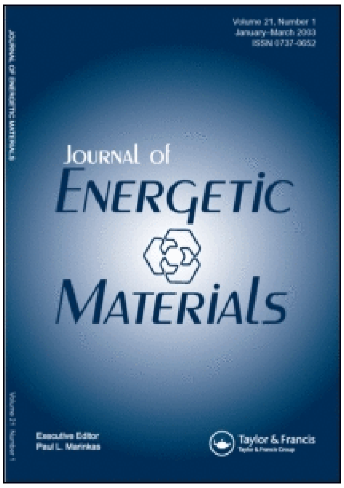

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Analysis of anionic impurities in ammonium dinitramide (ADN), Part I: Ion chromatographic analysis

Stuart A. Oehrle[a]
[a] Waters Corporation, Milford, MA

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Analysis of Anionic Impurities in Ammonium Dinitramide (ADN)

Part I: Ion Chromatographic Analysis

Stuart A. Oehrle
Waters Corporation
34 Maple St.
Milford, MA 01757

ABSTRACT

A method has been developed to analyze ammonium dinitrimide, a new energetic material, as well as other anionic impurities in it. This method employs ion chromatography with UV detection. Analysis of ADN samples could be done in under 20 minutes employing this method. Analysis of pure samples as well as aged samples was accomplished.

INTRODUCTION

Several new energetic materials have attracted attention as possible replacements or inclusion in various military and space applications.[1] Ammonium dinitramide (ADN), $NH_4N(NO_2)_2$, is one such compound under consideration.[2-5] Possible applications for ADN include use as an oxidizer in solid rocket motors or as a general purpose replacement for ammonium nitrate or ammonium perchlorate (AP). AP is currently the primary compound used as an oxidizer in most military and space motors. ADN offers several advantages over AP. These include higher boost and environmental acceptability.

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As is common with most manufacturing processes, monitoring impurities in the final product is important. In the case of ADN, anionic impurities (i.e. NO_2^-, and NO_3^-) can cause several problems. One of these include the lowering of the melting point of the product which would lead to a lowering of rocket performance. ADN is also light sensitive with the anionic impurities NO_2^- and NO_3^- being the primary degradation products. One technique that can monitor for these ions is ion chromatography (IC).

Ion chromatography is a liquid chromatographic technique developed for the analysis of ions in solution. An ion exchange column is used to separate the ions with detection typically achieved using conductivity since most ions do not have UV activity. The dinitramide anion (DN^-) has several resonance states that delocalize the negative charge as shown in figure 1. This is responsible for the high stability. However, because of the delocalisation of the charge DN^- has poor conductivity which makes the analysis difficult. Unlike most ions, DN^- does absorb UV light as does NO_2^- and NO_3^-, it's primary degradation products. Figure 2 is the spectra of DN^-, NO_2^-, and NO_3^-. Based on the UV spectra of all three, 214nm was chosen as the wavelength to monitor. UV detection offers greater sensitivity and selectivity as compared to conductivity. Figure 3 is a chromatogram of a 20 mg/L ADN sample with both UV (figure 3a) and conductivity detection (figure 3b). As seen in figure 3 the UV chromatogram offers higher sensitivity as compared to conductivity.

One disadvantage of UV detection is that sulfate can not be detected. This impurity is found in the original sample as well as the aged sample but does not change in amount. Table I displays the method detection limit (MDL) for both UV and conductivity detection for DN^-, NO_2^-, and NO_3^-. This method employs a UV transparent mobile phase which allows for fast analysis times and good peak shape which is an improvement over previous methods. To allow for a fast analysis times a short (50 mm) column was used as well as organic modifiers in the mobile phase (20% acetonitrile). This prevented DN^- absorption on the column which has in past methods lead to peak tailing and column degradation.[6]

EXPERIMENTAL

The IC system consisted of a Waters 616 Pump with a fixed loop rheodyne injector, 431 conductivity detector, a 996 photodiode array (PDA) detector collecting from 200-350 nm, and a Millennium 2010 Workstation for control and data acquisition (Waters Corp., Milford, MA). Ammonium dinitramide (ADN) was obtained from SRI International (Menlo Park, CA). All other anion standards were prepared from their salts and were of ACS grade or better. All solvents were of HPLC grade or better. High purity water was obtained from a Milli-Q™ system (Millipore Corp., Bedford, MA). The column used was a 5 cm IC Pak-A IC column (Waters Corp., Milford, MA). The eluent was a 3.0 mM lithium hydroxide and 20% acetonitrile mix. The mobile phase was filtered and degassed prior to use with helium sparging. Samples of ADN were aged by taking solutions of known standards and placing them in 2 mL sealed vials and leaving them exposed to light for periods of 12 -24 hours.

RESULTS AND CONCLUSIONS

Figure 4 is a chromatogram of a 20 mg/L ADN sample before (figure 4a) and after (figure 4b) aging. As can be seen NO_2 and NO_3 formation occurs. These are the most common contaminants for ADN in both pure and impure samples.

Linearity of the method was evaluated by injecting duplicate injections of five different standards (8, 10, 20, 40, and 60 mg/L) and forcing the line through zero. A correlation coefficient (r^2) of 0.998 was obtained. Ion chromatography can be used for the analysis of ADN and anionic impurities in it. Little sample preparation is required and good linearity can be obtained with total run times of under 20 minutes possible. Further, detection of ADN, nitrite and nitrate anions can be done with a high degree of sensitivity and selectivity by using UV detection. Conductivity detection can be used in series with UV detection to provide sulfate and chloride analysis if needed.

ACKNOWLEDGMENTS

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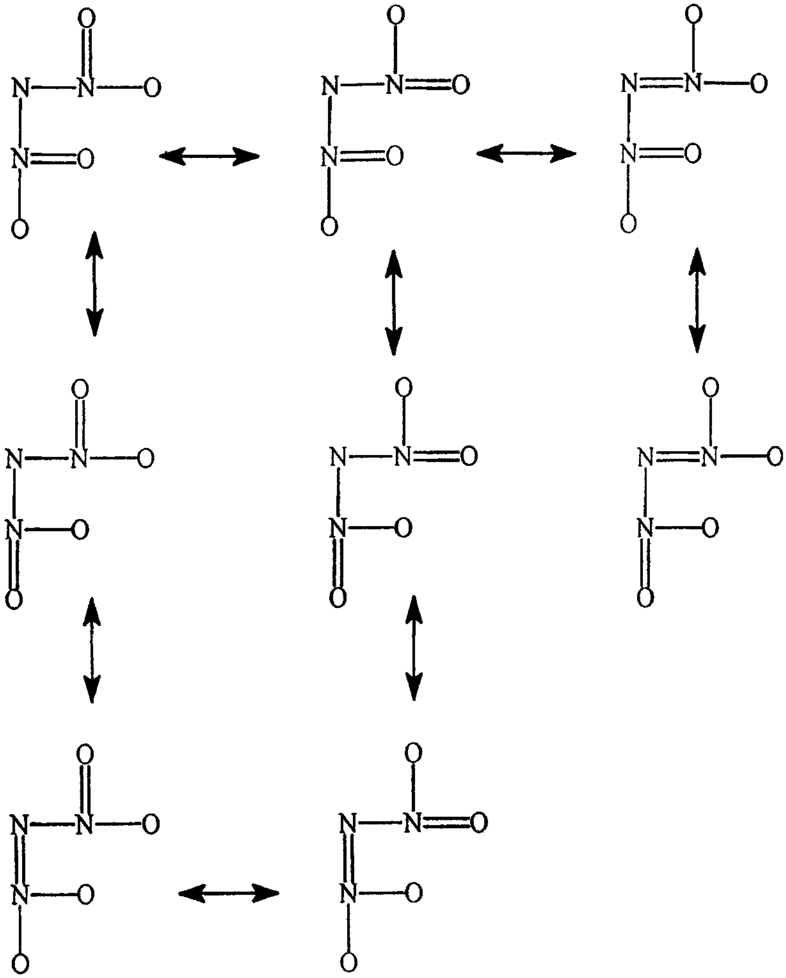
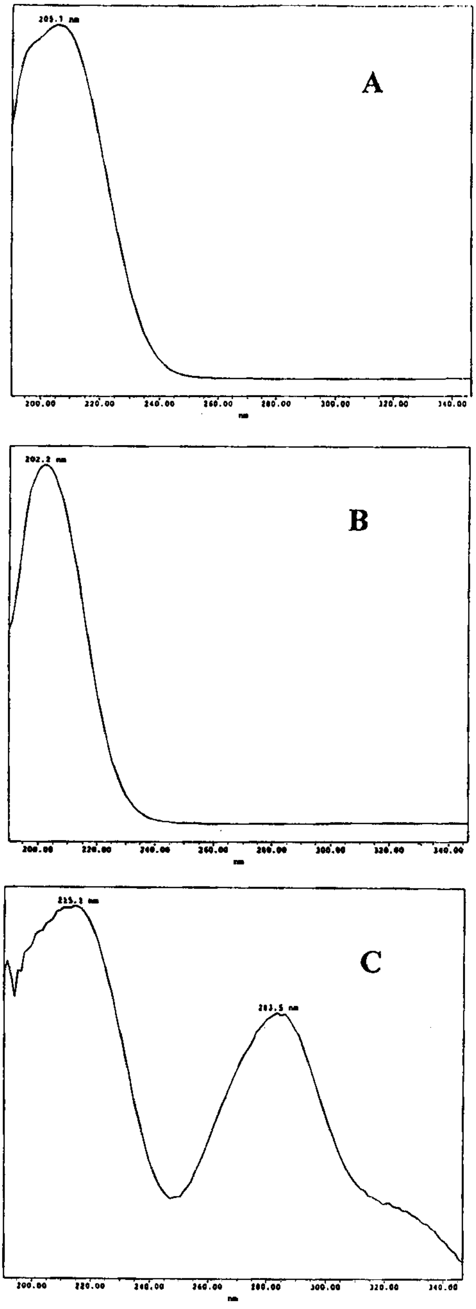


Figure 1: Various resonance states of the dinitramide anion (DN^-).



<u>Figure 2:</u> UV spectra of (A) NO_2^- ; (B) NO_3^- , and (C) DN^-.

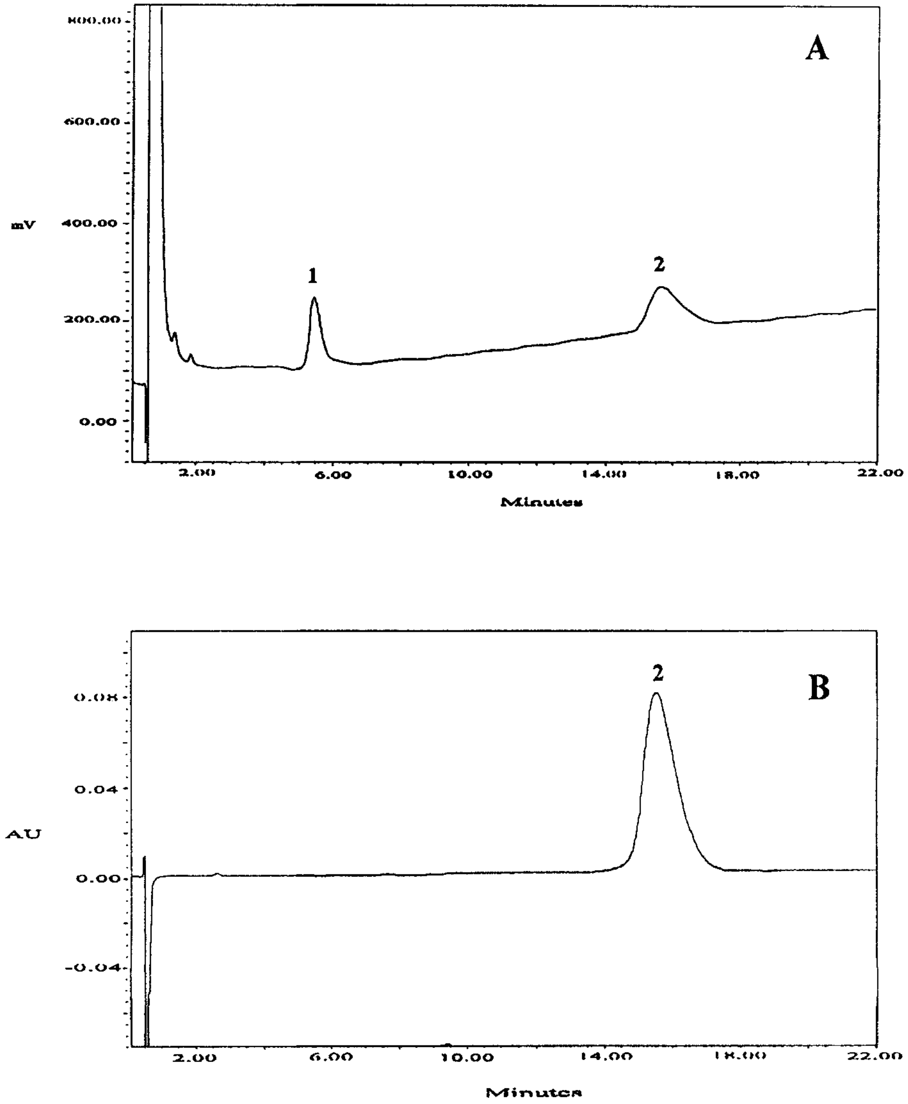


Figure 3: Chromatograms of a 20 mg/L ADN standard. **A:** Conductivity detection. **B:** UV detection at 214 nm.Peaks: **1:** SO_4^{-2}, and **2**: DN^-. Conditions as stated in experimental.

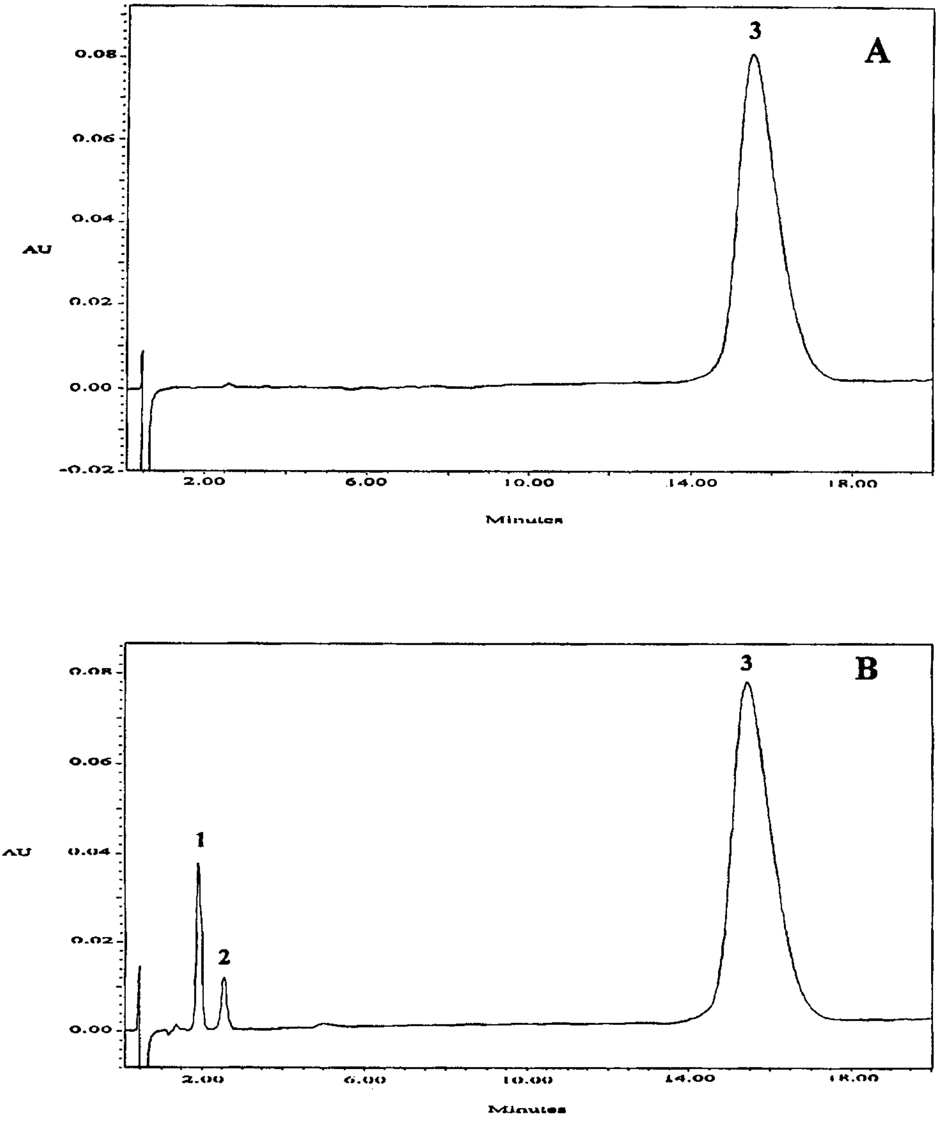


Figure 4: Chromatograms of a 20 mg/L sample before (A) and after (B) aging. UV detection at 214nm. Peaks: **1**: NO_2^-, **2**: NO_3^-, and **3**: DN^-. Conditions as stated in experimental.

Table I

Method detection limit (MDL) for anions

Anion	MDL (ng/mL) UV at 214nm	Conductivity
NO_2^-	2.8[a]	30[a]
NO_3^-	0.5[a]	30[a]
DN^-	38	261

[a] MDL values obtained from reference 7 and reverified.

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