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Comparative evaluation of purity of green energetic material (ammonium dinitramide) depending on refining method

Wooram Kim*, Younja Kwon*, Seong Yun Hwang, and Youngmin Jo*,†**

*Department of Environmental Science and Engineering, Kyung Hee University, Yongin-si, Gyeonggi-do 17104, Korea
**Department of Food and Biotechnology, Hankyong National University, Ansung-si, Gyeonggi-do 17579, Korea
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Abstract−Although the solid propellant, ammonium dinitramide (ADN, $NH_4N(NO_2)_2$) is safe and thermally stable, it requires high purity for practical commercial applications. Even a small amount of impurities in ADN can create negative effects, including catalyst poisoning and thruster nozzle cloggings when it is used as a liquid propellant. Thus, we explored several purification processes for the precipitated ADN particles, such as repetition extraction, adsorption by activated carbons, and low-temperature extraction. These purifying methods help to improve the chemical purity as evaluated by FTIR, UV-vis, DSC, and IC analyses. Among the purification processes, adsorption was found to be the best method, showing a final purity of 99.768% based on relative quantification by ion chromatography.

Keywords: Green Propellant, Ammonium Dinitramide, Purification, Adsorption

INTRODUCTION

ADN (ammonium dinitramide), which is an ionic oxidizer composed of ammonium cation (NH_4^+) and dinitramide anion ($N(NO_2)_2^-$), has a very high energy density of 23 kJ/cm^3 [1]. To utilize it as a high performance green propellant (HPGP) in a thruster system instead of ammonium perchlorate or hydrazine, its purity is very important [2]. Even in small amounts impurities may deteriorate the performance and lifetime of catalysts due to poisoning, degrade thermal properties such as stability and decomposition, and reduce the energy capacity of the liquid-phase monopropellant [3]. In addition, some impurities, including non-volatile residues, clog the injection nozzles of a thruster [4]. ADN purity is reduced by nitric acid ions and other ionic salts such as $KHSO_4$, KNO_3, K_2SO_4, NH_4NO_3 and $(NH_4)_2SO_4$, which are frequently observed as by-products from the neutralization of excess nitric acid and sulfuric acid. These impurities are precipitated in an early reactant concentration. However, some of the impurities can remain dissolved in aqueous solution and may coexist with ADN, since water is seldom removed completely from the final product. Most impurities or by-products can be removed during secondary recrystallization using selective solvents. However, ammonium nitrate or potassium nitrate, which exhibit physical properties similar to those of ADN, may remain even after purification processes. Furthermore, unidentified materials such as the ionic structure of ADN with trinitro functionalities, residual reagents, or other impurities that are likely from contaminated reaction vessels could be present after the reaction is complete. Additionally, metallic species that are a result of handling during synthesis might bind with ADN, causing the purity to decrease.

†To whom correspondence should be addressed.
E-mail: ymjo@khu.ac.kr

Nazeri et al. (2008) attempted to improve the purity by studying the key reactant of sulfamate counterion [5]. This resulted in a 1 : 3.5 optimum ratio of sulfuric acid to nitric acid, producing an ADN yield of 50.8%. The final purity of ADN is determined by the synthesis procedure or by post-synthesis treatment. We explored several post-synthesis purification methods such as repetition extraction, low-temperature extraction, and adsorption. The prepared ADN samples were characterized with a focus on the purity using several techniques such as FTIR, UV-vis spectroscopy, DSC, and IC.

MATERIALS AND METHODS

1. Materials

We used potassium sulfamate (NH_2SO_3K, assay >99%), sulfamic acid (NH_2SO_3H, assay >99%), sulfuric acid (assay >98%), fuming nitric acid (assay >99.5%), ammonium sulfate ($(NH_4)_2SO_4$, assay >99.5%), and potassium hydroxide (KOH, assay >99.5%) as starting materials for ADN synthesis. All chemicals were procured from Sigma Aldrich (USA). All solvents were reagent grade with purities over 99%; isopropyl alcohol (C_3H_8O), acetone (C_3H_6O), ethyl ether ($C_4H_{10}O$) and ethyl acetate ($C_4H_8O_2$) (Daejung Co., Korea) were used for the extraction processes. PAC (powdered activated carbon, 100 mesh), which is used for selective adsorption, and Celite 545, which is used as a porous filter layer, were also obtained from Sigma-Aldrich (USA).

2. Ammonium Dinitramide Synthesis

Potassium sulfamate (NH_2SO_3K) that was synthesized in our lab was slowly added to a mixture of fuming nitric acid and sulfuric acid, and then the mixture was cooled to −35 °C - −45 °C [6]. After allowing sufficient time for reaction with continuous stirring at a temperature below −10 °C, the solution was neutralized to pH 7-8 by adding 1 M-KOH solution. The neutralized solution was added to ammonium sulfate ($(NH_4)_2SO_4$) at ambient temperature in order

to exchange ammonium salts. The solution was cooled, and the precipitated by-products were filtered off. The remaining solution was concentrated by a rotary evaporator. The extracted crude ADN particles were then cleaned through several purification methods.

3. Purification Methods

3-1. Repeated Extraction (RE)

The synthesized ADN product was dissolved in acetone and then extracted with gradual addition of isopropyl alcohol. Some impurities were then separated from the product based on selective dissolution by adding warm ethyl acetate. The precipitated ADN was recovered by filtration using filter paper.

3-2. Adsorption by Activated Carbon (AA)

Charcoal based (PAC) was used as an adsorbent to extract the final product by selective capture of the ionic species in solution. First, PAC (10 g) was added to an aqueous solution (100 ml) containing the ionic phase of ADN. The solution with PAC was gently agitated by a magnetic stirrer for 30 minutes, then poured to the porous celite layer (1 cm thick) in an aspiration separator to collect the ADN adsorbed on PAC. The adsorbed ADN was then eluted with warm water (50 °C). This process was repeated three times.

3-3. Low-temperature Extraction (LT)

An aqueous solution containing the ionic phase of ADN was cooled very slowly to 0-5 °C for 24 hours. The precipitate was filtered and dried at 50 °C. Five batches of test samples were simultaneously prepared varying the extraction time up to 48 hours. However, since no further precipitation occurred after 24 hours, the test reaction time was fixed at 24 hours.

3-4. Characterization

The relative purities of the synthesized ADN samples with and without post-synthesis purification were evaluated through several analytical techniques. First, the synthesis of ADN was confirmed by Fourier transform infrared spectroscopy (FTIR, Spectrum One, Perkin-Elmer, USA) in the region from 4,000 cm^{-1} to 500 cm^{-1} and Ultraviolte-visible spectroscopy, (UV-vis, CARY 300 Bio, Varian, USA) at a wavelength of 284 nm. Differential scanning calorimetry (DSC) analysis was used to measure the characteristic thermal properties including thermal decomposition. The elemental composition of the particulate ADN was examined by an elemental analyzer (EA, Flash EA 1112, Thermo Fisher, USA) and compared to the theoretical molecular formula. Some potential impurities such as nitrate ions were more closely investigated by ion chromatography (IC). The instrumental setup for IC included a SUPP 5 150/4.0 analytical column, Na_2CO_3 and $NaHCO_3$ eluent solution, sample injections of 20 L, and a flow rate of 0.7 mL/min. The impurity peaks of SO_4, NO_3, and PO_4 on the chromatograms were integrated and quantitatively calculated for each sample.

RESULTS AND DISCUSSION

The nitric acid and sulfuric acid mixture likely contained a small amount of water due to exposure to the moisture in the ambient air of the laboratory during nitration, which thereby may have formed nitrate cations, and/or at the same time produced HSO_4^- or NO_3^- anions. These anions are expected to form KNO_3 or $KHSO_4$ through reactions with potassium cations from the starting reactant: potassium sulfamate. Besides, $(NH_4)_2SO_4$, which is added at the final step of the synthesis procedure, can be ionized by H_2O, leading to K_2SO_4 formation. The dissociated NO_3^- anion may react with potassium or ammonium cations, forming additional KNO_3 or NH_4NO_3. Alternatively, the synthesized ADN can also form NH_4NO_3 due to immediate decomposition by ambient humidity and temperature.

1. Synthesis Yield with Purification Processes

Recovery of particulate ADN is one significant factor in the synthesis process. This section details the effect of each purification method on the final synthesis yield.

1-1. Repeated Extraction

High-purity ADN was achieved by repeated purification steps of separation-evaporation-extraction-evaporation-crystallization. This method utilizes the different solubilities in the applied solvents of ADN and the synthesis by-products such as $KHSO_4$, K_2SO_4, KNO_3. While ADN was well dissolved in acetone, K_2SO_4 and KNO_3 could not be dissolved. Therefore, in this work, the by-products K_2SO_4 or KNO_3 were precipitated in an acetone solution, and separated by filtration. ADN was extracted from the filtrate by using a rotary evaporator for 15 minutes at 35 °C. Then, isopropyl alcohol was added to the ADN emulsion since it is difficult to dissolve ADN in isopropyl alcohol. After sufficient stirring of the precipitated ADN emulsion, ethyl acetate was gently added dropwise until yellowish solids were no longer generated. Thus, isopropyl alcohol concentrated the aqueous solution after extraction, segregated the coagulated crystals, and facilitated extraction of the crystalline products. In practice, crystalline forms could not be achieved by immediate crystallization using ethyl acetate or ether after concentration. Therefore, it is believed that isopropyl alcohol acted as an intermediate solvent.

After completion of the first extraction step, undissolved solids were separated from the resulting liquid extract by filtration. Other impurities were soluble in aqueous isopropyl alcohol or ethyl acetate. Separation of the solid from the liquid solution was carried out in a rotary evaporator.

The effective use of the isopropyl alcohol and ethyl acetate solvent mixture led to efficient extraction of the solid precipitates. Ethyl acetate assists in reducing the polarity of isopropyl alcohol, which leads to rapid crystallization. The extracted particulate ADN was washed by ethyl ether at 50 °C, and the final obtained yield improved to 73%. Repeated extraction with solvents and washing increased the purity of the final product despite the loss of some ADN precipitates.

However, the solubility of ammonium nitrates, some of which are formed during synthesis, is very similar to that of ADN, so it is difficult to completely remove them from the recrystallization process. Thus, these nitrates can remain as impurities even after the final recovery of the precipitated salt. Nevertheless, this method is an economical process that is relatively simple to use and results in products that can be quickly separated.

1-2. Extraction by PAC Adsorption

The carbonaceous adsorbents only capture the ionic phase of ADN due to the characteristic interaction between the carbon surface and ADN. The adsorption of ADN follows Langmuir or Freundlich isotherm models, which indicate single layer adsorption on the activated carbon surface. In this work, ADN was dissolved

in water and mixed with a charcoal based-PAC. Then PAC was gradually filtered out through a Cellite layer with a thickness of approximately 2 cm. The porous Cellite layer prevented PAC loss and movement into the filtrate. Desorption of the adsorbed ADN on the PAC surface was achieved with warm water at 50 °C. Finally ADN was crystallized in a rotary evaporator maintained at 45 °C.

According to our preliminary experiments, PAC showed better adsorption capacity (100 mg-ADN/g-AC) than granular activated carbon. Experimental observation suggests that ADN should be separated and purified carefully to avoid ammonium nitrate (AN) contamination. The crystalline ADN yield was 70% at mass basis. As the repeated washing method, the ion phase ADN could be recovered with small loss.

1-3. Low-temperature Extraction

The ionic phase of ADN in highly purified water can be naturally extracted in particulate form at low temperatures (0 °C to 5 °C) if the water is prevented from freezing [7]. Crystallization was carried out for 24 hours; this duration was selected because no further solid extraction was found after 24 hours based on simultaneous examination of five separate test batches. Overall, the solubility of ADN decreased in a low-temperature environment. Thus, a gradual decrease in the concentration of ADN in the solution might increase the relative solubility of impurities. Thus the purity of the extracted ADN could be improved using slow cooling. After completion of the extraction step, undissolved solids were separated from the resulting liquid extract by filtration. The final ADN product yield was only 31%, because a significant amount of ADN still could remain in a cold aqueous solution due to its high hydrophilic property.

In constrast, observation through SEM (Fig. 1) did not show a critical difference between samples. The superficial shapes were very irregular because they were not prilled with systematic treatment. However, particle surfaces seemed comparatively smoother than those of the crude sample.

2. Purity Evaluation of Synthesized ADN Samples

Analytical methods, including FTIR, UV-Vis, DSC, and IC, were used to determine the purity of the particulate ADN samples obtained from the different processes in this work. According to the molecular formula of ADN ($NH_4N(NO_2)_2$), oxygen is present in the highest proportion by weight at 51.58% and nitrogen at 45.17%. Theoretically, no other elements except hydrogen (3.25%) must be present. However, as seen in Table 1, some carbonaceous impurities were found in the crude ADN (CA), RE and LT samples. Carbon constituents might be introduced into the precipitated ADN from the reactants or from insufficiently cleaned experimental tools.

Table 1. Elemental composition as determined by EA

Sample	N (%)	C (%)	H (%)	O (%)
Theoretical comp.	**45.17**		**3.25**	**51.58**
CA	43.18	0.02	2.92	53.87
RE	44.25	0.01	3.45	52.29
AA	44.67	0	3.23	52.10
LT	41.84	0.07	2.88	55.21

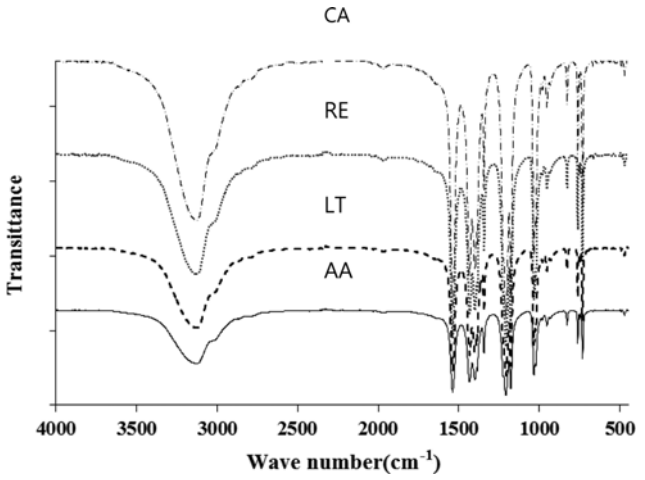

Fig. 2. FT-IR spectrum of ADN samples.

Although most of the carbon impurities could be filtered by various purification steps, a small amount of impurities totaling 0.013% for RE and 0.067% for LT remained after purification. However, adsorption using PAC can separate out these carbon species; thus, no carbon was detected by the elemental analyzer for this sample. So, the AA sample had an elemental composition that was the closest to the theoretical composition of ADN.

2-1. Fourier Transform Infrared Spectroscopy

FT-IR analysis identified the functionalities of ADN as seen in Fig. 2. The characteristic peaks for ADN are 3,124 cm^{-1} (N-H signal of NH_4^+), 1,537 cm^{-1} (asymmetric in-phase signal of the NO_2 group), and 1,343 cm^{-1} (symmetric in-phase signal of the NO_2 group). The peaks at 1,433 cm^{-1}, 1,208 cm^{-1} and 1,032 cm^{-1} represent the theo-

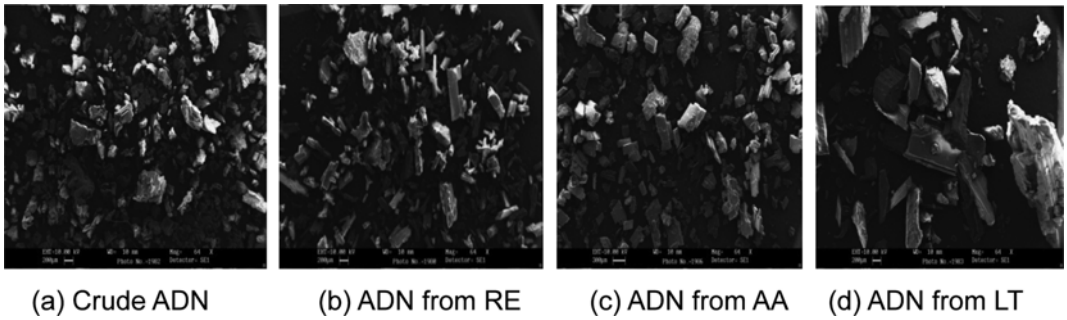

Fig. 1. SEM images of the ADN samples.

retical structural features of ADN [8]. A peak seen at 1,040 cm^{-1} might indicate AN, which deteriorates purity. Although the sharpness of the peaks at this wavenumber was different for each sample, most samples contained a small amount of impurities. However, some possible groups, such as NH- (3,151 cm^{-1}) and OH- (2,455 cm^{-1}), which were found in other works, did not appear in this work.

In addition, the unreacted sulfamic acid remains as an unidentified ionic impurity. The FT-IR analysis also could not directly measure the quantitative degree of purity. Nevertheless, this analysis enabled us to identify the chemical structure and representative functionalities in order to demonstrate that we obtained the target materials.

2-2. Ultraviolet-visible Spectroscopy

UV-Vis can trace the extent of reaction as the reactants are converted to dinitramidic acid, and provide an estimation of the quantitative purity based on Beer's law [9]. The molar extinction coefficient was 5.246×10^3 L/mol·cm, which was obtained from the concentration calibration curves. The degree of absorbance for ADN in the aqueous phase prepared at a concentration 10 mg/L was calculated in order to evaluate the purity from each purification method.

The apparent peaks at 212 and 284 nm in UV-vis spectrum indicate the presence of ADN. Since NO_2 contains many unshared electron pairs, very strong absorbance peaks appeared in these two regimes. The peak at 212 nm represents the electronic transition of π-π*, and 284 nm is the n-π* transition in the ultraviolet range. In particular, the structure of -$N(NO_2)_2$ exhibits strong absorption in the area of NO (max: 284 nm) [10]. Accordingly, since the peak at 284 nm is the most noticeable, this peak is known as a representative peak for ADN. In addition, the anions in dinitramide intensively absorb the UV signal, thereby enabling us quantify the concentration with high accuracy.

However, UV-Vis spectroscopy does not allow for accurate identification of the peaks due to interference by the broad absorption band of nitrate ions from 220 nm to 320 nm in presence of large quantities of nitrate mixtures. This work focused on the peak signal at 284 nm (Fig. 3), which is a characteristic absorption area of dinitramide (-$N(NO_2)_2$)) [11]. The relative values of the degree of peak absorption were 0.4151 for the RE sample, 0.4152 for AA, and 0.4125 for LT. Thereby, the calculated purities, as summarized in Table 2, were 98.51%, 99.3%, and 97.89%, respectively.

Table 2. Sample purities determined by UV

Sample	Absorbance	Purity (%)
CA	0.4077	96.8
RE	0.4151	98.51
AA	0.4182	99.3
LT	0.4125	97.89

2-3. Differential Scanning Calorimetry

Thermo analytical techniques are very useful to estimate the component properties as well as to understand the phase behavior of energy materials. To avoid strong exothermic decomposition reactions, we used only a small amount of each sample (less than 1 mg). The heating rate was also carefully controlled at 5 °C/min. Potential impurities including AN may cause a negative impact on the thermal stability by reducing the melting point. Powdered ADN can be melted over a certain temperature range through an endothermic mechanism under an inert nitrogen atmosphere. Sharper endothermic peaks imply higher purity.

According to the literature, the melting point of ADN crystals ranges from 92 °C to 95 °C, and varies with the amount or species of impurities such as AN [12]. It is assumed that samples with identical thermal properties will have the same melting point. In particular, the samples prepared from adsorption extraction (AA) and repetition extraction (RE) have shown similar thermal properties.

Purity analysis of the ADN crystals by DSC, based on the enthalpy measurement at a melting point at 93 °C, can be highly reliable for purities greater than 98%. With more unwanted by-products such as AN, the melting point will be lowered. For example a composite of ADN/AN (70/30 mole fraction) eutectic showed a melting point of 55 °C [13].

Fig. 4 shows the first endothermic peaks for the prepared samples. The sample prepared by AA had the highest peak, corresponding a melting point of 93.2 °C, followed by 92.9 °C for RE and 90.6 °C for RT.

2-4. Ion Chromatography

Ion chromatography analysis can indirectly determine relative

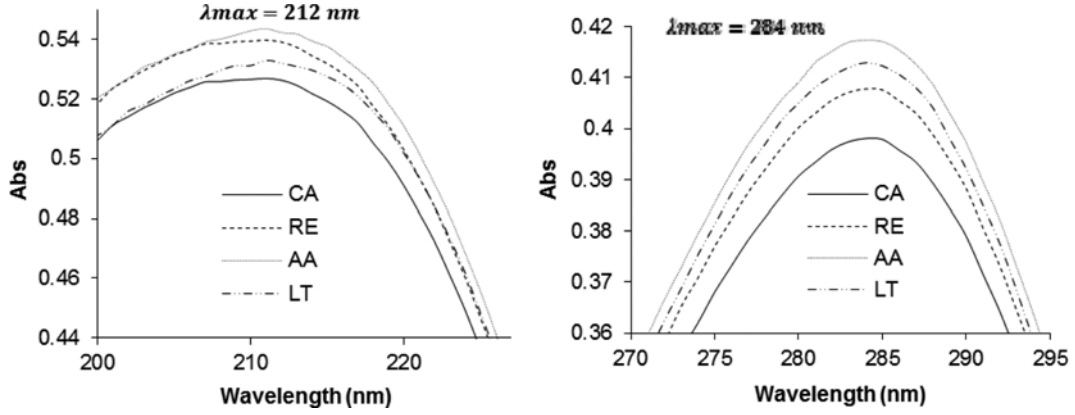

Fig. 3. UV-vis spectroscopy absorbance of ADN samples.

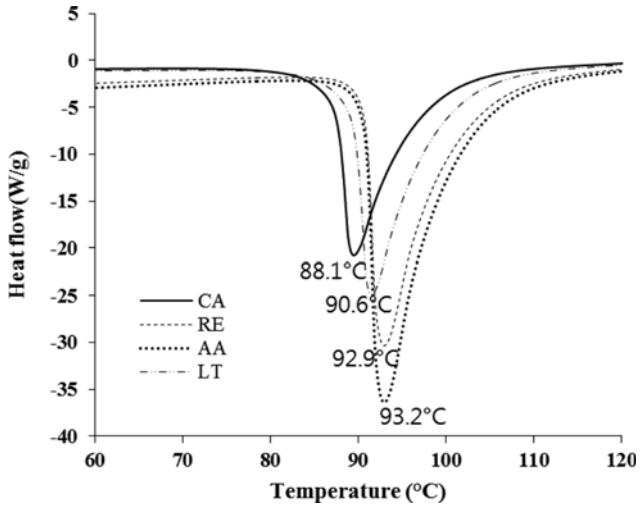

Fig. 4. DSC curves showing the endothermic peaks of the ADN samples.

purities through measurement of ionic impurities dissolved in solution [14]. However, ammonium salts such as sulfates or nitrates can interfere with accurate measurements [15]. Amongst these, ammonium nitrate, which is a typical by-product that can be formed from the decomposition of ADN, is a frequently observed anionic species that deteriorate the particulate ADN purity. In practice, some cations of K, NH_4, and H are present in salts bound to NO_3, SO_4 and $N(NO_2)_2^-$. Thus, anion measurements can show the quantitative amount of impurities in the solution by subtracting the ammonium nitrate content from the total ammonium content. The IC spectra of the prepared ADN samples are displayed in Fig. 5. As can be seen in the spectra, an obvious peak appears in the AA sample during analysis, indicating NO_3^- with minor peaks of Cl^- and PO_4^{3-}. While the CA sample contains apparent peaks for PO_4^{3-} and SO_4^{2-}.

In practice, ionic impurities can be formed during the nitration process in ADN synthesis and ammonium sulfate during ion-exchange of the ammonium cation. Ammonium nitrate can be present in a condensed phase due to the decomposition of ADN. Table 3 shows the quantitative analysis results for the $NO_3$and SO_4^{2-} ions, which shows that more than 100 times of the NO_3^- content was detected. The ADN obtained through adsorption extraction has the highest purity (99.768%) as determined by excluding impurities.

CONCLUSIONS

This study characterized the precipitated ADN samples, prepared through different purification methods. The focus was on chemical purity as determined by a several analytical techniques, including FTIR, UV-Vis, DSC, IC, and EA. FTIR indicated that

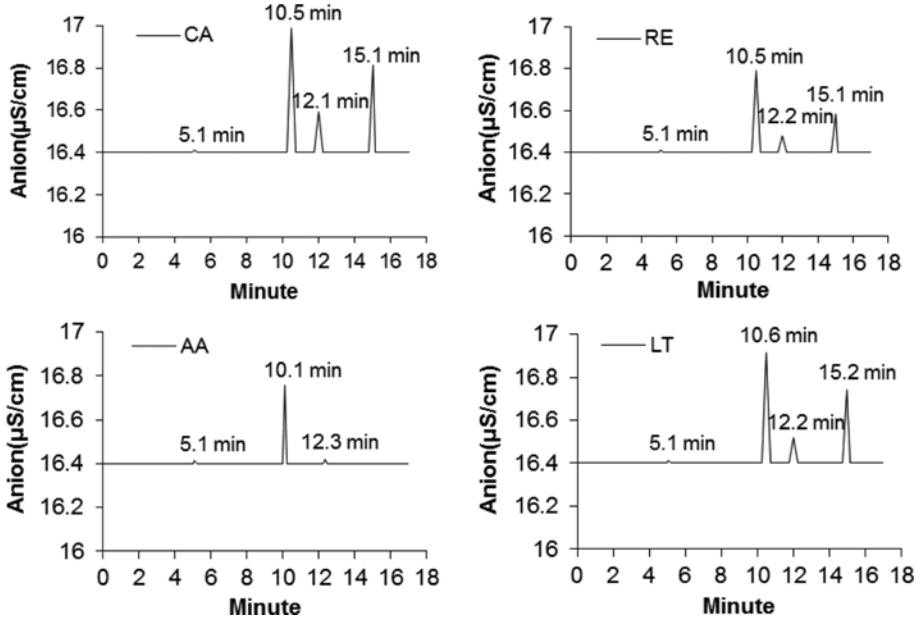

Fig. 5. IC chromatograms of purified ADN samples.

Table 3. Detection of anionic species in ion chromatography

Sample	NO_3^- (%)	PO_4^{2-} (%)	SO_4^{2-} (%)	Cl^- (%)	Relative purity (%)
CA	1.245	0.271	0.982	0.007	97.495
RE	0.682	0.012	0.282	0.005	99.019
AA	0.217	0.006	-	0.009	99.768
LT	1.125	0.122	0.714	0.007	98.032

the chemical functionalities representing ADN were present. UV-Vis resulted in a maximum purity of 99.3% based on absorbance at 284 nm. DSC analysis demonstrated single melting points for each sample, and the highest temperature, 93.2 °C, appeared for the AA sample. IC analysis revealed the highest purity at 99.768% relative to ionic impurities, which was also obtained for the AA sample. In particular, presumed impurities of carbonaceous or sulfuric species were not detected in the ADN purified by PAC adsorption. These post-synthesis purification methods for precipitated ADN can be used to improve the purity of the final solid phase of ADN compared to the crude sample.

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