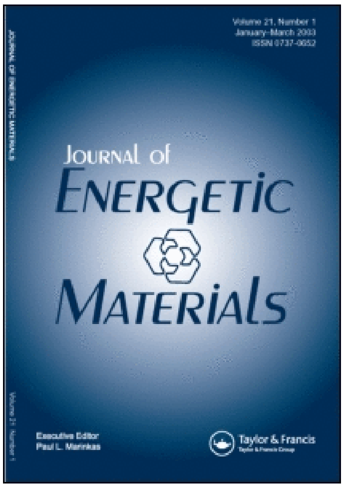

Journal of Energetic Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713770432

Analysis of anionic impurities in ammonium dinitramide (ADN), Part II: Capillary ion electrophoresis

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To cite this Article Oehrle, Stuart A.(1996) 'Analysis of anionic impurities in ammonium dinitramide (ADN), Part II: Capillary ion electrophoresis', Journal of Energetic Materials, 14: 1, 37 — 45
To link to this Article: DOI: 10.1080/07370659608216056
URL: http://dx.doi.org/10.1080/07370659608216056

Analysis of Anionic Impurities in Ammonium Dinitramide (ADN)

Part II: Capillary Ion Electrophoresis

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ABSTRACT

A method has been developed to analyze ammonium dinitrimide (ADN), a new energetic material, as well as other anionic impurities in it. This method employs capillary ion electrophoresis with UV detection. Analysis of ADN samples could be done in under 5.5 minutes employing this method. Analysis of pure samples as well as aged samples was accomplished.

INTRODUCTION

As discussed in part I of this paper[1], ammonium dinitramide (ADN), $NH_4N(NO_2)_2$, is one of several new energetic materials that have attracted attention as possible replacements for, or inclusion in, various military and space applications.[2] 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).[3-6] 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

Journal of Energetic Materials Vol. 14, 37-45 (1996)
Published in 1996 by Dowden, Brodman & Devine, Inc.

performance. ADN is also light sensitive with the anionic impurities NO_2^- and NO_3^- being the primary degradation products. One technique that was discussed earlier for monitoring these anions and the dinitramide ion (DN^-) was ion chromatography (IC). The method developed could analyze for NO_2^- and NO_3^-, the main degradation products, and DN^- in less than 20 minutes. In this paper capillary ion electrophoresis (CIE), a newer technology for the rapid analysis of ions, is used to analyze ADN and the degradation products found. Two methods, one employing indirect UV detection, and the other using direct UV detection were used. Total analysis time of less than 5.5 minutes could be achieved.

Capillary ion electrophoresis (CIE) is a capillary electrophoretic technique which has been optimized for the detection of ions. Figure 1 shows the basic components of a CIE instrument. Since most ions do not absorb UV light, detection is done by adding a UV absorbing chemical to the electrolytic buffer. As the non-absorbing ions pass by the cell the loss of absorbance is measured. The resulting data of absorbance versus time is called an electropherogram. Separation is accomplished by using a fused silica capillary and an appropriate electrolyte buffer which allows for the ions of interest to migrate. To allow for rapid analysis of anions an osmotic flow modifier (OFM) is also added to the electrolyte. This OFM reverses the normally cathodic direction of the electrosmotic flow, thus augmenting the separation and allowing for the migration of both small anions and larger anions. A high voltage (typically around 15-20 kV) is applied and the ions migrate toward the oppositely charged electrode. Sample introduction is done by raising the sample a fixed height for a short period of time. This injection technique is known as hydrostatic injection; volumes injected using this technique are typically in the low nL range. Hydrostatic injection is typically done for high ng/L (ppb) to mg/L (ppm) level analysis. Another injection technique used is called electromigration. In this technique a low voltage is applied to the sample and the ions migrate and concentrate on the head of the capillary. This technique is typically used as a preconcentration step and is applicable for low to mid ng/L (ppb) analysis.

One recent development in CIE chemistries has been the use of direct UV for the detection of anions.[7,8] This is only possible by using low UV (185nm) detection and a highly UV transparent (phosphate) electrolyte. Using this electrolyte most anions and organic acids can be separated and detected. The only notable exceptions are fluoride, sulfate, and phosphate. The mobility of this electrolyte is also less than the typical chromate (indirect UV) electrolyte thus allowing for more symmmetrical peak shapes for larger anions. A chromate (indirect detection) and phosphate (direct detection) electrolyte were investigated for use in analyzing ADN and it's degradation products.

EXPERIMENTAL

Instrumentation:

The capillary electrophoresis (CE) system employed was the Quanta™ 4000E Capillary Ion Analyzer (Waters Corporation, Milford, MA, U.S.A.). A Hg lamp was used for either indirect or direct UV detection at 254nm and 185nm. AccuSep™ polyimide fused silica capillaries of dimension 75um I.D. X 60cm were used throughout. Data acquisition and CIE control was carried out with a Waters Millennium™ 2010 Chromatography Manager with a SAT/IN module connecting the CIE to the data station with the signal polarity inverted from the CIE.

Preparation of electrolytes:

The chromate electrolyte used for indirect UV detection was prepared from a concentrate containing 100 mM sodium chromate tetrahydrate (Fisher Scientific, Pittsburgh, PA, U.S.A.) and 0.0056 mM sulfuric acid (J.T. Baker, Phillipsburg, NJ, U.S.A.; Ultrex Grade). Osmotic flow modifier (OFM) for reversal of the direction of the electroosmotic flow (EOF) was a 20 mM concentrate (CIA-Pak OFM anion BT) obtained from Waters. The working electrolyte for indirect anion analysis consisted of 4.0 mM Chromate-0.3 mM OFM. The electrolyte used for direct UV detection consisted of 25 mM Phosphate-0.5 mM OFM All working electrolytes were prepared fresh daily and degassed prior to use. CIA methods are covered under U.S. Patents 5,104,506, 5,128,055 and 5,156,724.

Chemicals:

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. Phosphate electrolyte packets were obtained from Waters. High purity water was obtained from a Milli-Q™ system (Millipore Corp., Bedford, MA). 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

Indirect UV detection employing the chromate electrolyte was first investigated. Figure 2 shows an electropherogram of the separation achieved for a sample of ADN which had been aged. As can be seen ADN has a negative peak due to it's strong UV absorbance at 254nm. This tends to make quantitation of ADN challenging if it was needed. Also the high tailing of the DN^- is indicative of a mismatch between the mobility of the electrolye and analyte; for this reason the phosphate electrolyte was used.

Using the phosphate electrolyte a reasonable separation of ADN and the main degradation products could be achieved. This is shown in figure 3 which is an electropherogram of a 20.0 mg/L ADN sample before (figure 3a) and after (figure 3b) aging. The formation of the NO_2^- and NO_3^- peaks are clearly evident.

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 0.9995 was obtained. Capillary ion electrophoresis 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 6 minutes possible.

ACKNOWLEDGMENTS

The author acknowledges Dr. Robert J. Schmitt of SRI for his valuable assistance and helpful discussions related to this work.

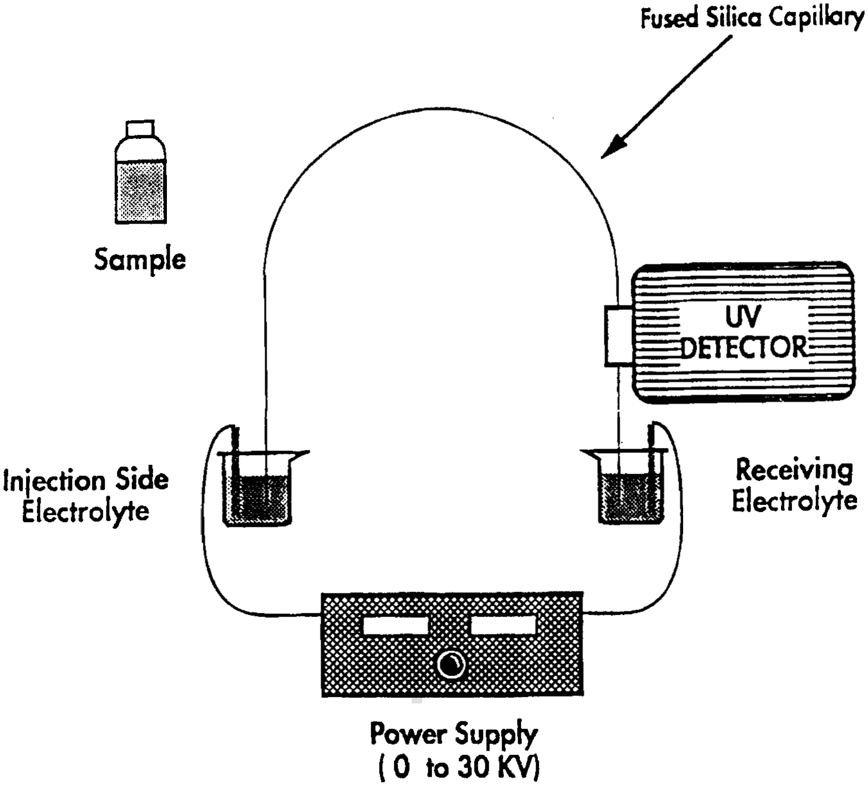

Figure 1: Basic diagram of a capillary electrophoresis system.

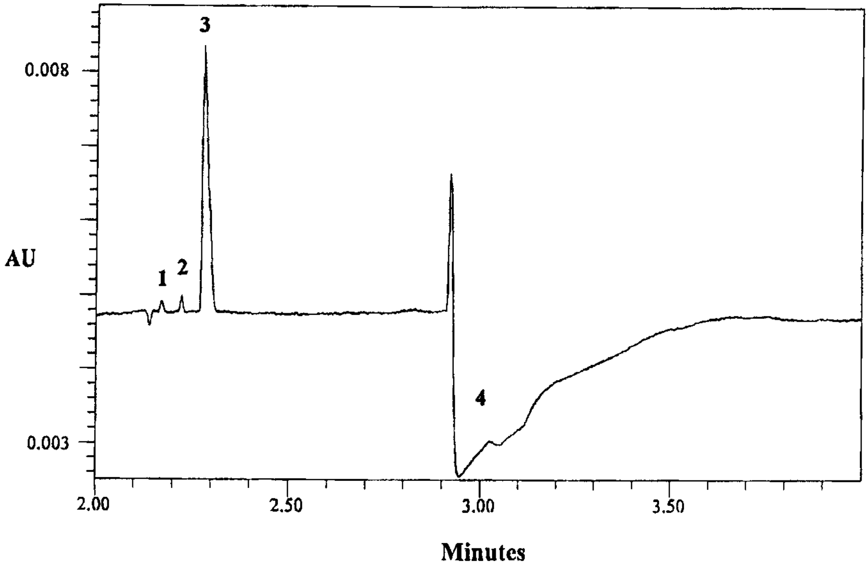

Figure 2: Electropherogram of a sample of an aged ADN sample analyzed using indirect UV detection. Experimental conditions: Fused-silica capillary; 60cm X 75um I.D. voltage 15kV (negative); 4.0 mM chromate-0.3 mM CIA-Pak OFM Anion (patented); indirect UV detection at 254nm; Hydrostatic Injection (9.8 cm for 30 seconds). Peaks: 1=chloride; 2=sulfate; 3=nitrate; 4=dinitramide (DN^-)

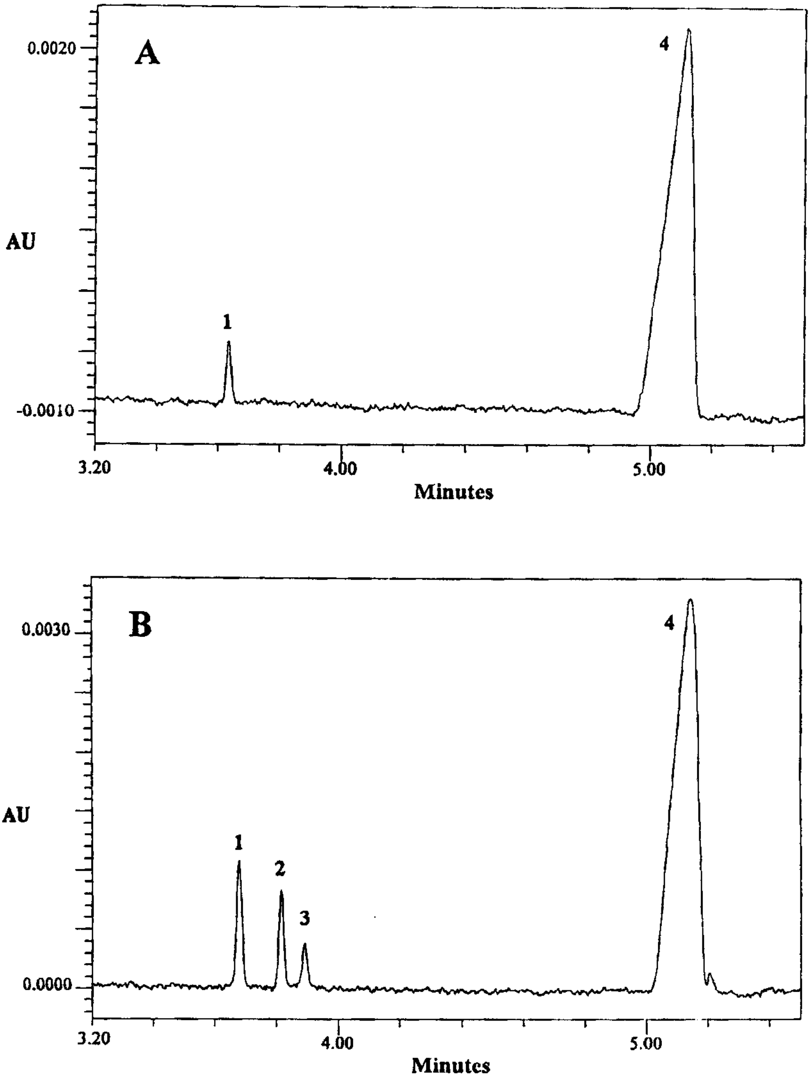

Figure 3: Electropherogram of a 20 mg/L sample of ADN analyzed before (figure 3a) and after aging (figure 2b) using direct UV detection. Experimental conditions: Fused-silica capillary; 60cm X 75um I.D. voltage 15kV (negative); 25 mM phosphate-0.5 mM CIA-Pak OFM Anion (patented); direct UV detection at 185nm; Hydrostatic Injection (9.8 cm for 30 seconds). Peaks: 1=chloride; 2=nitrite; 3=nitrate; 4=dinitramide (DN^-)

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