ENERGETIC SALTS: DEGRADATION AND TRANSFORMATION

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ENERGETIC SALTS: DEGRADATION AND TRANSFORMATION

BY

SRAVANTHI VADLAMANNATI

A DISSERTATION SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY

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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°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 collected 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 groundwater 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.
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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.

\[ \text{NH}_4\text{NO}_3 \rightleftharpoons \text{H}_2\text{NNO}_2 + \text{H}_2\text{O} \]  

\[ [\text{HN}=\text{C}(\text{NH}_2)\text{NH}_3]^+\text{NO}_3^- \rightleftharpoons \text{HN}=\text{C}(\text{NH}_2)\text{NHNO}_2 + \text{H}_2\text{O} \]  

\[ [\text{NH}_2\text{CONH}_3]^+\text{NO}_3^- \rightleftharpoons \text{NH}_2\text{CONHNO}_2 + \text{H}_2\text{O} \]  

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°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. 156.60°C, Hf 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 °C/minute from 40°C to 400°C. For some samples decomposition gases were transferred via a heated (250°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 \(^1\)H 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 (CCl₄) 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 CCl₄ (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 + NO₃⁻ (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 + NH₄⁺ in NU and urea + H⁺ in UN (for the same reasons as the positive CCl₄ 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°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 CO₂ and N₂O gas (second spectrum from top). Overlapping spectra of neat CO₂ and N₂O 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 CO₂/N₂O mixture suggest that UN decomposition produced significant amounts of CO₂ while NU and urea decomposition did not. Further, N₂O 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 N₂O peak (2240 cm⁻¹) and CO₂ 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 (H₂NNO₂) is believed to decompose via eq. 5.

\[ \text{H}_2\text{N-C(O)-NH-NO}_2 \rightarrow \text{HN}=\text{C}=\text{O} + \text{H}_2\text{NNO}_2 \]  \hspace{1cm} (4)

\[ \text{H}_2\text{NNO}_2 \rightarrow \text{H}_2\text{O} + \text{NNO} \] \hspace{1cm} (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.

\[
HN=\text{C}=\text{O} \quad \text{H}_2\text{O} \rightarrow \quad \text{NH}_3 + \text{CO}_2
\]  

(6)

The first weight-loss event for UN (~140°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].

\[
[\text{NH}_2\text{C(OH)NH}_2]^+\text{NO}_3^- \leftrightarrow \text{O=C(NH}_2)_2 + \text{HNO}_3
\]  

(7)

\[
\text{O=C(NH}_2)_2 \rightarrow \text{NH}_3 + \text{HCNO}
\]  

(8)

\[
\text{NH}_3 + \text{HCNO} \rightarrow \text{NH}_4\text{CNO}
\]  

(9)

\[
\text{NH}_3 + \text{HCNO} \rightarrow \text{NH}_4\text{CNO}
\]  

(9)

\[
\text{O=C(NH}_2)_2 \rightarrow \text{NH}_2\text{CN} \rightarrow \text{N}_3(\text{CNH}_2)_3 \quad \text{melamine (C}_3\text{H}_6\text{N}_6)
\]  

(10)

\[
\text{O=C(NH}_2)_2 + \text{HNCO} \rightarrow \text{O=C(NH}_2)(\text{NH-NC}) + \text{H}_2\text{O} \quad \text{cyanourea (C}_2\text{H}_5\text{N}_3\text{O})
\]  

(11)

\[
\text{O=C(NH}_2)_2 + \text{HNCO} \rightarrow \text{NH}_2\text{CONHCONH}_2 \quad \text{biuret (C}_2\text{H}_5\text{N}_3\text{O}_2)
\]  

(12)

\[
3 \text{HNCO} \rightarrow \text{O}_3\text{C}_3(\text{NH})_3 \quad \text{cyanuric acid (C}_3\text{H}_6\text{N}_3\text{O}_3)
\]  

(13)

![Diagram](image1.png)  

![Diagram](image2.png)
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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| Property                        | UN                  | NU                  |
|--------------------------------|---------------------|---------------------|
| Melting point °C               | 157-159             | 153-155             |
| Density g/cm³                  | 1.67±0.011          | 1.73±0.026          |
| DSC 200 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         |
| ¹H NMR δ-D-acetone ppm         | 8                   | 7.12                |
| ¹³C NMR δ-DMSO ppm             | 163                 | 151                 |
| MS negative nitrate            | NU-H⁺               |                    |
| MS negative with CCl₄ urea + Cl⁻ or 2 urea + Cl⁻ | NU + Cl⁻        |
| MS positive urea + H⁺          | methyl carbonate=NH₃⁺  |
|                                | cyanide+NH₄⁺         |
| Solubility mg/mL               |                     |                    |
| Water                          | 167.2±0.5           | 20±4                |
| 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. Summary of HRMS Fragmentation

| Solvent & Additive | Size | Nitrourea Size | Nitrourea Charge | Urea Nitrate Size | Urea Nitrate Charge |
|--------------------|------|----------------|------------------|-------------------|--------------------|
| methanol/water     | large| NU-H⁺          | isocyanic acid+NH₄⁺ | urea-H⁺           |
| CCl₄               | M-S  | NU+Cl⁻         | methyl carbamate+NH₄⁺ | 2(urea)+H⁺        |
|                    |      | dicynanic acid-H⁺ | methyl carbamate+H⁺ | 3(urea)+H⁺         |
|                    |      | nitramide+Cl⁻   | methyl carbamate+NH₄⁺ | methyol urea+H⁺    |
| methanol           | large| NU-H⁺          | isocyanic acid+NH₄⁺ | urea+Cl⁻          |
| CCl₄               | M-S  | NU+Cl⁻         | methyl carbamate+NH₄⁺ | 2(urea)+H⁺        |
|                    |      | dicynanic acid-H⁺ | methyl carbamate+H⁺ | 3(urea)+H⁺         |
|                    |      | nitramide+Cl⁻   | methyl carbamate+NH₄⁺ | methyol urea+H⁺    |
| Direct Inject      |      | N/A            | NO₃⁻             | urea+H⁺           |
| methanol/water     | large| NO₃⁻           | isocyanic acid+NH₄⁺ | 2(urea)+H⁺        |
| CCl₄               | M-S  | NO-H⁺          | NO₃⁻             | urea+H⁺           |
|                    |      | nitramide-H⁺    | NO₃⁻             | methyol urea+H⁺    |
| methanol/water     | large| urea-H⁺        | isocyanic acid+NH₄⁺ | NO₃⁻              |
| NH₄ acetate        | M-S  | dicynanic acid-H⁺ | NO₃⁻             | urea-H⁺           |
| no additive        | large| urea+H⁺        | isocyanic acid+NH₄⁺ | NO₃⁻              |
|                    | M-S  | dicynanic acid-H⁺ | NO₃⁻             | Biuret-H⁺          |
**Table 3.** Fragmentation patterns of NU and UN. Assignments with Cl− adduct were supported by additional mass peaks corresponding to the $^{37}$Cl− adduct.

### Negative Mode

| Additive | Mode | Solvent          | Nitrourea | Urea Nitrate |
|----------|------|------------------|-----------|--------------|
|          |      |                  | Obs. Mass | Calc. Mass | Assignment | Size | Obs. Mass | Calc. Mass | Assignment | Size  |
| CCl₄     | LC   | Fresh 50-50 MeOH-H₂O | 85.0050   | 85.0044    | [Dicynic acid - H⁻] | 85.0044 | 95.0008  | [Urea + Cl⁻] | 95.0018 | L       |
|          |      |                  | 96.9799   | 96.9810    | [Nitramide + Cl⁻] | 96.9810 | 96.9978  | [Urea + $^{37}$Cl⁻] | 96.9988 | M       |
|          |      |                  | 104.0930  | 104.0102   | [Nitrourea - H⁺] | 104.0102 | 102.0299 | [Biuret - H⁺] | 102.0309 | T       |
|          |      |                  | 139.9858  | 139.9868   | [Nitrourea + Cl⁻] | 139.9868 | 127.0271 | [Ammelide - H⁺] | 127.0262 | S       |
|          |      |                  |           |           |             |       | 155.0334 | [2xUrea + Cl⁻] | 155.0341 | S       |
|          | Direct Inject | One Week Old 50-50 MeOH-H₂O | 85.0050   | 85.0044    | [Dicynic acid - H⁻] | 85.0044 | Urea nitrate was not run with aged samples |
|          |      |                  | 96.9810   | 96.9810    | [Nitramide + Cl⁻] | 96.9810 |         |             |         |         |
| NH₄⁺ Acetate | Direct Inject | 50-50 MeOH-H₂O | 61.9871   | 61.9884    | [Nitrate⁻] | 61.9871 | 61.9884  | [Nitrate] | 61.9884 | L       |
|          |      |                  | 96.9799   | 96.9810    | [Nitramide + Cl⁻] | 96.9810 | 124.9829 | [Nitric acid + NO₃⁻] | 124.9840 | T       |
|          |      |                  | 104.0930  | 104.0102   | [Nitrourea - H⁺] | 104.0102 |         |             |         |         |
|          |      |                  | 139.9859  | 139.9868   | [Nitrourea + Cl⁻] | 139.9868 |         |             |         |         |

### Positive Mode

| Additive | Mode | Solvent          | Nitrourea | Urea Nitrate |
|----------|------|------------------|-----------|--------------|
|          |      |                  | Obs. Mass | Calc. Mass | Assignment | Size | Obs. Mass | Calc. Mass | Assignment | Size  |
| CCl₄     | LC   | Fresh 50-50 MeOH-H₂O | 61.0401   | 61.0396    | [Isocyanic acid + NH₄⁺] | 61.0396 | 61.0396  | [Urea + H⁺] | 61.0396 | L       |
|          |      |                  | 76.0395   | 76.0393    | [Methylcarbamate + H⁺] | 76.0393 | 78.0665  | [Urea + NH₄⁺] | 78.0662 | T       |
|          |      |                  | 93.0659   | 93.0659    | [Methylcarbamate + NH₄⁺] | 93.0659 | 93.0660  | [Methylol urea + H⁺] | 93.0659 | S       |
|          |      |                  |           |           |             |       | 121.0721 | [2xUrea + H⁺] | 121.0720 | L       |
|          |      |                  |           |           |             |       | 181.1045 | [3xUrea + H⁺] | 181.1044 | T       |
|          | Direct Inject | One Week Old 50-50 MeOH-H₂O | 61.0401   | 61.0396    | [Isocyanic acid + NH₄⁺] | 61.0396 | Urea nitrate was not run with aged samples |
|          |      |                  | 93.0658   | 93.0659    | [Methylcarbamate + NH₄⁺] | 93.0659 |         |             |         |         |
| NH₄⁺ Acetate | Direct Inject | 50-50 MeOH-H₂O | N/A       |            |             |       |            |             |         |         |
|          |      |                  |           |           |             |       | 61.0394  | [Urea + H⁺] | 61.0396 | M       |
|          |      |                  |           |           |             |       | 121.0724 | [2xUrea + H⁺] | 121.0720 | L       |
|          |      |                  |           |           |             |       | 130.0525 | [Cyanuric acid + H⁺] | 130.0523 | S       |
|          |      |                  |           |           |             |       | 181.1049 | [3xUrea + H⁺] | 181.1044 | T       |
|          |      |                  |           |           |             |       | 62.0435  | [Nitromethane + H⁺] | 62.0237 | M       |
|          |      |                  |           |           |             |       | 93.0666  | [Methylol urea + H⁺] | 93.0659 | M       |
**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                    | 158.75  | 166.55    | 433.5      | 10                    | 148.19    | 1089       |
| 10                    | 143.67  |           |            | 10                    | 143.67    | 1045       |

**Table 4.** DSC Summary of Urea Nitrate & Nitrourea
Figure 1. Chemical Structures of Nitrourea (NU) and Urea Nitrate (UN)
Figure 2. Stacked transmission mode IR spectra of recrystallized Nitrourea (Top) and Urea Nitrate (Bottom)
Figure 3. Raman Spectrum, from top, of UN, Urea, NU, Ammonium Nitrate, respectively. Ammonium nitrate exhibited additional small peak at ~2900cm\(^{-1}\).
Figure 4. Negative mode mass spectra of NU and UN in 50-50 MeOH-H$_2$O with CCl$_4$. a) direct inject NU, b) LC NU, c) direct inject UN, d) LC UN.
Figure 5. Positive mode mass spectra of NU and UN in 50-50 MeOH-H$_2$O with CCl$_4$.

a) LC NU, b) direct inject UN, c) LC UN.
Figure 6. DSC thermograms of nitrourea (top) & urea nitrate (bottom) scanned at 10 °C/minute.
Figure 7. TGA trace of nitrourea
Figure 8. Stacked TGA Trace of urea (top) and recrystallized Urea Nitrate (bottom)
Figure 9. Stacked IR spectra of urea nitrate, CO$_2$ and N$_2$O mixture, nitrourea, and urea from top to bottom, respectively. Selected wavenumbers are shown.
**Figure 10.** Overlap spectra of $\text{CO}_2$ (—), $\text{N}_2\text{O}$ (⋯), and a mixture of both (---).
**Figure 11.** Overlap magnified IR spectra of urea nitrate, nitrourea, urea, and a mixture of CO$_2$ and N$_2$O.
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 to 18 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 fireworks 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. Perchlorate 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 ($\text{ClO}_3^-$) then chlorite ($\text{ClO}_2^-$) then chloride ($\text{Cl}^-$). 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 $\mu$g/mL can be reduced to less than 0.5 $\mu$g/mL. In the present study we monitored the occurrence of perchlorate anion following fireworks displays.

Prior to the July 4$^{th}$ 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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| Location | Geographical Description (Lat. & Long.) | Years         |
|----------|----------------------------------------|---------------|
| Site 1   | Municipal Park                         | 2007, 2009-2012 |
| Site 2   | Academic Campus                        | 2011-2012    |
| Site 3   | Municipal Park                         | 2011-2012    |
| Site 4   | Public Beach                           | 2011         |

*Table 1: Locations with geographical description and years specimens collected*
| Location | Distance from firing site (ft) |        |        |        |        |        |
|----------|-------------------------------|--------|--------|--------|--------|--------|
| 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**
| 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
| 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: 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. 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. 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.

Figure 1 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). The phase transitions of AN are believed to be facilitated through thermally induced vibronic couplings. 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. These can be added while the AN is aqueous or when it is a hot melt, or they can be introduced by chemical reaction. 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. Although a number of potential solutions to the III/IV problem have been fielded, 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….” As water content is increased from 0.01 to 0.35% it is
reported that the temperature of the IV $\rightarrow$ III transition temperature decreased,\textsuperscript{23} and an increase in water content also increases the rate of the IV $\rightarrow$ III phase change. One way to reduce water content is temperature cycling across the III/IV transition.\textsuperscript{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\textsubscript{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).\textsuperscript{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), polyvinyl butyral (PVB), polystyrene (PS), acrylonitrile (AcrN), ethyl cellulose (EC), polyurethane (PU), poly (lactic-co-glycolic acid) (PLGA), poly methyl methacrylate (PMMA), polyethylenimine (PEI), poly (diallyldimethylammonium chloride) (PDA), poly (sodium4-styrenesulfonate) (PSS), Polyallylaminehydrochloride (PAH), polydiallyldimethylammonium chloride (PDADMA), polymethacrylate (PMA).

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)]. 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 µm. 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). 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 μm. 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. As a crystal phase stabilizer, APSP has two effects; the potassium ion replaces the NH₄⁺ 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. 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. Reduction in hygroscopicity has also been observed using precipitation polymerization of acrylonitrile (AcrN) in cyclohexane to ammonium nitrate.
2.0. Experimental Procedure:

Raw materials:

Ammonium nitrate (Certified 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 x 10⁻⁵ mol) and BPO (100 mg, 9.83 x 10⁻³ mol) were added. The mixture was heated to 60°C 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. 156.60°C, 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). Samples were run in triplicate. Samples were run in triplicate at a scan rate of 20ºC/minute from -10 to 225°C if only the endotherms were to be examined or up to 500ºC 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°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.\textsuperscript{41}

\[
\text{NH}_4\text{NO}_3 \rightarrow 2 \text{H}_2\text{O} + \text{N}_2\text{O}
\]

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°C and one at 52°C—and the other shows only one endotherm but it is at 41°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°C where it is often cited in the literature;\textsuperscript{40, 52} and is pictured in the top of Table 2. Instead it was observed as low as 41°C and as high as 56°C (Table 3). The variability in the temperature at which the phase changes between 32°C and 84°C occur has been previously reported. It has been suggested that this endotherm around 50°C may actually be two endotherms: the IV to III phase transition of dry AN and the IV to II transition.\textsuperscript{22, 23, 43} This may also explain the two endotherms near 50°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°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°C 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°C) to I (129°C) and melt (170°C).49-53

Since the DSC traces suggested AN was successfully dried, encapsulation techniques were sought to act as a long-term moisture barrier. Polystyrene29 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°C. 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°C 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 polystyrene (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 \( \text{NH}_4^+ \) stretching, symmetric and asymmetric modes, near 3234 cm\(^{-1}\), 3058 cm\(^{-1}\) and 3025 cm\(^{-1}\). Total stretching and in-plane and out-of-plane deformation modes of \( \text{NO}_3^- \) were observed around 2500 cm\(^{-1}\). In the region 1300-1500 \( \text{NH}_4^+ \) and \( \text{NO}_3^- \) 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 characteristic band around 2200 cm$^{-1}$ 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$^\circ$C, its melting point, and resulted in complete loss by 250$^\circ$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$^\circ$C). Figure 13 overlays the TGA traces of neat polystyrene (which shows little weight loss up to 320$^\circ$C) to that of uncoated AN (maximum weight loss 250$^\circ$C) and PS-coated AN (maximum weight loss 270$^\circ$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 | AN with alkyl naphthalene sulfonate (Gurley) & Na sulfonate SKFert | fluidized bed | det velocity | for ANFO-coating of granules so smooth, hard & don't breakdown & prevent caking |
| Fernandez-perez, M.; no Coa | 2007, 46, 3304-3311 | AN with dibutyl sebacate & dibutyl phthalate (PVB) in chloroform, add AN heat at 60C for 4 hrs add hexane | 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 butyral (PVB) in chloroform add AN heat at 60C for 4 hrs add hexane | DSC, anti caking, XPS | solid rocket propellents |
| Yue, J | Advances in fine petrochemical engineering, (CHINA) 2008, vol 9, 12, 15-37 | 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 Styrene in chloroform, add AN, BPO heat at 60C for 4 hrs add cyclohexane | DSC, anti caking, XPS | |
| Saihi | Reactive & Functional polymers, 64, 2005, 127-138 | Ammonium phosphate with polyurethane | CP-DD-MAS NMR 13C , DTG, FTIR, intumescent flame retardant system | |
| Saihi | Reactive & Functional polymers, 66, 2006, 1118-1125 | Ammonium phosphate with polyurethane shell | 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 control release of drugs |
| Kim, Y. H | J Polymer Sci, part A: Polymer Chem. 42, 2004, 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 electrolyte coating with Poly diallyldimethylammonium 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 DCM, add BSA-FTIC and centrifuge, discard supernatant, repeat; save supernatant layer and discard ppt. Layer by layer deposition niPMA & niPDADMA. | fluorescence microscope & thermal stability | biological materials like e.coli,proteins |
| Hirsjarvi, S | Colloids and surface Interfaces, 2006, 9/3-99 | Polyelectrolyte coating with PAH and PSS Nano precipitation method, poly lactic acid (PLA) in DCM & ethanolic solution, slow evaporation, collect nanoparticles disperse 2min in polyelectrolyte with 0.02M NaCl, EBL, done with vacuum filtration. Particles shifted to polyacrylate for 5min after 2 cycles of washing & coating continued till all oppositely charged PEs added. new membrane used before each addition. | SEM, zeta potential, Photon correlation spectroscopy, DSC | Patented is a way to encapsulate small soluble low molecular materials, e.g. NaCl |
| Temperature | Phase Change | Percent Volume Change |
|-------------|--------------|-----------------------|
| -17°C       | V ↔ IV       | 1.5%                  |
| 32°C        | IV ↔ III     | 3.5%                  |
| 84°C        | III ↔ II     | 1.4%                  |
| 126°C       | II ↔ I       | 2.0%                  |
| 169°C       | I ↔ melt     |                       |

Table 2: Phase changes of Ammonium Nitrate & Percent Volume Change
### Table 3

| Sample | mg  | 1\(^{\text{st}}\) (30-50\(^{\circ}\)C) | 2\(^{\text{nd}}\) (80-90\(^{\circ}\)C) | 3\(^{\text{rd}}\) (120-130\(^{\circ}\)C) | 4\(^{\text{th}}\) (160-170\(^{\circ}\)C) | (300\(^{\circ}\)C) |
|--------|-----|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------|
| 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 | | | | | | | |
| AN     | 0.517 | 52 | 27 | | | | | | | |
| AN     | 0.497 | 52 | 15 | 5 | 90 | 17 | 128 | 54 | 169 | 62 | NR | NR |
| AN     | 0.481 | 41 | 18 | 90 | 17 | 128 | 51 | 170 | 58 | NR | NR |
| AN     | 0.496 | 43 | 14 | 3 | 91 | 17 | 128 | 49 | 169 | 56 | NR | NR |
| AN     | 0.505 | 45 | 13 | 2 | 91 | 19 | 128 | 55 | 169 | 62 | NR | NR |
| AN     | 0.506 | 44 | 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 |

Table 3: DSC Results for AN “as received” (NR-not record, run terminated early)
| 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     | 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 | 15 | 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 |

Table 4: DSC Data for AN “Dried” Vacuum Dried 110˚C (NR-not record, run terminated early)
| Sample | mg | 1st (30-50°C) | 2nd (80-90°C) | 3rd (120-130°C) | 4th (160-170°C) | Exotherm (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  | 0.530 | 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°C & Coating with Polystyrene (NR-not record)
| 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  |                |                |                |       |
| AN/PS    | 0.520| 54 12 102 24  |                |                |                |       |
| AN/PS    | 0.480| 54 11 107 24  |                |                |                |       |
| AN/PS    | 0.525| 54 11 105 20  |                |                |                |       |
| AN/PS    | 0.507| 55 13 89 12   | 130 37 170 49  |                |                |       |
| AN/PS    | 0.502| 53 16 93 10   | 128 46 168 56  |                |                |       |
| AN/PS    | 0.519| 54 21 88 7    | 128 44 167 49  |                |                |       |
| AN/PS    | 0.514| 53 20 87 12   | 127 54 167 67  |                |                |       |
| AN/PS    | 0.482| 54 21 98 2    | 128 44 169 55  |                |                |       |
| AN/PS    | 0.485| 49 16 90 14   | 129 42 170 58  |                |                |       |
| AN/PS    | 0.484| 49 16 90 8    | 128 50 168 64  |                |                |       |
| AN/PS    | 0.501| 51 15 91 16   | 129 43 169 52  |                |                |       |
| AN/PS    | 0.501| 54 12 116 26  |                |                |                |       |
| AN/PS    | 0.495| 53 19 90 7    | 128 45 169 54  |                |                |       |
| AN/PS    | 0.513| 55 18 90 4    | 130 36 172 45  |                |                |       |
| AN/PS    | 0.487| 55 18 91 7    | 128 46 168 62  |                |                |       |
| AN/PS    | 0.520| 55 9 106 11   |                |                |                |       |
| AN/PS    | 0.490| 54 20 92 2    | 129 42 170 51  |                |                |       |
| AN/PS    | 0.487| 54 12 92 9    | 128 43 168 53  |                |                |       |
| AN/PS    | 0.485| 53 20 92 9    | 128 58 170 77  |                |                |       |
| AN/PS    | 0.489| 55 18 92 2    | 128 39 169 44  |                |                |       |
| AN/PS    | 0.490| 52 16 115 52  |                |                |                |       |
| AN/PS    | 0.499| 54 16 92 12   | 129 42 170 55  |                |                |       |
| AN/PS    | 0.760| 54 17 93 7    | 129 41 169 51  |                |                |       |
| AN/PS    | 0.487| 53 14 93 16   | 129 39 163 32  |                |                |       |
| AN/PS    | 0.523| 53 24 93 4    | 128 50 169 64  |                |                |       |
| AN/PS    | 0.518| 49 15 93 15   | 129 34 160 25  |                |                |       |
| AN/PS    | 0.512| 54 20 95 9    | 129 47 169 60  |                |                |       |
| AN/PS    | 0.478| 54 22 93 6    | 128 50 169 62  |                |                |       |
| AN/PS    | 0.498| 55 11 121 27  |                |                |                |       |
| AN/PS    | 0.481| 46 19 94 15   | 129 45 167 45  |                |                |       |
| AN/PS    | 0.503| 53 15 94 10   | 128 31 159 23  |                |                |       |
| AN/PS    | 0.482| 54 18 96 17   | 129 44 165 37  |                |                |       |
| AN/PS    | 0.476| 53 19 95 13   | 128 54 168 72  |                |                |       |
| AN/PS    | 0.482| 56 14 96 5    | 130 30 171 38  |                |                |       |
| AN/PS    | 0.487| 54 21 96 2    | 128 45 169 61  |                |                |       |
| AN/PS    | 0.512| 53 23 96 2    | 128 48 168 61  |                |                |       |
| AN/PS    | 0.523| 54 16 120 48  |                |                |                |       |
| AN/PS    | 0.484| 55 15 99 4    | 129 30         |                |                |       |
| AN/PS    | 0.497| 56 20 100 3   | 131 37 170 38  |                |                |       |
| AN/PS    | 0.525| 54 19         | 128 39 170 46  |                |                |       |
| AN/PS    | 0.503| 55 18         | 130 34 172 41  |                |                |       |
| AN/PS    | 0.482| 55 21         | 129 44 169 53  |                |                |       |
| AN/PS    | 0.496| 53 24         | 128 52 170 64  |                |                |       |
| AN/PS    | 0.517| 54 20         | 129 4095 167 46|                |                |       |
| AN/PS    | 0.512| 54 21         | 129 42 167 48  |                |                |       |
| AN/PS    | 0.484| 54 18         | 129 36 169 36  |                |                |       |
| AN/PS    | 0.514| 53 21         | 128 42 168 44  |                |                |       |
| AN/PS    | 0.520| 53 25         | 129 52 167 58  |                |                |       |
| AN/PS    | 0.479| 53 20         | 128 39 166 38  |                |                |       |
| AN/PS    | 0.487| 54 15         | 129 28 165 25  |                |                |       |
| AN/PS    | 0.523| 55 19         | 130 35 170 36  |                |                |       |
| AN/PS    | 0.511| 54 20         | 129 37 162 27  |                |                |       |

Table 5: DSC data of AN vacuum dried at 110°C and Coating with Polystyrene (cont)
### Table 5: DSC data of AN vacuum dried at 110°C and Coating with Polystyrene (cont)

| Sample | mg   | 1st (30-50°C) | 2nd (80-90°C) | 3rd (120-130°C) | 4th (160-170°C) | (300°C) |
|--------|------|---------------|---------------|----------------|----------------|---------|
|        |      | C Jg          | C Jg          | C Jg           | C Jg           | C Jg    |
| 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        | 142 3          | NR NR          |         |
| AN/PS  | 0.499| 55 18         | 127 20        | 158 20         | NR NR          |         |
| AN/PS  | 0.505| 54 18         | 128 30        | 152 15         | 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        |              |                |         |
| AN/PS  | 0.513| 55 16         | 121 32        |              |                |         |
| AN/PS  | 0.489| 54 15         | 126 37        |              |                |         |
| AN/PS  | 0.503| 53 18         | 127 51        |              |                |         |
| 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        |              |                |         |
| AN/PS  | 0.494| 57 10         | 132 23        |              |                |         |
| 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        |              |                |         |
| 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         |              |                |                |         |
| 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        |              |                |         |
| 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 (Cont’d)**

| Sample | mg | Endotherms | Exotherm |
|--------|----|------------|----------|
|       |    | 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 | 0.508 | 53 22 | 127 28 | 149 14 | NR | NR |
| AN/PS | 0.521 | 54 20 | 129 20 | 174 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°C and Coating with Polystyrene (cont)
| 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           |
| 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           |
| AN/AcrN | 0.491 | 54  | 13            | 92  | 14            | 128 | 33            | 162 | 22           |
| 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             | 130 | 23            | 153 | 11            | NR  | NR           |
| average |     | 54  | 20            | 90  | 11            | 129 | 44            | 165 | 53           |
|         |     |     |               |     |               |     |               |     | 312          |

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$_0$) | RH%=(|AN$_f$-AN$_0$|/AN$_0$)*100 |
|---------------|-----------------------------|---------------------------------------------|-----------------|
|               | AN/PS | AN/ACrN | Neat AN | AN/PS | AN/ACrN | Neat AN | Neat AN | Neat AN | Neat AN | Neat AN | Neat AN | Neat AN | Neat AN | Neat AN | Neat AN | Neat AN | Neat AN | Neat AN | Neat AN | Neat AN | Neat AN | Neat AN | Neat AN | Neat AN | Neat AN | Neat AN | Neat AN | Neat AN | Neat AN | Neat AN | Neat AN |
| 0 min(A$_0$ weight) | 0.500 | 0.501 | 0.501 | 0.000 | 0.000 | 0.000 | 0.068 | 0.062 | 0.069 | 13.6 | 12.4 | 13.8 |
| 30 min        | 0.505 | 0.505 | 0.505 | 0.005 | 0.000 | 0.005 | 0.068 | 0.062 | 0.069 | 13.6 | 12.4 | 13.8 |
| 60 min        | 0.507 | 0.507 | 0.507 | 0.006 | 0.005 | 0.007 | 0.068 | 0.062 | 0.069 | 13.6 | 12.4 | 13.8 |
| 90 min        | 0.509 | 0.509 | 0.508 | 0.008 | 0.006 | 0.008 | 0.068 | 0.062 | 0.069 | 13.6 | 12.4 | 13.8 |
| 120 min       | 0.511 | 0.510 | 0.510 | 0.011 | 0.008 | 0.009 | 0.068 | 0.062 | 0.069 | 13.6 | 12.4 | 13.8 |
| 150 min       | 0.510 | 0.511 | 0.511 | 0.010 | 0.011 | 0.011 | 0.068 | 0.062 | 0.069 | 13.6 | 12.4 | 13.8 |
| 180 min       | 0.511 | 0.512 | 0.511 | 0.011 | 0.010 | 0.011 | 0.068 | 0.062 | 0.069 | 13.6 | 12.4 | 13.8 |
| 210 min       | 0.512 | 0.512 | 0.512 | 0.012 | 0.011 | 0.012 | 0.068 | 0.062 | 0.069 | 13.6 | 12.4 | 13.8 |
| 240 min       | 0.513 | 0.514 | 0.513 | 0.012 | 0.012 | 0.012 | 0.068 | 0.062 | 0.069 | 13.6 | 12.4 | 13.8 |
| 270 min       | 0.512 | 0.515 | 0.513 | 0.012 | 0.012 | 0.013 | 0.068 | 0.062 | 0.069 | 13.6 | 12.4 | 13.8 |
| 300 min       | 0.513 | 0.515 | 0.514 | 0.013 | 0.012 | 0.013 | 0.068 | 0.062 | 0.069 | 13.6 | 12.4 | 13.8 |
| 15hrs         | 0.556 | 0.557 | 0.557 | 0.056 | 0.013 | 0.057 | 0.068 | 0.062 | 0.069 | 13.6 | 12.4 | 13.8 |
| 20hrs         | 0.562 | 0.564 | 0.562 | 0.062 | 0.056 | 0.062 | 0.068 | 0.062 | 0.069 | 13.6 | 12.4 | 13.8 |
| 24hrs         | 0.568 | 0.571 | 0.569 | 0.068 | 0.062 | 0.069 | 0.068 | 0.062 | 0.069 | 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 (ANf-AN0) |
|--------|-----------------------------|----------------------------------------|
|        | 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 (A0 weight) | 0.4974 | 0.5057     | 0.0023 | 0.0060     |
| A0 weight | 0.4997 | 0.5000     | 0.4997 | 0.5000     |
| Empty vial weight | 9.0633 | 9.0510   | 9.0633 | 9.0510      |
| [(Af-A0)] |        |            | 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$_4$NO$_3$ (IV) and (III) Crystals
Figure 2: DSC Thermogram of Ammonium Nitrate "as received"
Figure 3: Expanded AN “as received” endotherms only
Figure 4: DSC Thermogram of Dried Ammonium Nitrate.
FIGURE 5

Figure 5: DSC Thermogram of Ammonium Nitrate Coated with Polystyrene
Figure 6: DSC Thermogram of Ammonium Nitrate Coated with Acrylonitrile.
FIGURE 7

Figure 7: FESEM Image of uncoated AN
Figure 8: FESEM image of AN Coated with Polystyrene
Figure 9: ATR spectra: uncoated AN (top), PS neat (middle), PS-coated AN (bottom).
Figure 10: ATR spectra: uncoated AN (top), AcrN neat (middle), AcrN-coated AN (bottom).
Figure 11: TGA of Uncoated AN
Figure 12: TGA of PS coated AN
Figure 13: TGA of Polystyrene (neat), AN, and PS-coated AN
Figure 14: TGA of AcrN coated AN
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 chemical ionization using methane as reagent gas for recrystalized nitrourea synthesized by method 1 (left) and method 2 (right).
Figure A.2 IR spectrum (transmission mode) of recrystallized Nitrourea using sulfuric acid method
Figure A.3 IR spectrum (transmission mode) of recrystallized Nitrourea made using acetic anhydride method 2.
Figure A. 4 1H-NMR (top) and 13C-NMR (bottom) of Nitrourea (2) and Urea Nitrate(1)
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 | 2007 | Prior | Area(μS*Min) | Peak Ht(μS) | Ret. Time(Min) | ng/ml | ng/g of soil |
|-------------|------|-------|--------------|-------------|----------------|------|-------------|
| 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    | 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        | 9.024          | 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              | 9.091 | 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 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              | 9.054 | 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 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 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.
| ID | 2009 Prior | Area(μS*Min) | Peak Ht(μS) | Ret. Time(Min) | ng/ml | ng/g of soil |
|---|---|---|---|---|---|---|
| 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 2 | 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 3 | X | 0.016 | X | 0.06 | X | 9.014 | X | 121.5 | X | 243 |
| 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 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 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
| 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 | 0.0072 | X | 0.02 | X | 9.041 | X | 69.5 | X | 139 |
| O 1 | 0.0055 | X | 0.02 | X | 9.031 | X | 61 | X | 122 |
| O 2 | 0.0047 | X | 0.02 | X | 8.997 | X | 63 | X | 126 |
| O 2 | 0.0055 | X | 0.02 | X | 8.984 | X | 57 | X | 114 |
| O 3 | 0.0064 | X | 0.03 | X | 9.007 | X | 65.5 | X | 131 |
| O 3 | 0.0168 | X | 0.06 | X | 9.011 | X | 117.5 | X | 235 |
| O 4 | 0.1389 | X | 0.52 | X | 9.001 | X | 728 | X | 1456 |
| O 4 | 0.1234 | X | 0.46 | X | 9.001 | X | 650.5 | X | 1301 |
| O 4 | 0.0907 | X | 0.34 | X | 9.004 | X | 487 | X | 974 |
| O 5 | 0.0035 | X | 0.01 | X | 8.981 | X | 51 | X | 102 |
| O 5 | 0.0057 | X | 0.02 | X | 9.017 | X | 62 | X | 124 |
| O 5 | 0.0034 | X | 0.01 | X | 8.994 | X | 50.5 | X | 101 |
| O 6 | 0.0261 | X | 0.09 | X | 9.004 | X | 164 | X | 328 |
| O 6 | 0.0147 | X | 0.06 | X | 9.008 | X | 107 | X | 214 |
| O 6 | 0.0097 | X | 0.04 | X | 9.004 | X | 82 | X | 164 |
| O 7 | 0.1659 | X | 0.65 | X | 9.007 | X | 863 | X | 1726 |
| O 7 | 0.2233 | X | 0.84 | X | 9.001 | X | 1150 | X | 2300 |
| O 7 | 0.1759 | X | 0.66 | X | 9.004 | X | 913 | X | 1826 |
| O 8 | X | X | X | X | X | X | X | X | X |
| O 8 | X | X | X | X | X | X | X | X | X |
| O 9 | 0.0015 | X | 0.01 | X | 9.048 | X | 41 | X | 82 |
| O 9 | 0.0261 | X | 0.05 | X | 9.081 | X | 164 | X | 328 |
| O 10 | X | X | X | X | X | X | X | X | X |
| O 10 | X | X | X | X | X | X | X | X | X |
| O 11 | 0.0044 | X | 0.01 | X | 9.011 | X | 55.5 | X | 111 |
| O 11 | 0.0023 | X | 0.01 | X | 8.848 | X | 45 | X | 90 |
| O 11 | 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

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| ID   | Area(μS*Min) | Peak Ht(μS) | Ret. Time(Min) | ng/ml | ng/g of soil |
|------|--------------|-------------|----------------|-------|-------------|
|      | Prior | After | Prior | After | Prior | After | Prior | After |
| O 1  | X     | 0.026  | X     | 0.03  | X     | 8.588 | X     | 185.5 |
| O 1  | X     | 0.0048 | X     | 0.02  | X     | 8.704 | X     | 79.5  |
| O 2  | X     | 0.0984 | X     | 0.39  | X     | 8.671 | X     | 547.5 |
| O 2  | X     | 0.0907 | X     | 0.36  | X     | 8.668 | X     | 509   |
| O 3  | X     | 0.0939 | X     | 0.37  | X     | 8.668 | X     | 525   |
| O 4  | X     | 0.0056 | X     | 0.02  | X     | 8.684 | X     | 83.5  |
| O 4  | X     | 0.0015 | X     | 0.01  | X     | 8.678 | X     | 63    |
| O 4  | X     | 0.0011 | X     | 0.01  | X     | 8.664 | X     | 61    |
| O 5  | X     | 0.0038 | X     | 0.01  | X     | 8.664 | X     | 74.5  |
| O 5  | X     | 0.0051 | X     | 0.02  | X     | 8.681 | X     | 81    |
| O 5  | X     | 0.0026 | X     | 0.01  | X     | 8.664 | X     | 68.5  |
| O 6  | X     | 0.0038 | X     | 0.01  | X     | 8.664 | X     | 149   |
| O 6  | X     | 0.0051 | X     | 0.02  | X     | 8.681 | X     | 162   |
| O 6  | X     | 0.0026 | X     | 0.01  | X     | 8.664 | X     | 137   |
| O 7  | X     | 0.0039 | X     | 0.02  | X     | 8.704 | X     | 75    |
| O 7  | X     | 0.0003 | X     | 0.01  | X     | 8.701 | X     | 70.5  |
| O 8  | X     | 0.0029 | X     | 0.01  | X     | 8.714 | X     | 70    |
| O 8  | X     | 0.0006 | X     | 0.01  | X     | 8.708 | X     | 87    |
| O 9  | X     | 0.0102 | X     | 0.04  | X     | 8.697 | X     | 106.5 |
| O 9  | X     | 0.0063 | X     | 0.02  | X     | 8.708 | X     | 87    |
| O 10 | X     | 0.0003 | X     | 0.01  | X     | 8.701 | X     | 70.5  |
| O 10 | X     | 0.0029 | X     | 0.01  | X     | 8.714 | X     | 70    |
| O 11 | X     | 0.0003 | X     | 0.01  | X     | 8.701 | X     | 70.5  |
| O 11 | X     | 0.0029 | X     | 0.01  | X     | 8.714 | X     | 70    |

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 |
|-----|--------------|-------------|----------------|-------|--------------|
|     | Prior        | After       | Prior          | After | Prior        | After | Prior | After |
| O 1 | X            | X           | X              | X     | X            | X     | X     | X     |
| O 1 | X            | X           | X              | X     | X            | X     | X     | X     |
| O 2 | X            | X           | X              | X     | X            | X     | X     | X     |
| O 2 | 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 0.02      | X 9.348        | X     | 38           | X 75  |
| O 4 | 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     |
| O 5 | X            | X           | X              | X     | X            | X     |
| O 5 | X            | X           | X              | X     | X            | X     |
| O 6 | X            | X           | X              | X     | X            | X     |
| O 6 | X            | X           | X              | X     | X            | X     |
| O 7 | X            | X           | X              | X     | X            | X     |
| O 7 | X            | X           | X              | X     | X            | X     |
| O 8 | X            | X           | X              | X     | X            | X     |
| O 8 | X            | X           | X              | X     | X            | X     |
| O 9 | X            | X           | X              | X     | X            | X     |
| O 9 | X            | X           | X              | X     | X            | X     |
| O 9 | X            | X           | X              | X     | X            | X     |
| O 9 | 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     |
| O 11| X            | X           | X              | X     | X            | X     |
| O 11| 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
| ID   | Area(μS*Min) | Peak Ht(μS) | Ret. Time(Min) | ng/ml | ng/g of soil |
|------|--------------|-------------|----------------|-------|-------------|
|      | Prior | After | Prior | After | Prior | After | Prior | After | Prior | After |
| 2011 | X | X | X | X | X | X | X | X | X | X |
| B1-1 | 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 |
| 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          |
| 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 0.1587     | X           | 0.34           | X     | 9.158        | X           | 346            | X           | 693            |
| B2-2 | 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           | 165            |
| 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 |
|------|--------------|-------------|----------------|-------|--------------|
|      | Prior | After | Prior | After | Prior | After | Prior | After | Prior | After |
| 2011 |       |       |       |       |       |       |       |       |       |       |
| 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     | 0.4877 | 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
| ID     | 2012 Area (μS*Min) | 2012 Peak Ht (μS) | 2012 Ret. Time (Min) | 2012 ng/ml | 2012 ng/g of soil | 2013 Prior Area (μS*Min) | 2013 After Area (μS*Min) | 2013 Peak Ht (μS) | 2013 Ret. Time (Min) | 2013 ng/ml | 2013 ng/g of soil |
|--------|--------------------|------------------|----------------------|------------|------------------|--------------------------|--------------------------|------------------|----------------------|------------|------------------|
| M1-1   | X 1.4119           | X 5.06           | X 8.998              | X 4735     | X 9469           | X                        | X                       | X                | X                    | X          | X                |
| M1-2   | X 1.1463           | X 4.14           | X 9.014              | X 3849     | X 7699           | X                        | X                       | X                | X                    | X          | X                |
| M1-3   | X 1.0843           | X 3.92           | X 9.014              | X 3643     | X 7285           | X                        | X                       | X                | X                    | X          | X                |
| M2-1   | X 0.007            | X 0.03           | X 9.098              | X 52       | X 103            | X                        | X                       | X                | X                    | X          | X                |
| M2-2   | X 0.0018           | X 0.01           | X 9.118              | X 34       | X 69             | X                        | X                       | X                | X                    | X          | X                |
| M2-3   | X 0.0022           | X 0.01           | X 9.984              | X 36       | X 71             | X                        | X                       | X                | X                    | X          | X                |
| M3-1   | X X                | X X              | X X                  | X X        | X X              | X                        | X                       | X                | X                    | X          | X                |
| M3-2   | X X                | X X              | X X                  | X X        | X X              | X                        | X                       | X                | X                    | X          | X                |
| M3-3   | X X                | X X              | X X                  | 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           | X                        | X                       | X                | X                    | X          | X                |
| M4-2   | X 0.1738           | X 0.63           | X 9.078              | X 608      | X 1215           | X                        | X                       | X                | X                    | X          | X                |
| M4-3   | X 0.1013           | X 0.37           | X 9.087              | X 366      | X 732            | X                        | X                       | X                | X                    | X          | X                |
| M5-1   | X 0.2583           | X 0.94           | X 9.071              | X 889      | X 1779           | X                        | X                       | X                | X                    | X          | X                |
| M5-2   | X 0.2234           | X 0.82           | X 9.068              | X 773      | X 1546           | X                        | X                       | X                | X                    | X          | X                |
| M5-3   | X 0.1443           | X 0.5            | X 9.071              | X 509      | X 1019           | X                        | X                       | X                | X                    | X          | X                |
| M6-1   | X X                | X X              | X X                  | X X        | X X              | X                        | X                       | X                | X                    | X          | X                |
| M6-2   | X X                | X X              | X X                  | X X        | X X              | X                        | X                       | X                | X                    | X          | X                |
| M6-3   | X X                | X X              | X X                  | 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            | X                        | X                       | X                | X                    | X          | X                |
| M7-2   | X 0.0802           | X 0.29           | X 9.091              | X 296      | X 591            | X                        | X                       | X                | X                    | X          | X                |
| M7-3   | X 0.0283           | X 0.1            | X 9.091              | X 123      | X 245            | X                        | X                       | X                | X                    | X          | X                |
| M8-1   | X 0.0043           | X 0.02           | X 9.041              | X 43       | X 85             | X                        | X                       | X                | X                    | X          | X                |
| M8-2   | X 0.0161           | X 0.06           | X 9.071              | X 82       | X 164            | X                        | X                       | X                | X                    | X          | X                |

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 |
| J1-1 | X | X | X | X | X | X | X | X |
| J1-3 | 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 |
| J4-2 | 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 |
| J6-2 | X | X | X | X | X | X | X | X |
| J6-3 | X | X | X | X | X | X | X | X |
| J7-1 | X | X | X | X | X | X | X | X |
| J7-2 | X | X | X | X | X | X | X | X |
| J7-3 | 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 Locus map of Site 1
Figure B.2 Locus map of Site 2

Note: Sites 1-8 numbered left-to-right, B 1-8
Figure B.3 Locus map of Site 3
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           |

Area(μS*Min) Vs Concentration (ng/ml)

\[ y = 0.0002x - 0.002 \]

\[ R^2 = 0.9981 \]

Figure B. 5 A Standard Calibration Curve of Perchlorate ion in Water by Ion Chromatography
Figure B.6

![Graph](image)

| Concentration (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) | Concent. Rec. (ng/ml) | % Rec  |
|----------------------|---------------|--------------|-----------------|-----------------------|--------|
| 0.5 μg/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    |
| 0.5 μg/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    |
| 1.0 μg/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) | Concent. Rec. (ng/ml) | % Rec  |
|----------------------|---------------|--------------|-----------------|-----------------------|--------|
| 0.5 μg/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    |
| 0.5 μg/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    |
| 1.0 μg/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 Chromatogram of Water.
Figure B.8 Chromatogram of perchlorate in soils collected prior and after 2010 fireworks display from O4 at site 1.
Figure B. 9 Chromatogram of perchlorate in soils collected prior and after 2011 fireworks display from B4 at site 2.
Figure B.10 Chromatogram of perchlorate in soils collected prior and after 2011 fireworks display from M5 at site 3.
Figure B.11 Chromatogram of perchlorate in soils collected prior and after 2011 fireworks display from J2 at Site 4.
## List of Abbreviations

| Abbreviation  | Description                                      |
|---------------|--------------------------------------------------|
| 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            | ethylcellulose                                   |
| 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.................................polyethylenimine

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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