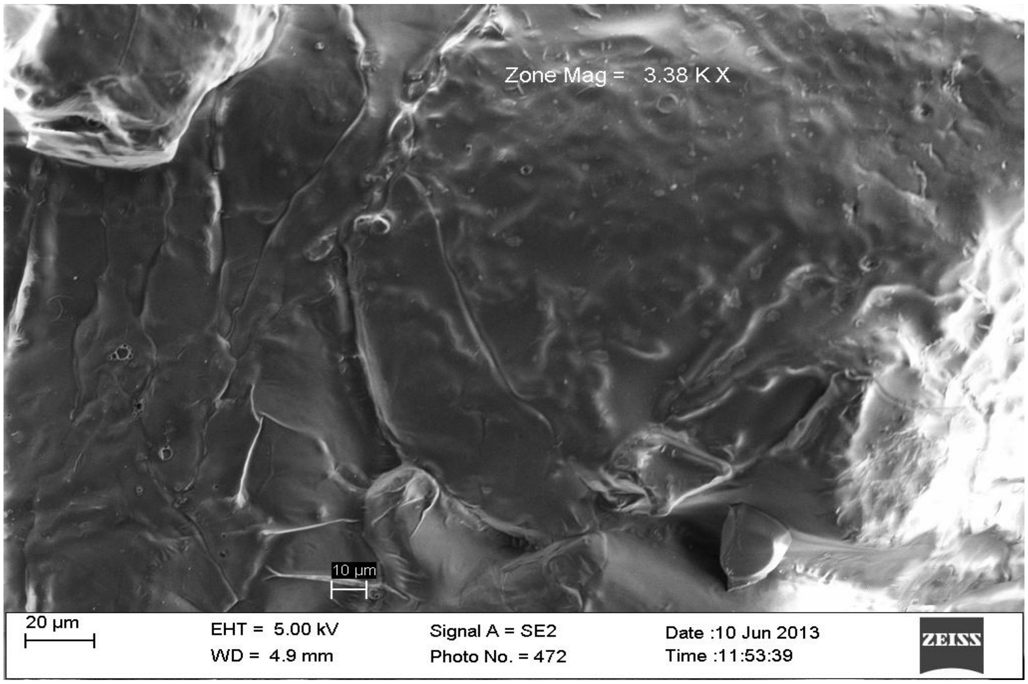


Figure 8: FESEM image of AN Coated with Polystyrene

FIGURE 9

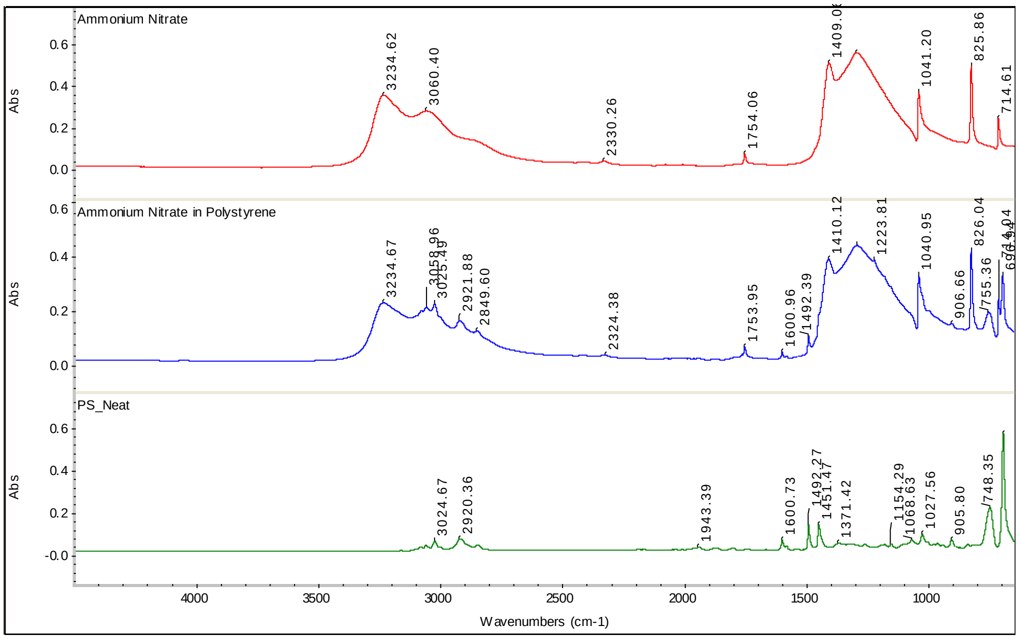


Figure 9: ATR spectra: uncoated AN (top), PS neat (middle), PS-coated AN (bottom).

FIGURE 10

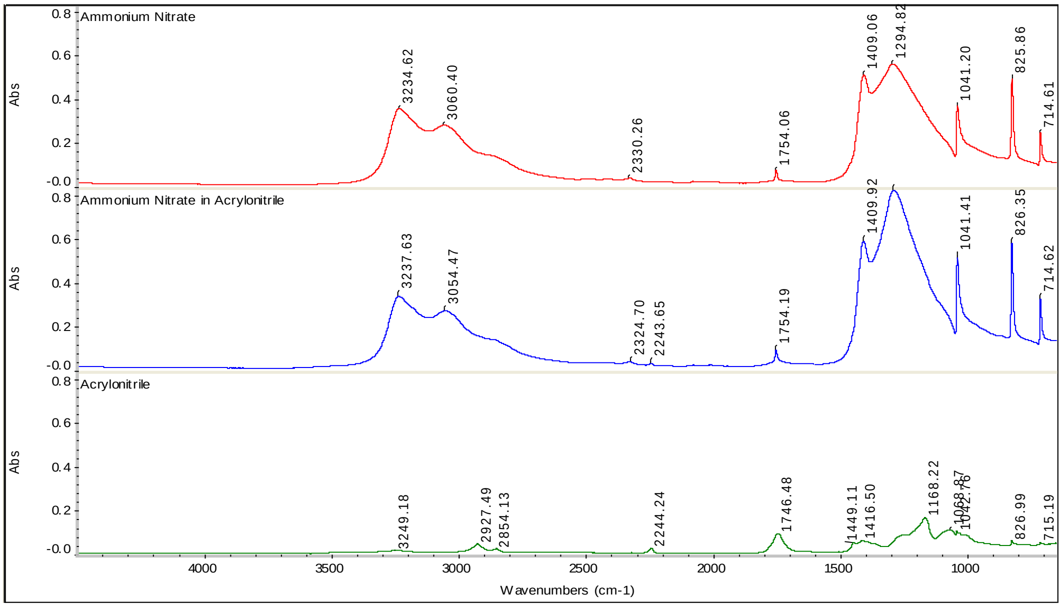


Figure 10: ATR spectra: uncoated AN (top), AcrN neat (middle), AcrN-coated AN (bottom).

FIGURE 11

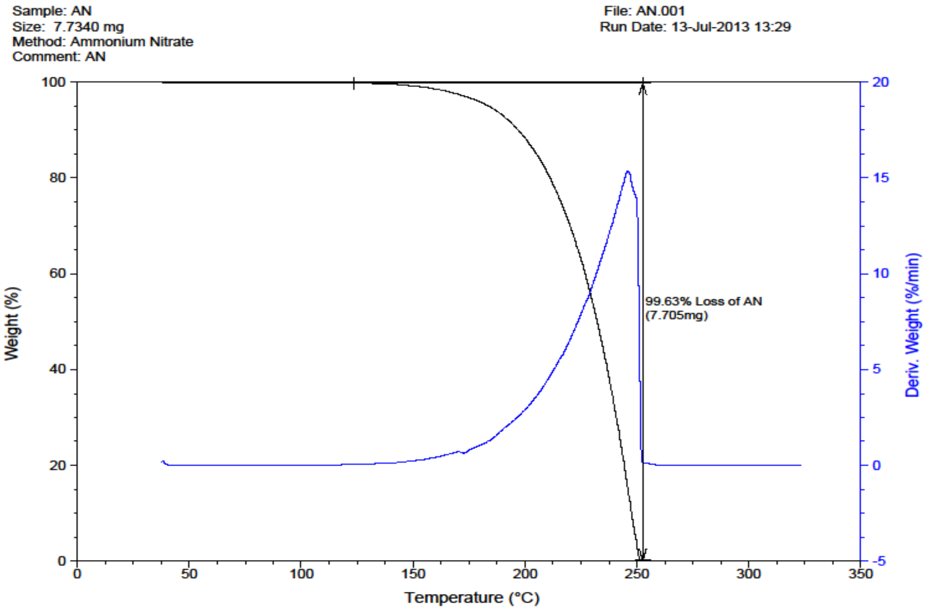


Figure 11: TGA of Uncoated AN

FIGURE 12

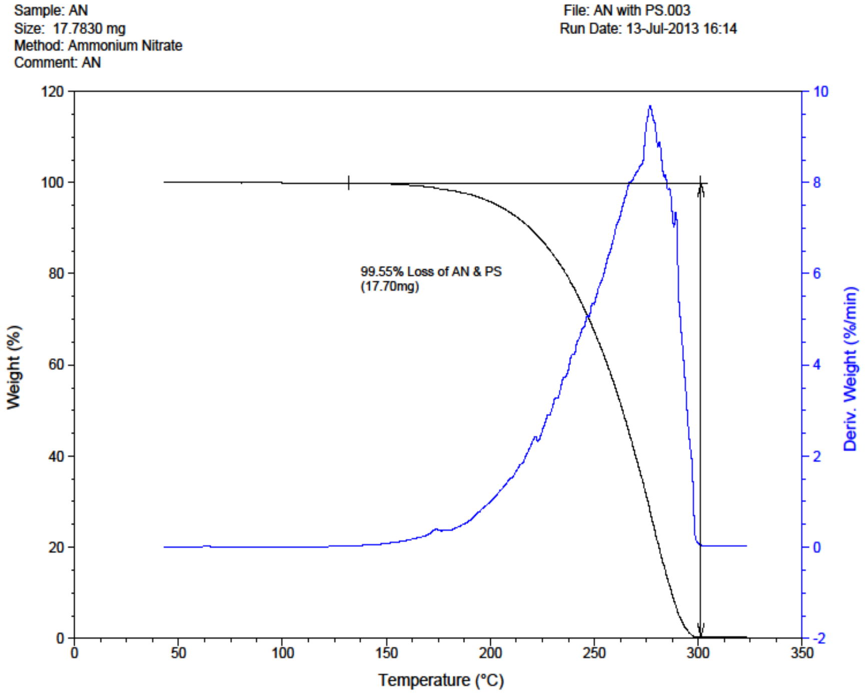


Figure 12: TGA of PS coated AN

FIGURE 13

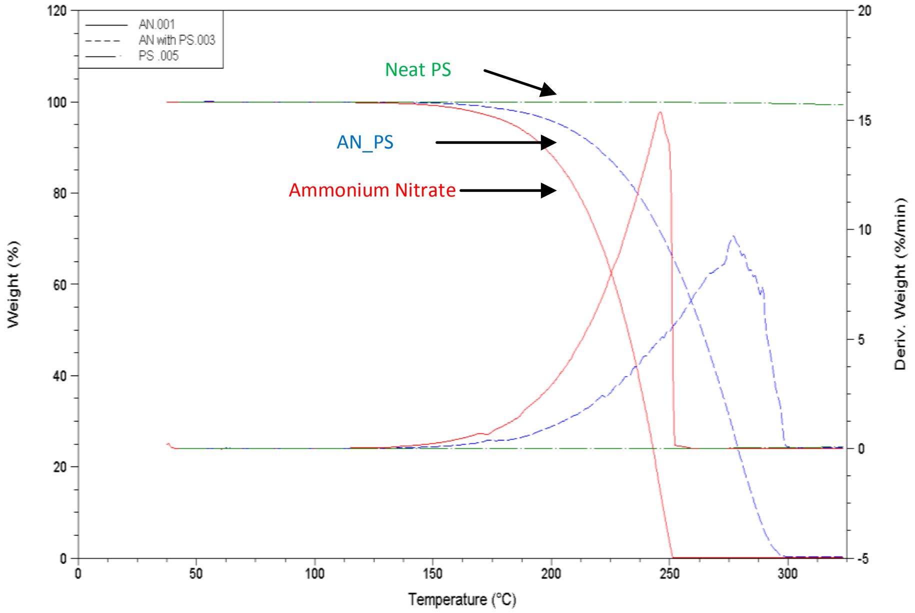


Figure 13: TGA of Polystyrene (neat), AN, and PS-coated AN

FIGURE 14

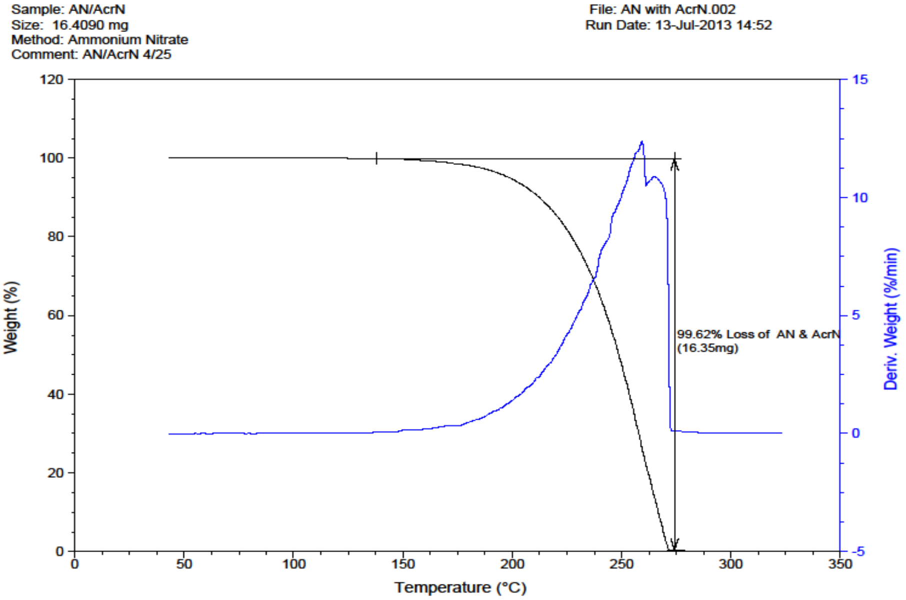


Figure14: TGA of AcrN coated AN

FIGURE 15

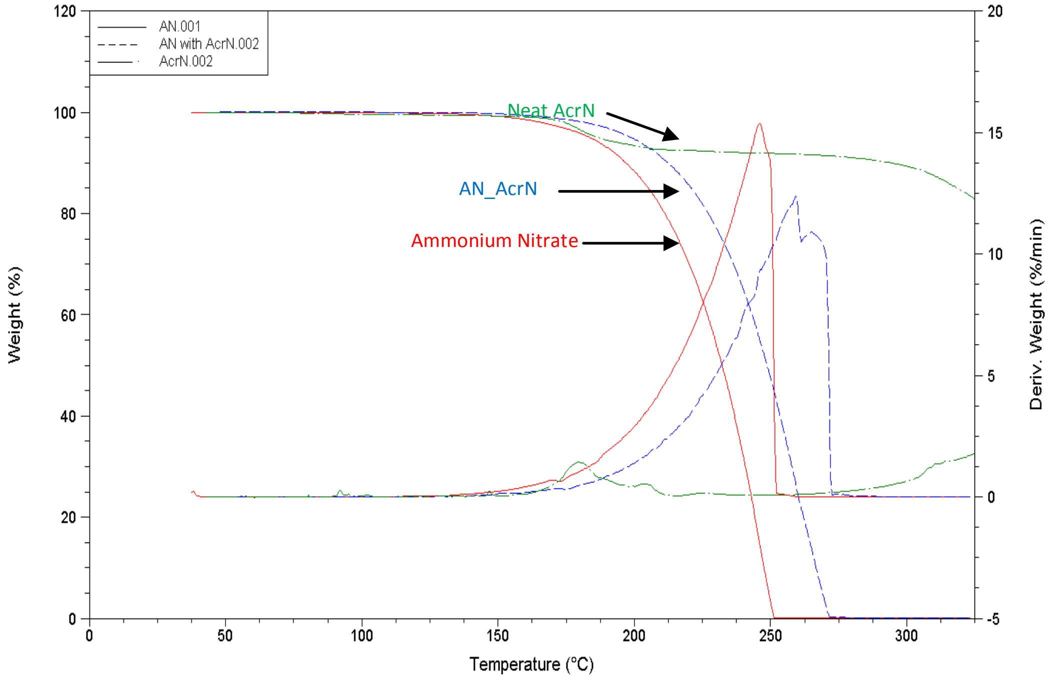


Figure 15: Overlay of AN, ACrN and AN coated with ACrN

Appendix A

FIGURE A.1

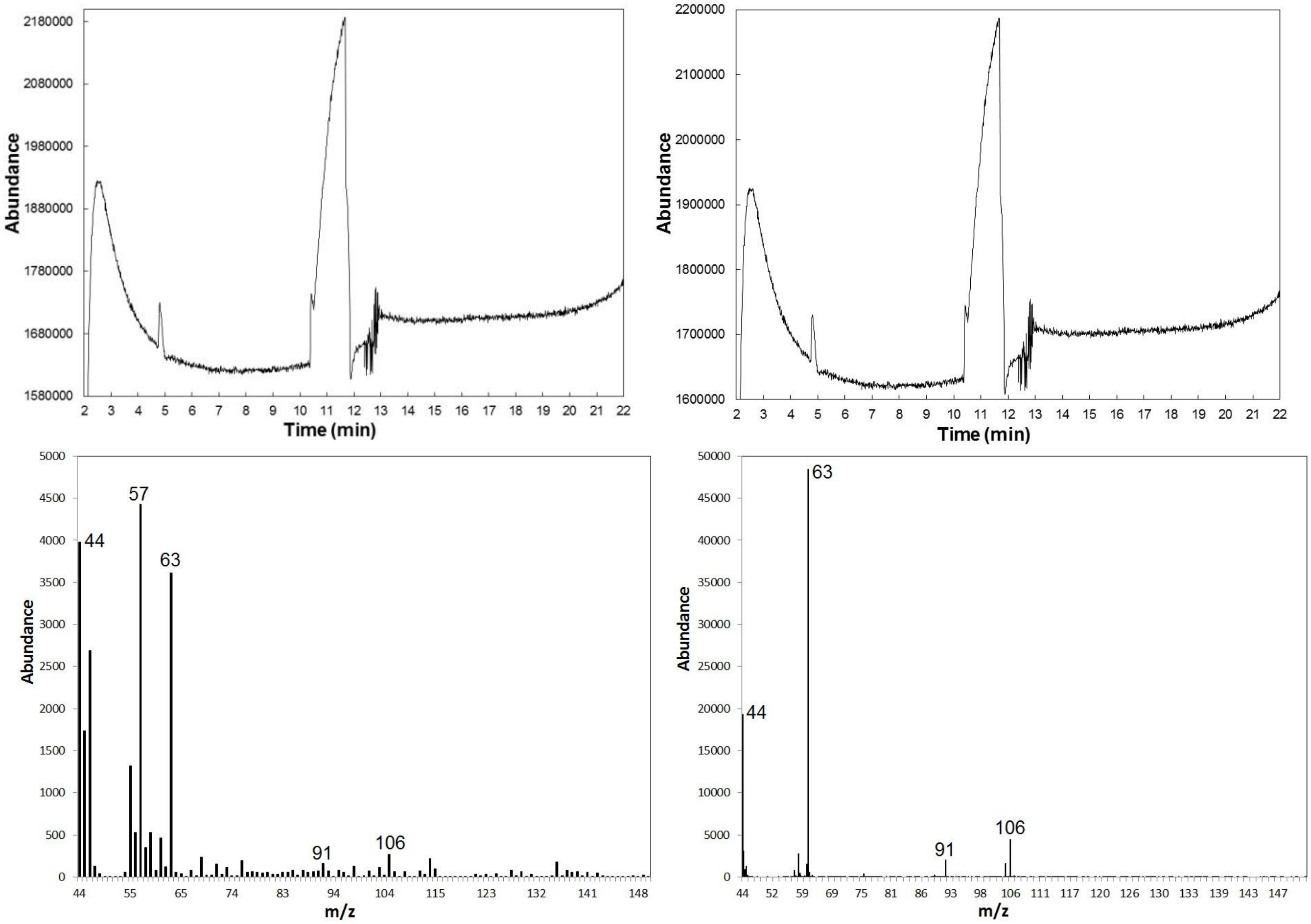


Figure A.1 GC/MS chromatograms and spectra with chenical ionization using methane as reagent gas for recrystalized nitrourea synthesized by method 1(left) and method 2 (right).

FIGURE A.2

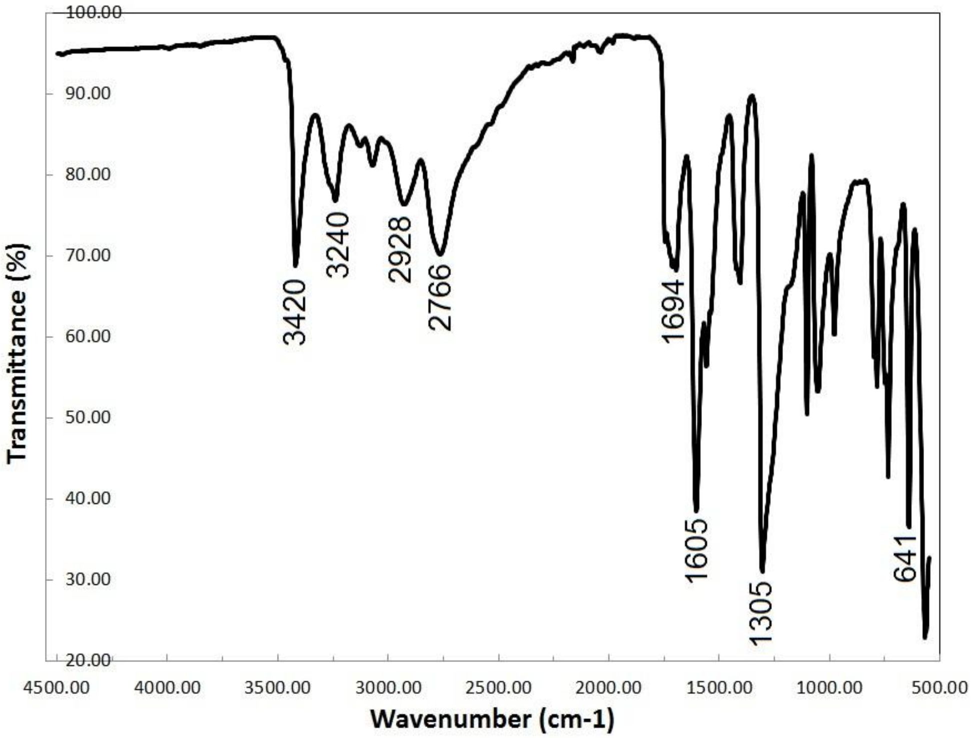


Figure A.2 IR spectrum (transmission mode) of recrystallized Nitrourea using sulfuric acid method

FIGURE A.3

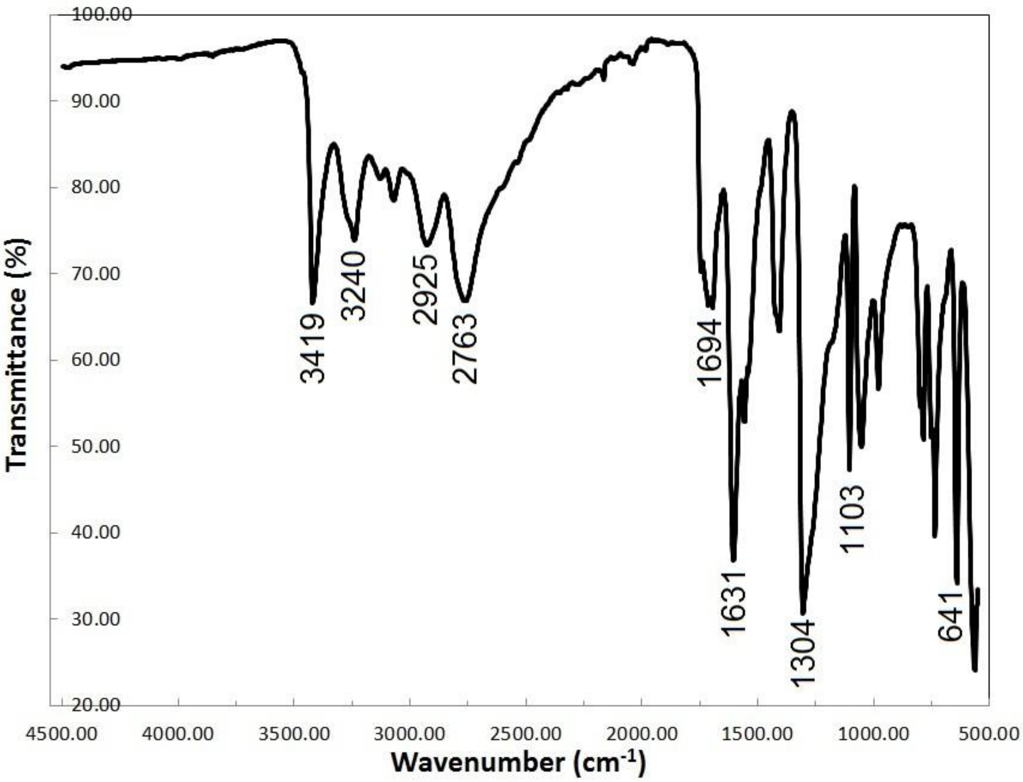


Figure A. 3 IR spectrum (transmission mode) of recrystallized Nitrourea made using acetic anhydride method 2.

FIGURE A. 4

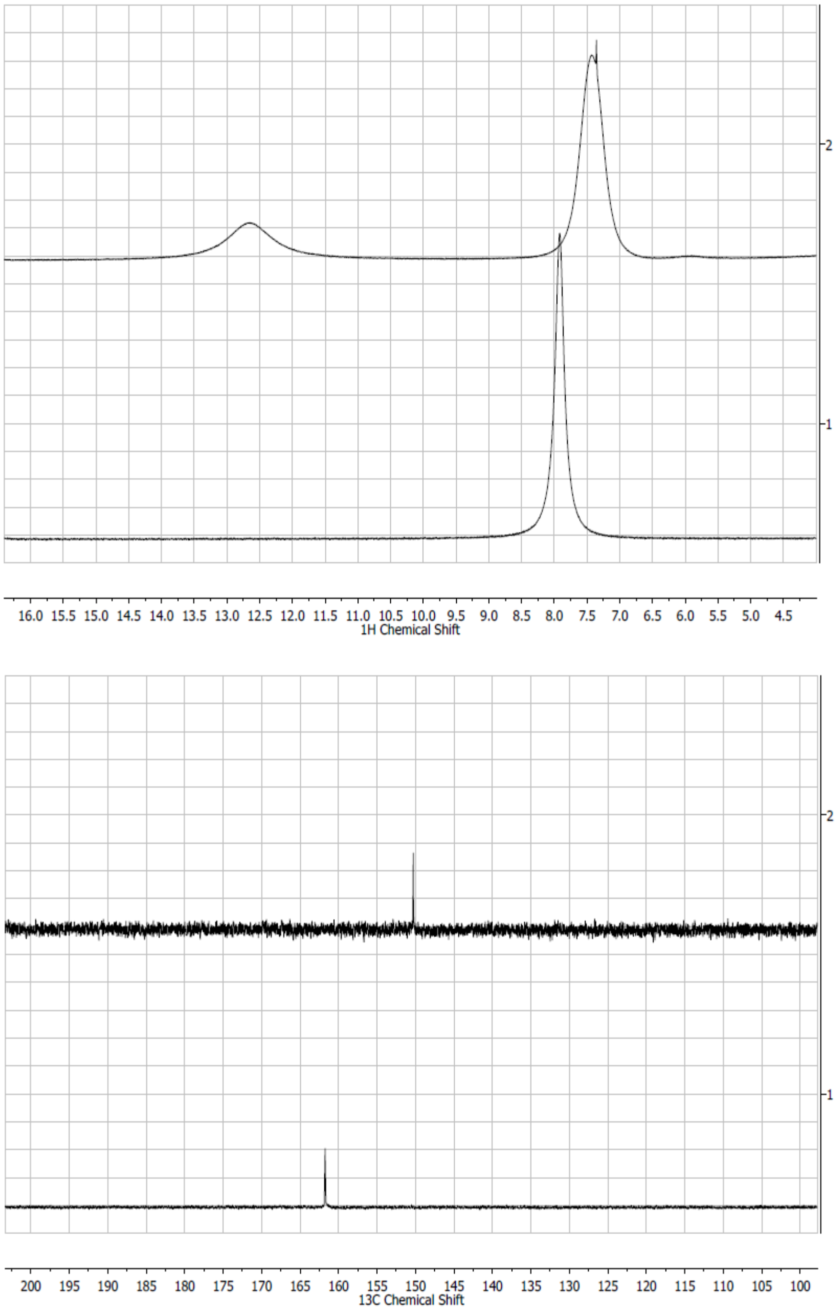


Figure A. 4 1H-NMR (top) and 13C-NMR (bottom) of Nitrourea (2) and Urea Nitrate(1)

FIGURE A. 5

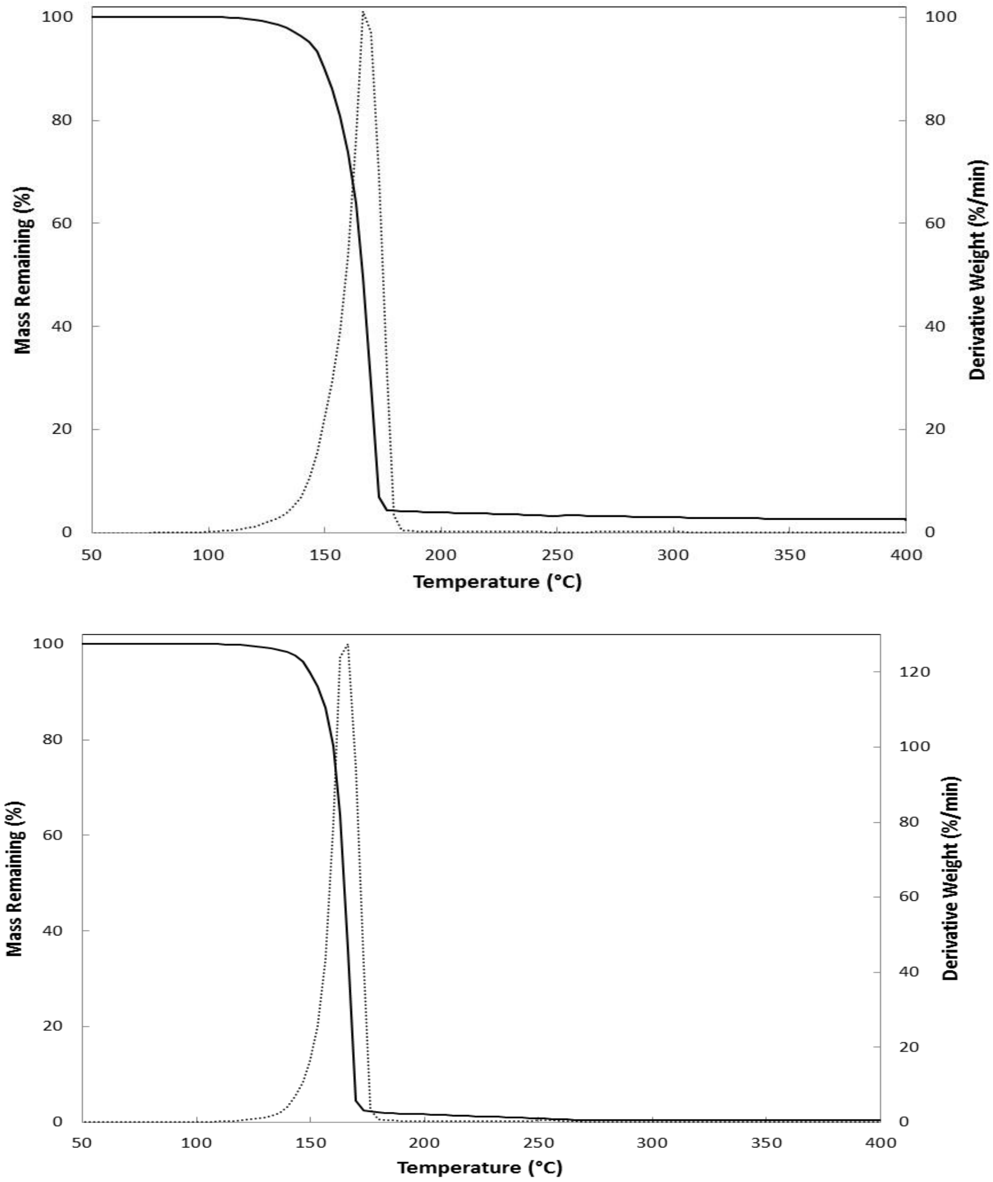


Figure A.5 TGA Trace Recrystallized Nitrourea synthesized using method 1 (top) & method 2 (bottom). Scan rate 20 °C/min.

Appendix B

TABLE B.1

Soil Sample	Area(µS*Min)		Peak Ht(µS)		Ret. Time(Min)		ng/ml		ng/g of soil	
2007	Prior	After	Prior	After	Prior	After	Prior	After	Prior	After
O 1	X	0.0022	X	0.01	X	9.074	X	53	X	105
O 1	X	0.0149	X	0.02	X	8.318	X	95	X	190
O 1	X	0.0031	X	0.01	X	9.071	X	56	X	111
O 2	X	0.019	X	0.05	X	8.941	X	125	X	249
O 2	X	X	X	X	X		X	X	X	X
O 2	X	0.0042	X	0.04	X	9.204	X	51	X	101
O 3	0.0079	0.0057	0.03	0.02	9.041	9.048	69	58	138	116
O 3	0.0076	0.005	0.03	0.02	9.034	9.021	67.5	55	135	109
O 3	0.0122	0.0062	0.04	0.02	9.061	8.998	90.5	61	181	121
O 4	X	0.009	X	0.03	X	9.001	X	74.5	X	149
O 4	X	0.0082	X	0.03	X	9.011	X	70.5	X	141
O 4	X	0.0086	X	0.03	X	9.024	X	72.5	X	145
O 5	X	X	X	X	X	X	X	X	X	X
O 5	X	X	X	X	X	X	X	X	X	X
O 5	X	X	X	X	X	X	X	X	X	X
O 6	X	X	X	X	X	X	X	X	X	X
O 6	X	X	X	X	X	X	X	X	X	X
O 6	X	X	X	X	X	X	X	X	X	X
O 7	X	0.0069	X	0.03	X	9054	X	68	X	137
O 7	X	0.008	X	0.03	X	9.121	X	72	X	144
O 7	X	0.0121	X	0.03	X	8.841	X	86	X	171
O 8	X	X	X	X	X	X	X	X	X	X
O 8	X	X	X	X	X	X	X	X	X	X
O 8	X	X	X	X	X	X	X	X	X	X
O 9	X	X	X	X	X	X	X	X	X	X
O 9	X	X	X	X	X	X	X	X	X	X
O 9	X	X	X	X	X	X	X	X	X	X
O 10	X	0.0085	X	0.03	X	9.104	X	74	X	147
O 10	X	0.0104	X	0.03	X	9.104	X	80	X	160
O 10	X	0.0073	X	0.03	X	9.108	X	70	X	139
O 11	X	X	X	X	X	X	X	X	X	X
O 11	X	X	X	X	X	X	X	X	X	X
O 11	X	X	X	X	X	X	X	X	X	X
O 12	X	X	X	X	X	X	X	X	X	X
O 12	X	X	X	X	X	X	X	X	X	X
O 12	X	0.0086	X	0.08	X	9.121	X	74	X	148
O 13	X	X	X	X	X	X	X	X	X	X
O 13	X	X	X	X	X	X	X	X	X	X
O 13	X	0.0041	X	0.02	X	9.008	X	50	X	100
O 14	X	X	X	X	X	X	X	X	X	X
O 14	X	X	X	X	X	X	X	X	X	X
O 14	X	X	X	X	X	X	X	X	X	X
X =Below Detection Limit (BDL)										

Table B.1 Amounts of Perchlorates Recovered before and after Fireworks display from 2007 at Site 1.

TABLE B.2

ID	Area(µS*Min)		Peak Ht(µS)		Ret. Time(Min)		ng/ml		ng/g of soil	
2009	Prior	After	Prior	After	Prior	After	Prior	After	Prior	After
O 1	X	0.018	X	0.06	X	9.031	X	133	X	266
O 1	X	0.018	X	0.07	X	9.001	X	130	X	260
O 1	X	0.017	X	0.06	X	9.024	X	127.5	X	255
O 2	X	0.016	X	0.06	X	9.014	X	122	X	244
O 2	X	0.016	X	0.06	X	9.004	X	121	X	242
O 2	X	0.016	X	0.06	X	9.014	X	121.5	X	243
O 3	X	X	X	X	X	X	X	X	X	X
O 3	X	X	X	X	X	X	X	X	X	X
O 3	X	X	X	X	X	X	X	X	X	X
O 4	X	0.003	X	0.01	X	9.057	X	58.5	X	117
O 4	X	0.002	X	0.01	X	9.014	X	54	X	108
O 4	X	0.004	X	0.01	X	9.011	X	61	X	122
O 5	X	X	X	X	X	X	X	X	X	X
O 5	X	X	X	X	X	X	X	X	X	X
O 5	X	X	X	X	X	X	X	X	X	X
O 6	X	0.013	X	0.04	X	9.008	X	109.5	X	219
O 6	X	0.015	X	0.05	X	9.017	X	118	X	236
O 6	X	0.012	X	0.04	X	9.024	X	100	X	200
O 7	X	X	X	X	X	X	X	X	X	X
O 7	X	X	X	X	X	X	X	X	X	X
O 7	X	X	X	X	X	X	X	X	X	X
O 8	X	0.008	X	0.02	X	9.018	X	83.5	X	167
O 8	X	0.007	X	0.02	X	9.004	X	76.5	X	153
O 8	X	0.017	X	0.06	X	9.048	X	125.5	X	251
O 9	X	X	X	X	X	X	X	X	X	X
O 9	X	0.006	X	0.04	X	98.114	X	73.5	X	147
O 9	X	X	X	X	X	X	X	X	X	X
O 10	X	X	X	X	X	X	X	X	X	X
O 10	X	X	X	X	X	X	X	X	X	X
O 10	X	X	X	X	X	X	X	X	X	X
O 11	X	X	X	X	X	X	X	X	X	X
O 11	X	X	X	X	X	X	X	X	X	X
O 11	X	X	X	X	X	X	X	X	X	X
X =Below Detection Limit (BDL)										

Table B.2 Amounts of Perchlorates Recovered before and after Fireworks display from 2009 at Site 1

TABLE B.3

ID	Area(μS*Min)		Peak Ht(μS)		Ret. Time(Min)		ng/ml		ng/g of soil	
2010	Prior	After	Prior	After	Prior	After	Prior	After	Prior	After
O 1	X	0.0072	X	0.02	X	9.041	X	69.5	X	139
O 1	X	0.0055	X	0.02	X	9.031	X	61	X	122
O 1	X	0.0059	X	0.02	X	8.997	X	63	X	126
O 2	X	0.0047	X	0.02	X	8.984	X	57	X	114
O 2	X	0.0055	X	0.02	X	8.981	X	61	X	122
O 2	X	0.0034	X	0.01	X	8.938	X	50.5	X	101
O 3	X	0.0064	X	0.03	X	9.007	X	65.5	X	131
O 3	X	0.0168	X	0.06	X	9.011	X	117.5	X	235
O 3	X	0.006	X	0.02	X	8.981	X	63.5	X	127
O 4	X	0.1389	X	0.52	X	9.001	X	728	X	1456
O 4	X	0.1234	X	0.46	X	9.001	X	650.5	X	1301
O 4	X	0.0907	X	0.34	X	9.004	X	487	X	974
O 5	X	0.0035	X	0.01	X	8.981	X	51	X	102
O 5	X	0.0057	X	0.02	X	9.017	X	62	X	124
O 5	X	0.0034	X	0.01	X	8.994	X	50.5	X	101
O 6	X	0.0261	X	0.09	X	9.004	X	164	X	328
O 6	X	0.0147	X	0.06	X	9.008	X	107	X	214
O 6	X	0.0097	X	0.04	X	9.004	X	82	X	164
O 7	X	0.1659	X	0.63	X	9.007	X	863	X	1726
O 7	X	0.2233	X	0.84	X	9.001	X	1150	X	2300
O 7	X	0.1759	X	0.66	X	9.004	X	913	X	1826
O 8	X	X	X	X	X	X	X	X	X	X
O 8	X	X	X	X	X	X	X	X	X	X
O 8	X	X	X	X	X	X	X	X	X	X
O 9	X	0.0015	X	0.01	X	9.048	X	41	X	82
O 9	X	X	X	X	X	X	X	X	X	X
O 9	X	0.0261	X	0.05	X	9.081	X	164	X	328
O 10	X	X	X	X	X	X	X	X	X	X
O 10	X	X	X	X	X	X	X	X	X	X
O 10	X	X	X	X	X	X	X	X	X	X
O 11	X	0.0044	X	0.01	X	9.011	X	55.5	X	111
O 11	X	0.0023	X	0.01	X	8.848	X	45	X	90
O 11	X	X	X	X	X	X	X	X	X	X

X =Below Detection Limit (BDL)

Table B.3 Amounts of Perchlorates Recovered before and after Fireworks display from 2010 at Site 1

TABLE B.4

ID	Area(µS*Min)		Peak Ht(µS)		Ret. Time(Min)		ng/ml		ng/g of soil	
2011	Prior	After	Prior	After	Prior	After	Prior	After	Prior	After
O 1	X	0.026	X	0.03	X	8.588	X	185.5	X	371
O 1	X	0.0048	X	0.02	X	8.704	X	79.5	X	159
O 1	X	0.0031	X	0.01	X	8.711	X	71	X	142
O 2	X	0.0984	X	0.39	X	8.671	X	547.5	X	1095
O 2	X	0.0907	X	0.36	X	8.668	X	509	X	1018
O 2	X	0.0939	X	0.37	X	8.668	X	525	X	1050
O 3	X	X	X	X	X	X	X	X	X	X
O 3	X	X	X	X	X	X	X	X	X	X
O 3	X	X	X	X	X	X	X	X	X	X
O 4	X	0.0056	X	0.02	X	8.684	X	83.5	X	167
O 4	X	0.0015	X	0.01	X	8.678	X	63	X	126
O 4	X	0.0011	X	0.01	X	8.664	X	61	X	122
O 5	X	X	X	X	X	X	X	X	X	X
O 5	X	X	X	X	X	X	X	X	X	X
O 5	X	X	X	X	X	X	X	X	X	X
O 6	X	0.0038	X	0.01	X	8.664	X	74.5	X	149
O 6	X	0.0051	X	0.02	X	8.681	X	81	X	162
O 6	X	0.0026	X	0.01	X	8.664	X	68.5	X	137
O 7	X	X	X	X	X	X	X	X	X	X
O 7	X	X	X	X	X	X	X	X	X	X
O 7	X	X	X	X	X	X	X	X	X	X
O 8	X	0.0039	X	0.02	X	8.704	X	75	X	150
O 8	X	0.003	X	0.01	X	8.701	X	70.5	X	141
O 8	X	0.0029	X	0.01	X	8.714	X	70	X	140
O 9	X	0.0097	X	0.03	X	8.721	X	104	X	208
O 9	X	0.0102	X	0.04	X	8.697	X	106.5	X	213
O 9	X	0.0063	X	0.02	X	8.708	X	87	X	174
O 10	X	X	X	X	X	X	X	X	X	X
O 10	X	X	X	X	X	X	X	X	X	X
O 10	X	X	X	X	X	X	X	X	X	X
O 11	X	X	X	X	X	X	X	X	X	X
O 11	X	X	X	X	X	X	X	X	X	X
O 11	X	X	X	X	X	X	X	X	X	X
X =Below Detection Limit (BDL)										

Table B.4 Amounts of Perchlorates Recovered before and after Fireworks display from 2011 at Site 1

TABLE B. 5

ID	Area(µS*Min)		Peak Ht(µS)		Ret. Time(Min)		ng/ml		ng/g of soil	
2012	Prior	After	Prior	After	Prior	After	Prior	After	Prior	After
O 1	X	X	X	X	X	X	X	X	X	X
O 1	X	X	X	X	X	X	X	X	X	X
O 1	X	X	X	X	X	X	X	X	X	X
O 2	X	X	X	X	X	X	X	X	X	X
O 2	X	X	X	X	X	X	X	X	X	X
O 2	X	X	X	X	X	X	X	X	X	X
O 3	X	0.0047	X	0.02	X	9.311	X	42	X	84
O 3	X	0.0071	X	0.03	X	9.301	X	50	X	100
O 3	X	0.0047	X	0.02	X	9.318	X	42	X	84
O 4	X	0.0034	X	0.01	X	9.348	X	38	X	75
O 4	X	X	X	X	X	X	X	X	X	X
O 4	X	0.0044	X	0.02	X	9.307	X	41	X	82
O 5	X	X	X	X	X	X	X	X	X	X
O 5	X	X	X	X	X	X	X	X	X	X
O 5	X	X	X	X	X	X	X	X	X	X
O 6	X	X	X	X	X	X	X	X	X	X
O 6	X	X	X	X	X	X	X	X	X	X
O 6	X	X	X	X	X	X	X	X	X	X
O 7	X	X	X	X	X	X	X	X	X	X
O 7	X	X	X	X	X	X	X	X	X	X
O 7	X	X	X	X	X	X	X	X	X	X
O 8	X	X	X	X	X	X	X	X	X	X
O 8	X	X	X	X	X	X	X	X	X	X
O 8	X	X	X	X	X	X	X	X	X	X
O 9	X	X	X	X	X	X	X	X	X	X
O 9	X	X	X	X	X	X	X	X	X	X
O 9	X	X	X	X	X	X	X	X	X	X
O 10	X	0.0235	X	0.09	X	9.338	X	105	X	209
O 10	X	0.0188	X	0.07	X	9.338	X	89	X	178
O 10	X	0.022	X	0.08	X	9.331	X	100	X	199
O 11	X	X	X	X	X	X	X	X	X	X
O 11	X	X	X	X	X	X	X	X	X	X
O 11	X	X	X	X	X	X	X	X	X	X
X =Below Detection Limit (BDL)										

Table B.5 Amounts of Perchlorates Recovered before and after Fireworks display from 2012 at Site 1

Table B.6

ID	Area(µS*Min)		Peak Ht(µS)		Ret. Time(Min)		ng/ml		ng/g of soil	
2011	Prior	After	Prior	After	Prior	After	Prior	After	Prior	After
B1-1	X	X	X	X	X	X	X	X	X	X
B1-2	X	0.0077	X	0.03	X	8.771	X	41.5	X	83
B1-3	X	X	X	X	X	X	X	X	X	X
B2-1	X	0.0037	X	0.02	X	8.754	X	21.5	X	43
B2-2	X	0.0042	X	0.02	X	8.758	X	24.0	X	48
B2-3	X	0.0040	X	0.01	X	8.758	X	23.0	X	46
B3-1	X	0.2407	X	0.98	X	8.704	X	1206.5	X	2413
B3-2	X	0.2953	X	1.21	X	8.694	X	1479.5	X	2959
B3-3	X	0.2690	X	1.10	X	8.701	X	1348.0	X	2696
B4-1	X	0.1358	X	0.53	X	8.738	X	682.0	X	1364
B4-2	X	0.1555	X	0.61	X	8.738	X	780.5	X	1561
B4-3	X	0.1181	X	0.47	X	8.741	X	593.5	X	1187
B5-1	X	0.0018	X	0.01	X	8.814	X	12.0	X	24
B5-2	X	X	X	X	X	X	X	X	X	X
B5-3	X	0.0014	X	0.01	X	8.754	X	10.0	X	20
B6-1	X	0.013	X	0.05	X	8.757	X	68.0	X	136
B6-2	X	0.0125	X	0.05	X	8.754	X	65.5	X	131
B6-3	X	0.0026	X	0.01	X	8.751	X	16.0	X	32
X =Below Detection Limit (BDL)										

Table B.6 Amounts of Perchlorates Recovered before and after Fireworks display from 2011 at Site 2

Table B.7

ID	Area(µS*Min)		Peak Ht(µS)		Ret. Time(Min)		ng/ml		ng/g of soil	
2012	Prior	After	Prior	After	Prior	After	Prior	After	Prior	After
B1-1	X	0.0199	X	0.07	X	9.181	X	98	X	197
B1-2	X	0.0186	X	0.07	X	9.167	X	94	X	188
B1-3	X	0.0207	X	0.08	X	9.158	X	101	X	202
B2-1	X	0.0943	X	0.34	X	9.161	X	346	X	693
B2-2	X	0.1057	X	0.37	X	9.158	X	384	X	769
B2-3	X	0.0997	X	0.36	X	9.154	X	364	X	729
B3-1	X	0.0031	X	0.01	X	9.141	X	42	X	85
B3-2	X	0.0051	X	0.02	X	9.171	X	49	X	98
B3-3	X	0.0031	X	0.01	X	9.167	X	42	X	85
B4-1	X	0.1587	X	0.57	X	9.151	X	561	X	1122
B4-2	X	0.1555	X	0.56	X	9.151	X	550	X	1101
B4-3	X	0.1487	X	0.54	X	9.158	X	528	X	1055
B5-1	X	0.019	X	0.07	X	9.167	X	95	X	191
B5-2	X	0.0188	X	0.07	X	9.161	X	95	X	189
B5-3	X	0.0245	X	0.09	X	9.164	X	114	X	227
B6-1	X	0.0074	X	0.03	X	9.184	X	57	X	113
B6-2	X	0.0063	X	0.02	X	9.177	X	53	X	106
B6-3	X	0.008	X	0.03	X	9.167	X	59	X	117
B7-1	X	0.0062	X	0.02	X	9.194	X	53	X	105
B7-2	X	0.0136	X	0.05	X	9.168	X	77	X	155
B7-3	X	0.0069	X	0.02	X	9.194	X	55	X	110
B8-1	X	0.0148	X	0.06	X	9.188	X	81	X	163
B8-2	X	0.0206	X	0.07	X	9.167	X	101	X	201
B8-3	X	0.0163	X	0.06	X	9.194	X	86	X	173
X =Below Detection Limit (BDL)										

Table B.7 Amounts of Perchlorates Recovered before and after Fireworks display from 2012 at Site 2

Table B.8

ID	Area(µS*Min)		Peak Ht(µS)		Ret. Time(Min)		ng/ml		ng/g of soil	
2011	Prior	After	Prior	After	Prior	After	Prior	After	Prior	After
M1-1	X	0.0416	X	0.16	X	8.741	X	250.0	X	500
M1-2	X	0.0561	X	0.21	X	8.744	X	322.5	X	645
M1-3	X	0.0313	X	0.11	X	8.744	X	198.5	X	397
M2-1	X	0.0524	X	0.20	X	8.754	X	304.0	X	608
M2-2	X	0.0633	X	0.24	X	8.748	X	358.5	X	717
M2-3	X	0.0531	X	0.20	X	8.748	X	307.5	X	615
M3-1	X	0.4967	X	1.98	X	8.704	X	2525.5	X	5051
M3-2	X	0.4872	X	1.93	X	8.701	X	2478.0	X	4956
M3-3	X	0.4466	X	1.78	X	8.707	X	2275.0	X	4550
M4-1	X	0.0240	X	0.09	X	8.747	X	162.0	X	324
M4-2	X	0.0216	X	0.08	X	8.744	X	150.0	X	300
M4-3	X	0.0230	X	0.09	X	8.738	X	157.0	X	314
M5-1	X	2.515	X	9.36	X	8.594	X	12617.0	X	25234
M5-2	X	2.4451	X	9.21	X	8.594	X	12267.5	X	24535
M5-3	X	2.3901	X	9.00	X	8.594	X	11992.5	X	23985
M6-1	X	0.0187	X	0.07	X	8.737	X	135.5	X	271
M6-2	X	0.0181	X	0.07	X	8.727	X	132.5	X	265
M6-3	X	0.0183	X	0.07	X	8.728	X	133.5	X	267
M7-1	X	0.0402	X	0.16	X	8.728	X	243.0	X	486
M7-2	X	0.0311	X	0.12	X	8.724	X	197.5	X	395
M7-3	X	0.0329	X	0.13	X	8.724	X	206.5	X	413
M8-1	X	0.0770	X	0.30	X	8.738	X	427.0	X	854
M8-2	X	0.0860	X	0.33	X	8.738	X	472.0	X	944
M8-3	X	0.0857	X	0.33	X	8.724	X	470.5	X	941
X =Below Detection Limit (BDL)										

Table B.8 Amounts of Perchlorates Recovered before and after Fireworks display from 2011 at Site 3

Table B.9

ID	Area(μS*Min)		Peak Ht(μS)		Ret. Time(Min)		ng/ml		ng/g of soil	
2012	Prior	After	Prior	After	Prior	After	Prior	After	Prior	After
M1-1	X	1.4119	X	5.06	X	8.998	X	4735	X	9469
M1-2	X	1.1463	X	4.14	X	9.014	X	3849	X	7699
M1-3	X	1.0843	X	3.92	X	9.014	X	3643	X	7285
M2-1	X	0.007	X	0.03	X	9.098	X	52	X	103
M2-2	X	0.0018	X	0.01	X	9.118	X	34	X	69
M2-3	X	0.0022	X	0.01	X	8.984	X	36	X	71
M3-1	X	X	X	X	X	X	X	X	X	X
M3-2	X	X	X	X	X	X	X	X	X	X
M3-3	X	X	X	X	X	X	X	X	X	X
M4-1	X	0.1686	X	0.62	X	9.077	X	590	X	1181
M4-2	X	0.1738	X	0.63	X	9.078	X	608	X	1215
M4-3	X	0.1013	X	0.37	X	9.087	X	366	X	732
M5-1	X	0.2583	X	0.94	X	9.071	X	889	X	1779
M5-2	X	0.2234	X	0.82	X	9.068	X	773	X	1546
M5-3	X	0.1443	X	0.5	X	9.071	X	509	X	1019
M6-1	X	X	X	X	X	X	X	X	X	X
M6-2	X	X	X	X	X	X	X	X	X	X
M6-3	X	X	X	X	X	X	X	X	X	X
M7-1	X	0.0994	X	0.36	X	9.087	X	360	X	719
M7-2	X	0.0802	X	0.29	X	9.091	X	296	X	591
M7-3	X	0.0283	X	0.1	X	9.091	X	123	X	245
M8-1	X	0.0043	X	0.02	X	9.041	X	43	X	85
M8-2	X	0.0161	X	0.06	X	9.071	X	82	X	164

X =Below Detection Limit (BDL)

Table B. 9 Amounts of Perchlorates Recovered before and after Fireworks display from 2012 at Site 3

Table B.10

ID	Area(µS*Min)		Peak Ht(µS)		Ret. Time(Min)		ng/ml		ng/g of soil	
2011	Prior	After	Prior	After	Prior	After	Prior	After	Prior	After
J1-1	X	X	X	X	X	X	X	X	X	X
J1-2	X	X	X	X	X	X	X	X	X	X
J1-3	X	X	X	X	X	X	X	X	X	X
J2-1	X	0.3011	X	1.19	X	8.744	X	1541.5	X	3083
J2-2	X	0.2668	X	1.04	X	8.654	X	1370	X	2740
J2-3	X	0.2713	X	1.07	X	8.641	X	1392.5	X	2785
J3-1	X	0.0735	X	0.29	X	8.698	X	403.5	X	807
J3-2	X	0.0651	X	0.26	X	8.711	X	361.5	X	723
J3-3	X	0.1147	X	0.45	X	8.754	X	609.5	X	1219
J4-1	X	X	X	X	X	X	X	X	X	X
J4-2	X	X	X	X	X	X	X	X	X	X
J4-3	X	X	X	X	X	X	X	X	X	X
J5-1	X	0.0576	X	0.23	X	8.698	X	324	X	648
J5-2	X	0.0998	X	0.39	X	8.694	X	535	X	1070
J5-3	X	0.0623	X	0.24	X	8.724	X	347.5	X	695
J6-1	X	X	X	X	X	X	X	X	X	X
J6-2	X	X	X	X	X	X	X	X	X	X
J6-3	X	X	X	X	X	X	X	X	X	X
J7-1	X	X	X	X	X	X	X	X	X	X
J7-2	X	X	X	X	X	X	X	X	X	X
J7-3	X	X	X	X	X	X	X	X	X	X
X =Below Detection Limit (BDL)										

Table B.10 Amounts of Perchlorates Recovered before and after Fireworks display from 2011 at Site 4

Figure B.1

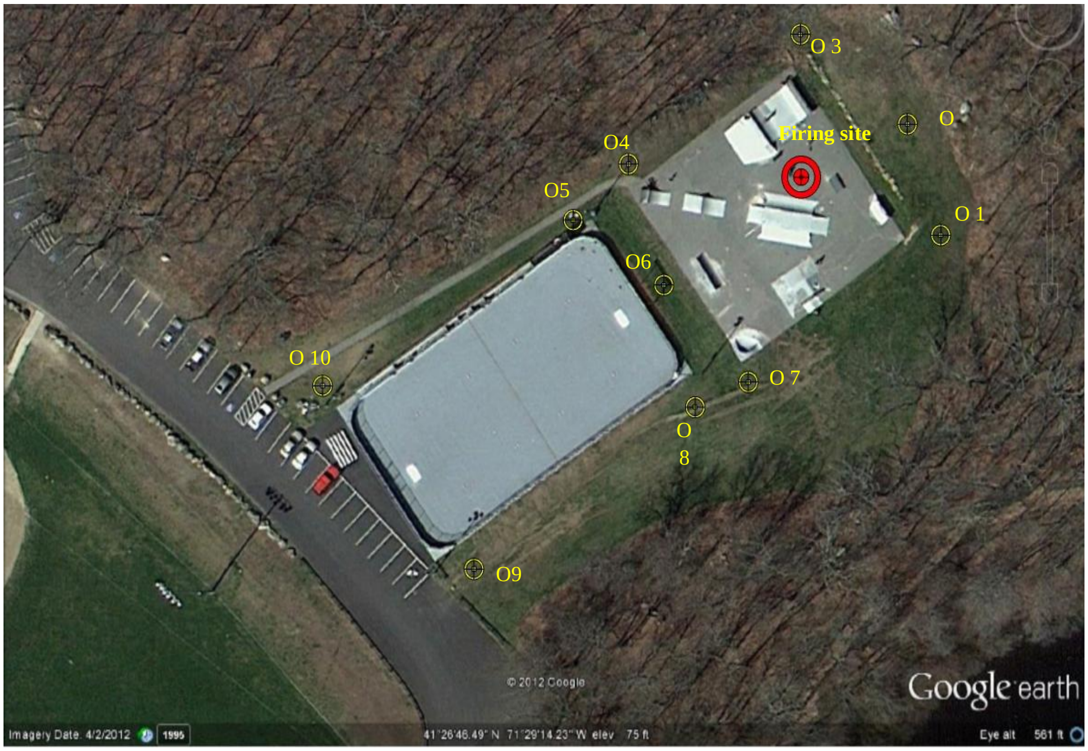


Figure B.1 Locus map of Site 1

Figure B.2

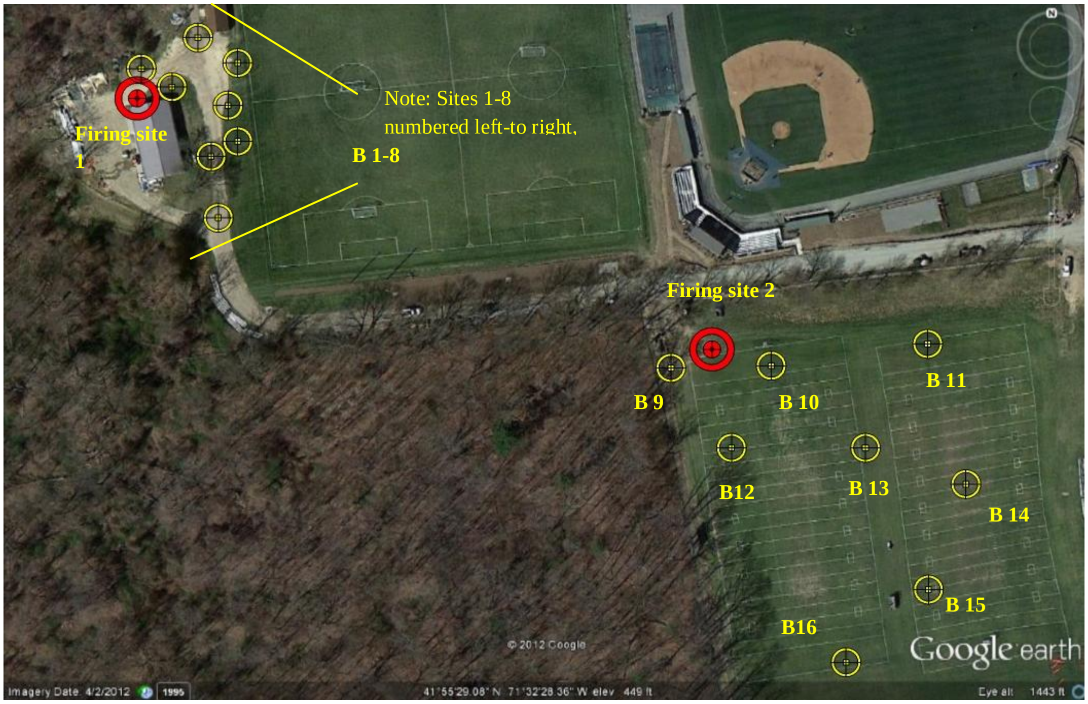


Figure B.2 Locus map of Site 2

Figure B.3

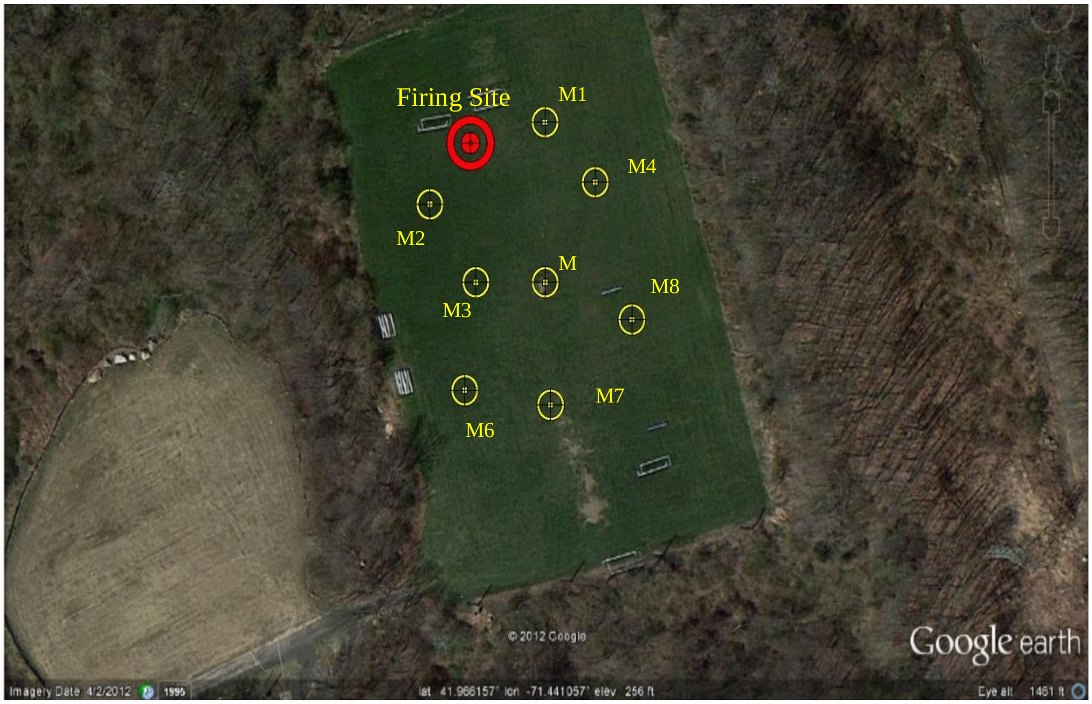


Figure B.3 Locus map of Site 3

Figure B.4

Figure B.4 Locus map of Site 4

Figure B.5

Concentration (ng/ml)	Area (µS*Min)	Peak Ht (µS)	Ret. Time (Min)
5	0.0015	0.01	9.011
10	0.0031	0.01	9.034
25	0.0043	0.02	9.044
50	0.0098	0.04	9.041
75	0.0139	0.05	9.041
100	0.0185	0.07	9.044
150	0.0291	0.11	9.038
200	0.037	0.14	9.038
500	0.1064	0.39	9.028
750	0.156	0.6	9.027
1000	0.2211	0.83	9.021

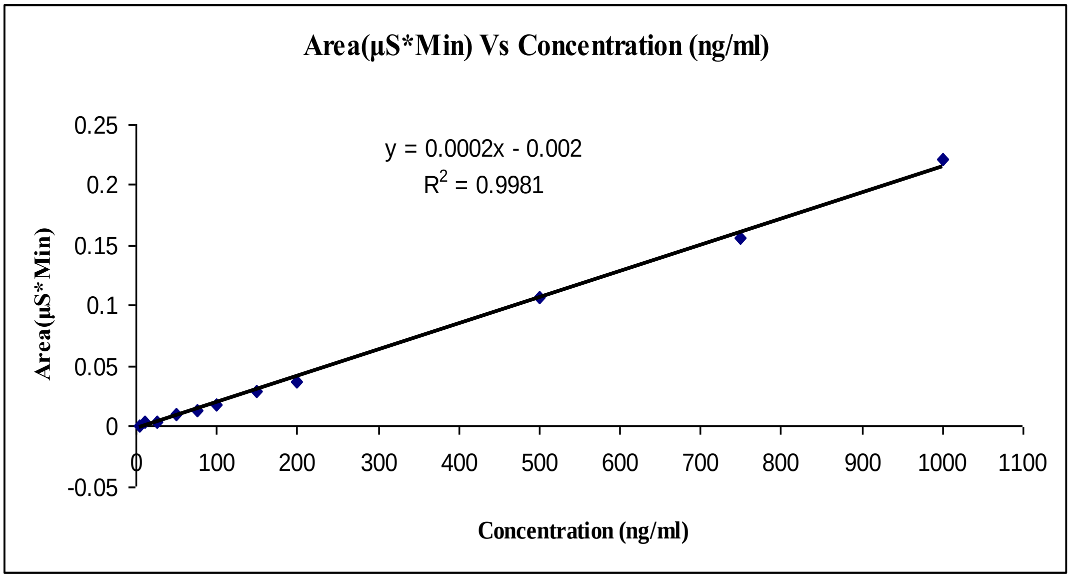
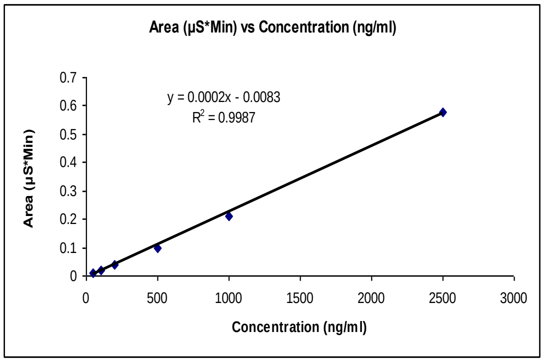


Figure B. 5 A Standard Calibration Curve of Perchlorate ion in Water by Ion Chromatography

Figure B.6

Conc (ng/ml)	Area (µS*Min)	Peak Ht(µS)	Ret. Time(Min)
50	0.0116	0.04	9.138
100	0.0178	0.07	9.148
200	0.041	0.13	9.141
500	0.0994	0.35	9.134
1000	0.2126	0.75	9.131
2500	0.5783	2.16	9.081



Blanks ID	Area (µS*Min)	Peak Ht. (µS)	Ret. Time (Min)	Conc. Rec. (ng/ml)	% Rec
0.5µg/ml water 1	0.1042	0.37	9.137	563	113
0.5 µg/ml water 2	0.1068	0.38	9.104	576	115
0.5µg/ml water 3	0.1021	0.37	9.067	552	110
1.0 µg/ml water 1	0.2078	0.77	9.101	1081	108
1.0µg/ml water 2	0.2107	0.79	9.094	1095	110
1.0 µg/ml water 3	0.2116	0.81	9.054	1100	110
2.5 µg/ml water 1	0.5781	2.19	9.084	2932	117
2.5 µg/ml water 2	0.5902	2.23	9.068	2993	120
2.5 µg/ml water 3	0.5957	2.26	9.027	3020	121

Sample ID	Area (µS*Min)	Peak Ht. (µS)	Ret. Time (Min)	Conc Rec (ng/ml)	% Rec
0.5µg/ml soil 1	0.1055	0.39	9.141	569	114
0.5 µg/ml soil 2	0.106	0.38	9.114	572	114
0.5µg/ml soil 3	0.1046	0.4	9.091	565	113
1.0 µg/ml soil 1	0.2234	0.8	9.108	1159	116
1.0µg/ml soil 2	0.2128	0.79	9.104	1106	111
1.0 µg/ml soil 3	0.2172	0.81	9.071	1128	113
2.5 µg/ml soil 1	0.5744	2.17	9.108	2914	117
2.5 µg/ml soil 2	0.5968	2.24	9.074	3026	121
2.5 µg/ml soil 3	0.4843	1.84	9.054	2463	99

Figure B.6 Recovery Studies Data

Figure B.7

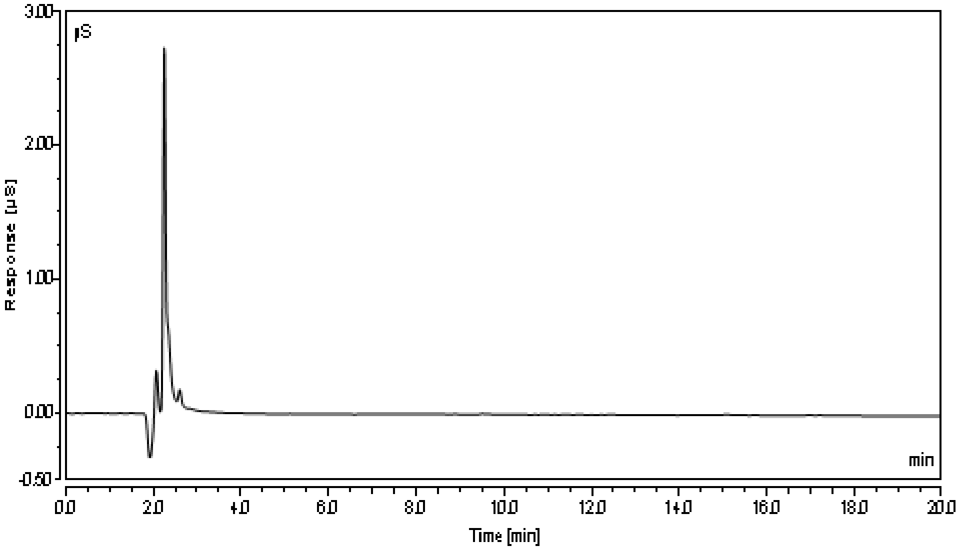


Figure B.7 Chromatogram of Water.

Figure B.8

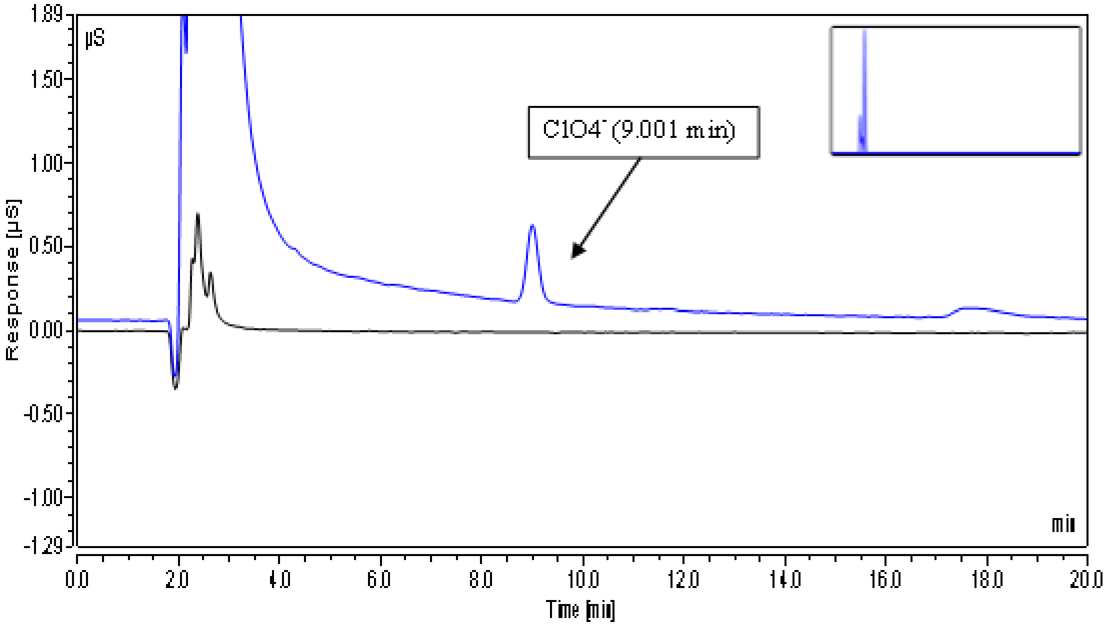


Figure B. 8 Chromatogram of perchlorate in soils collected prior and after 2010 fireworks display from O4 at site 1.

Figure B.9

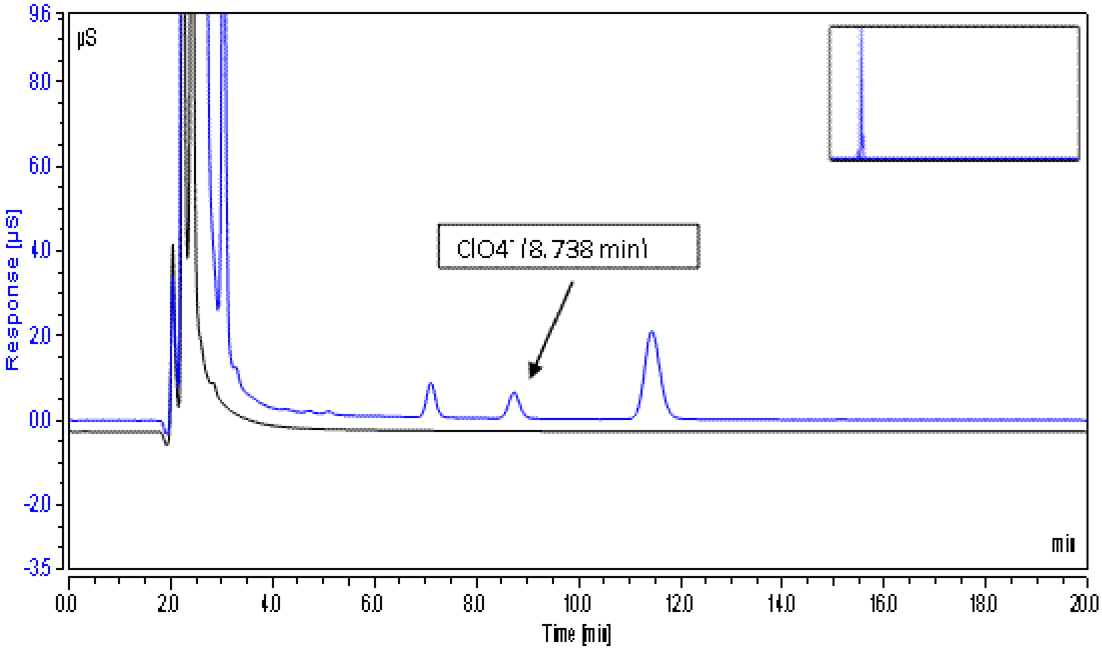


Figure B. 9 Chromatogram of perchlorate in soils collected prior and after 2011 fireworks display from B4 at site 2.

Figure B.10

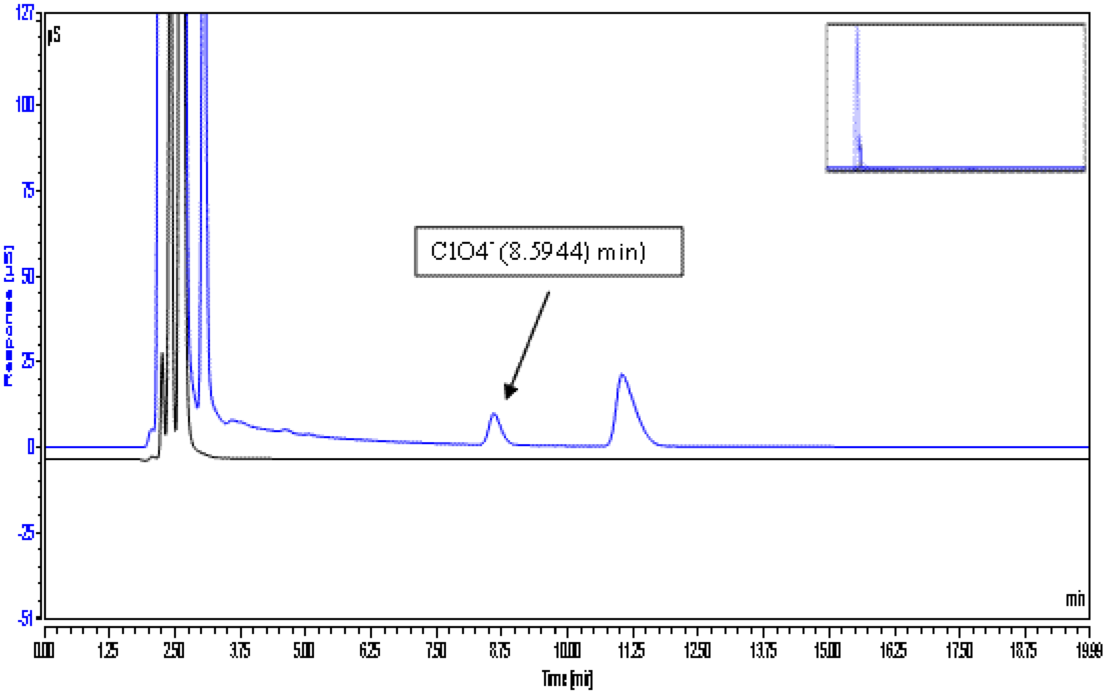


Figure B.10 Chromatogram of perchlorate in soils collected prior and after 2011 fireworks display from M5 at site 3.

Figure B.11

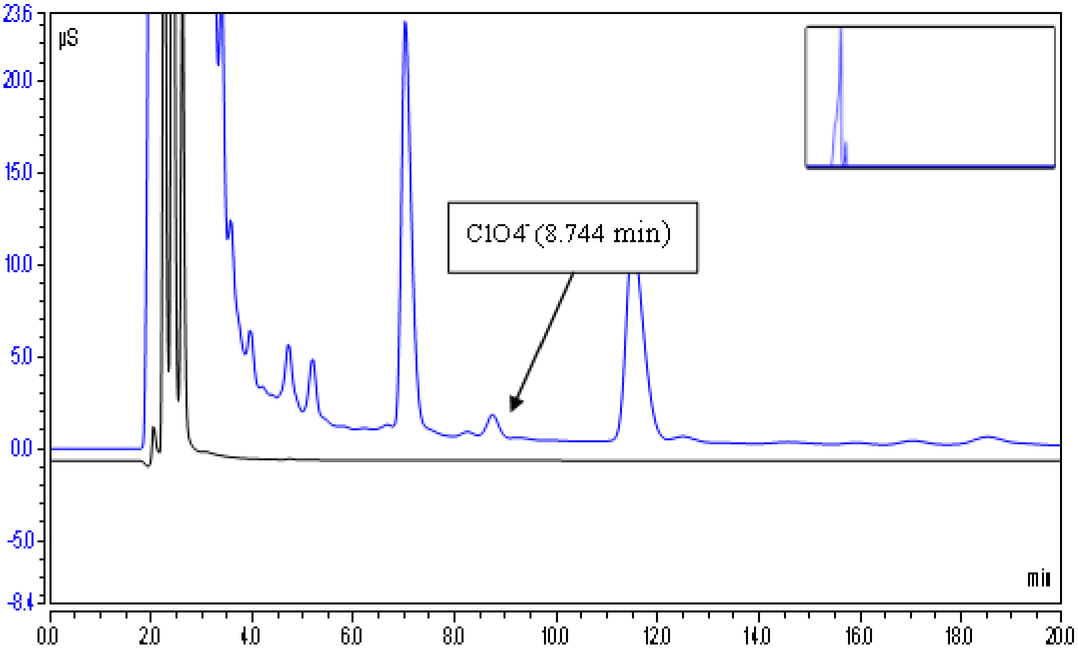


Figure B.11 Chromatogram of perchlorate in soils collected prior and after 2011 fireworks display from J2 at Site 4.

List of Abbreviations

AcrN…………………….………acrylonitrile

AN………………………………ammonium nitrate

APSP……………………………potassium salt of polyacrylate

ATR…………………………….attenuated total reflectance

APCI……………………………atmospheric pressure chemical ionization

BDL…………………………….below detection limit

DSC…………………………….differential scanning calorimeter

EC………………………………ethylcelluose

EPA…………………………….environmental protection agency

FTIR……………………………fourier transform infrared spectroscopy

GC/MS…………………………gas chromatography/ mass spectrometer

HPLC…………………………..high performance liquid chromatography

IR……………………………….infra red spectroscopy

LCMS………………………….liquid chromatography/ mass spectroscopy

NMR…………………………...nuclear magnetic resonance spectroscopy

NU……………………………...nitrourea

PAH……………………………polyallylaminehydrochloride

PDA……………………………poly (diacetylene)

PDADMA………………………..poly (diallyldimethylammonium chloride)

PEI……………………………..polyethylenime

PLGA…………………………..poly (lactic-co-glycolic acid)

PMA……………………………poly methyl methacrylate

PMMA…………………………polymethacrylate

PSS……………………………..poly (sodium 4- styrenesulfonate)

PS………………………………polystyrene

PVB……………………………poly vinyl butyral

TGA……………………………thermo gravimetric analyzer

U………………………………..urea

UN……………………………...urea nitrate

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