

Synthesis, characterization and purity determination of ammonium dinitramide (ADN) and its precursors

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Abstract

Dinitramidic acid (DNA) and its salts are recently the most studied nitramine compounds. The present work describes the synthesis, characterization and purity determination of ammonium dinitramide (ADN) and its precursors such as guanylurea dinitramide (GUDN) and potassium dinitramide (KDN). The synthesized ADN and its precursors were characterized using ultra violet Visible, Fourier transform-infra red (FTIR) spectroscopy and thermal techniques such as differential scanning calorimetry (DSC). The performance of ADN as an oxidizer in propellant compositions mainly depends on its purity. The presence of undesired impurities would be detrimental to its performance. Further, the overall yield of the product depends on the purity of the precursors. Hence, it becomes essential to analyze both the precursors and the final product using a suitable analytical technique prior to its application in propellant compositions. The reported method only analyzed the ion involved in ADN synthesis. In present study we have analyzed ions involved in GUDN, KDN and ADN using suitable ion chromatographic method for the direct analysis of anions and cations involved. The synthesized compounds have been subsequently characterized using atomic absorption spectrometry (AAS) to estimate their purity.

Keywords : ammonium dinitramide, guanylurea dinitramide, potassium dinitramide, purity estimation, ion chromatography.

1. Introduction :

The use of powerful, safer and ecofriendly explosives is the main criteria of ammunitions during propellant formulations. To meet the requirement there is always need of energetic compositions with low sensitivity, which should provide safety to ammunitions¹. Ammonium dinitramide (ADN) is a high performance solid oxidizer with positive oxygen balance than that of ammonium nitrate (AN)². ADN is a possible replacement for ammonium perchlorate (AP) in composite propellants^{3,4}. Guanylurea dinitramide (GUDN) is one the important precursor for the synthesis of ADN via potassium dinitramide (KDN).

GUDN is a white crystalline solid and is stable salt of dinitramidic acid with good thermal stability, low water solubility and non hygrscopic⁵. GUDN is low vulnerable energetic material to impact and friction stimuli and is a

good candidate for insensitive munitions⁶. Its thermal stability is comparable to cyclotrimethylene nitramine (RDX) and superior to that of ADN^{7,8}. GUDN can find applications in low vulnerable ammunitions (LOVA) propellants⁹; melt cast and plastic bonded explosives (PBX) high explosives formulations¹⁰⁻¹². Besides the advantage of low sensitivity, GUDN burns with an extremely low temperature, which is important in automatic guns where barrel erosion often is a problem. The synthesis of GUDN involves the nitration of ammonium salt of sulphamic acid with conc. HNO₃/H₂SO₄ at -20°C to -50°C with further treatment of aqueous suspension of guanylurea sulfate. KDN was prepared by the reaction of GUDN with alcoholic KOH. ADN was synthesized using KDN with the treatment of ammonium sulphate with isopropanol.

Ion chromatography is one of the important analytical

technique useful for the analysis of cations and anions from a particular compound. Atomic absorption spectrometry (AAS) is also a vital analytical tool often used for the determination of percentage of ions involved in the compounds. The objective of this work was to develop a suitable ion chromatographic method for the direct analysis of the anions involved in energetic dinitramides. Different ion exchanger phases were tested with organic ADN or inorganic eluants.

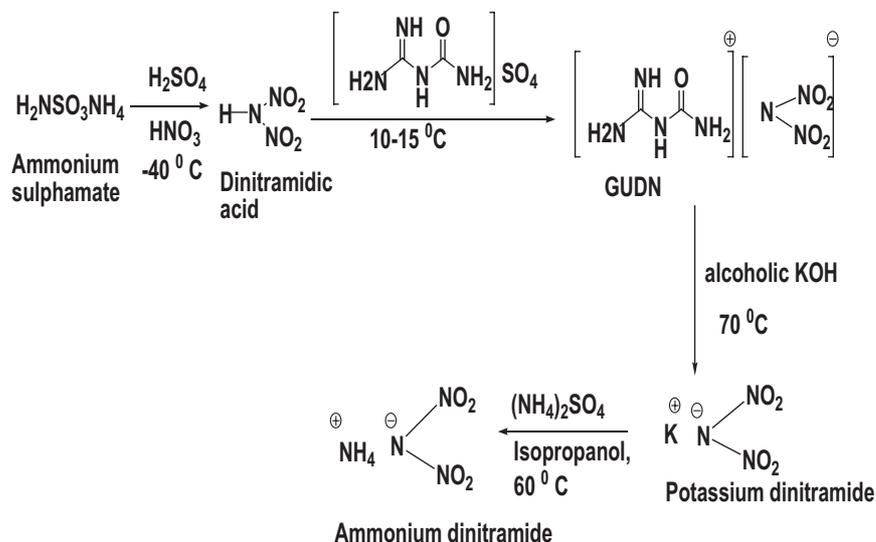
The reported method for the synthesis of energetic dinitramides (GUDN, KDN and ADN) involves the separate and different starting compounds. These methods were not specified and operational since the yield was very low for ADN. In order to overcome the limitations of the reported methods for ADN synthesis, in present study we report the synthesis of ADN via GUDN and KDN, starting from ammonium sulphamate as a starting compound. The same method is noteworthy in new of its safety, simplicity of execution of the process, and the use of commercial nitrating mixtures yielding in low yield of ADN, which makes the process quite expensive.

In present study the yield of ADN via GUDN and further KDN is appreciable and at the same time, the method is amenable to scale up. The literature says that, the dinitramides were characterized by UV, IR and DSC, but these techniques have their own limitations since they are not able to confer the quantitative information about the purity of GUDN, KDN and ADN. The evaluation of dinitramide ions is carried out by measuring the UV absorption of dinitramide ions at 285 nm. In presence of large quantities of nitrate ions, e.g.: during the estimation of dinitramide ions in a nitrating mixture, UV spectroscopy cannot be used accurately due to interference from the broad absorption band of nitrate ions from 220 nm to 320 nm. The purity determination of ADN by DSC, based on the measurement of enthalpy of melting of ADN at 93 °C, can be applied only with good reliability for samples containing more than 98% of ADN.

The reported method studied the ion chromatographic analysis of ADN only containing NH_4^+ ions since they have accounted the synthesis of ADN from ammonium sulphamate. In present study the synthesis of ADN was carried out from via GUDN and KDN. We report herein the IC analysis of each ions involved during synthesis of ADN, KDN and GUDN. The reported method only explained the IC analysis of ion involved in ADN not GUDN and KDN. These techniques do not quantify the percent purity of the ADN.

2. Experimental materials.

All the chemicals used were of analytical reagent grade (AR). GUDN was synthesized in-house by the nitration of



Scheme 1 Synthesis of ADN from GUDN.

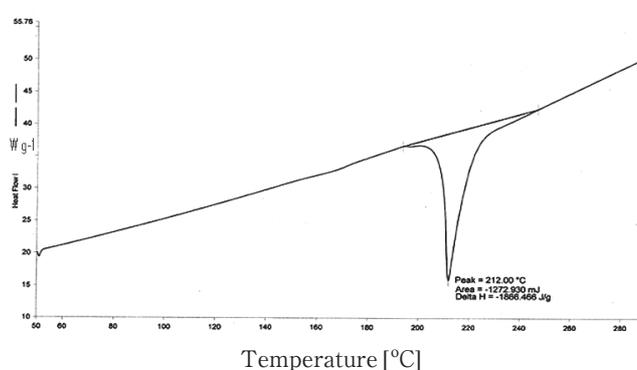


Figure 1 DSC curve of GUDN.

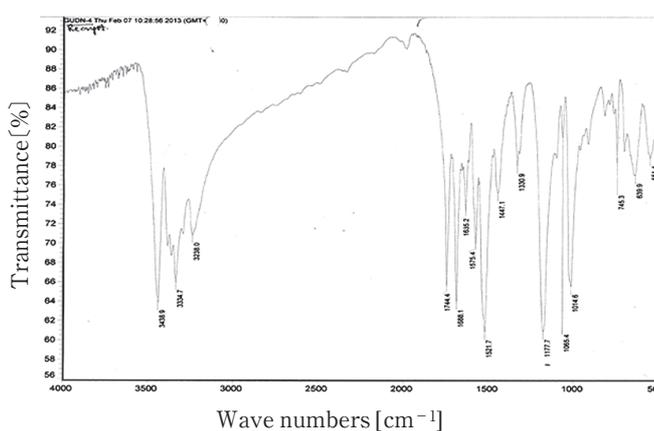
ammonium sulphamate at -40 °C the precursor guanylurea suplahte was synthesized from dicyandiamide with treatment with aqueous H_2SO_4 . KDN was prepared from the treatment of alcoholic KOH in ethanol and ADN was prepared from KDN by further cation exchange reaction with ammonium sulphamate in isopropanol. The thermal study was carried out using a differential scanning calorimeter (Perkin Elmer DSC-7). A sample weight of about 0.5 mg was taken for heating at $5^\circ\text{C}\cdot\text{min}^{-1}$ in the temperature range 50-350 °C for the determination of the decomposition temperature/exothermicity.

UV spectrum of GUDN was recorded using water as solvent in the range of 200 - 400 nm using quartz cell. The absorption spectrum was obtained as a plot of the intensity of the transmitted or absorbed light versus wavelength. Absorption maximum (λ_{max}) was obtained from the spectrum. UV spectrum of the sample was recorded in water solution. GUDN shows UV maximum in water at 222 nm and 283 nm. The absorbance at 283 nm is the characteristic of the $(-\text{NNO}_2)^-$ ion caused by low energy $n-\pi^*$ transitions¹³ while, the absorption maximum at 222 nm is attributed to high energy $\sigma-\sigma^*$ transition. Thermal analysis of GUDN was carried out by using DSC with open Al pan. The DSC of GUDN shows a sharp exothermic peak appearing at 212.12 °C.

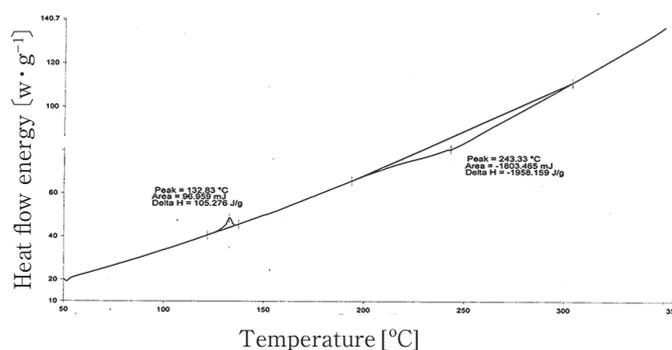
The AAS measurement was carried out on Analyst 800 Perkin Elmer. The standard solution of K for Merck

Table 1 Characterization data of GUDN, KDN and ADN. The characterization of these compounds was carried out by using UV, IR and DSC.

Method of characterisation	GUDN	KDN	ADN	Remark
UV (λ_{\max} , nm)	223 & 283	—	—	The evaluation of dinitramide ions is carried out by measuring the UV absorption of dinitramide ions at 285 nm. In presence of large quantities of nitrate ions, e.g.: during the estimation of dinitramide ions in a nitrating mixture, UV spectroscopy cannot be used accurately due to interference from the broad absorption band of nitrate ions from 220 nm to 320 nm.
IR (cm^{-1})	3441, 3335, 3237 (NH ₄ ⁺), 1524, 1329, 1179, 814, 745 (NO ₂) & =N-N=N= 1019, 915	1524, 1329, 1179, 814, 745 (NO ₂) & =N-N=N= 1019, 915	1524, 1329, 1179, 814, 745 (NO ₂) & =N-N=N= 1019, 915	The absence of absorption band at 3237, 3335 in KDN indicates the formation of KDN and complete conversion of GUDN to KDN.
DSC (°C)	Exo (Peak) : 214 °C	Endo (onset) : 131–135 °C	Endo (Peak) : 91, 184.67, 250.74 (Lit.= 92 °C)	The purity determination of ADN by DSC, based on the measurement of enthalpy of melting of ADN at 93 °C, can be applied only with good reliability for samples containing more than 98% of ADN.
AAS results	—	K ⁺ Ion Expected 27 %, Observed 28 %,		In addition to Ion chromatographic analysis and thermal characterisation, AAS results helped in determination of the percentage of K ⁺ ions in KDN.

**Figure 2** IR spectrum of GUDN.

having concentration of 1000 ppm was appropriately diluted to obtain solution having concentration of 350 ppm. This standard solution was aspirated into the flame and the absorbance is recorded. The flow rate for the fuel and oxidant was 2.0 L·min⁻¹ and 17.0 L·min⁻¹ respectively. The analyte sample was aspirated into the flame and the absorbance was recorded and from the calibration curve, the concentration of K in the solution was completed.

**Figure 3** DSC curve of KDN.

3. Results and discussion

3.1 Atomic absorption spectrometric analysis

The quantitative estimation of potassium using IC has already been described earlier. 0.1 % of CsCl was added to both standard and sample solution to avoid ionization interference. The Cs ions undergo ionization in preference to potassium ions due to lower ionization potential of Cs, which enhance the absorbance of potassium ions and thus generate realistic results. Atomic absorption spectrometry is useful for the selective estimation of alkali metals, alkaline earth metals and 3d elements. The confirmation of

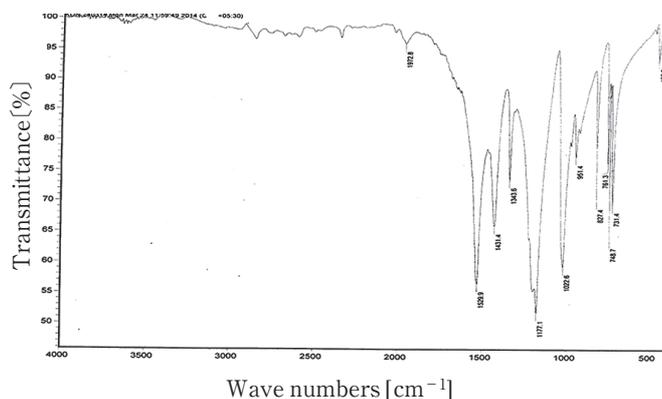


Figure 4 IR spectrum of KDN.

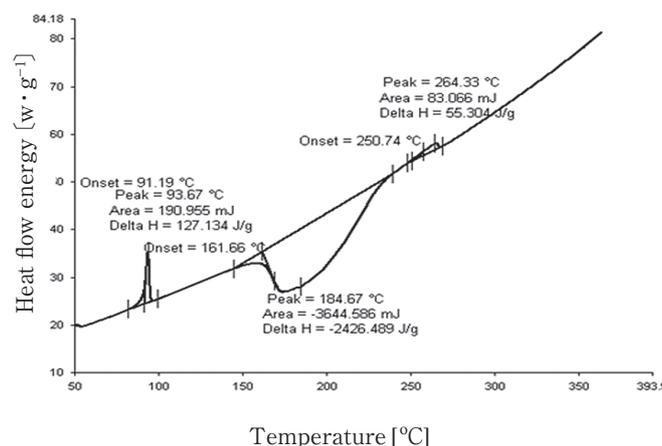


Figure 5 DSC curve of ADN.

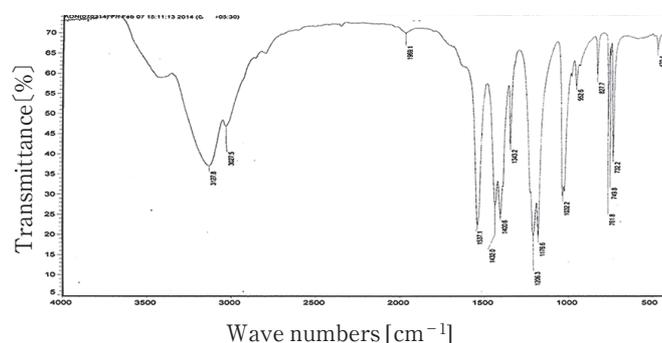


Figure 6 IR spectrum of ADN.

the purity of KDN is important since it affects the yield and the purity of the end product i.e. ADN. Hence, atomic absorption spectrometric analysis has also been employed to confirm the purity of KDN. The potassium content as estimated by AAS is in close agreement with that obtained by IC analysis which confirms the high purity of KDN for its conversion to ADN.

3.2 Ion chromatographic analysis

The Guanylurea cation shows a retention time (Rt) of 7.9 minutes, whereas, the dinitramide (DN^-) ion shows Rt = 3.14 minutes. Figure 7 (a) and 7 (b) shows the ion chromatogram of synthesized GUDN and standard GUDN sample for cation and anion respectively. The Rt of both cation and anion are in agreement with those of the standard GUDN. The Ion chromatogram of synthesized GUDN does not show the presence of any other ions which

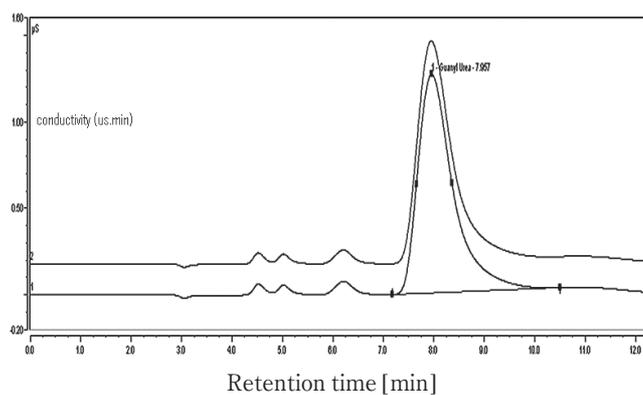


Figure 7 (a) Ion chromatogram of cation for GUDN.

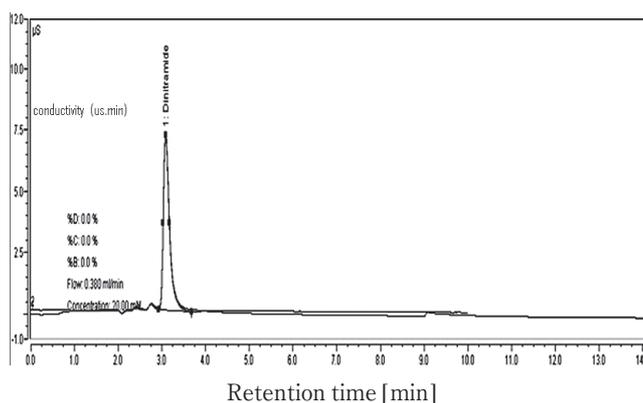


Figure 7 (b) Ion chromatogram of an anion for GUDN.

supports the high purity of GUDN. Hence, the synthesized GUDN is useful for its conversion to KDN. However, the quantification of both guanylurea cation and DN^- ion could not be carried out since the compounds have known concentrations of guanylurea cation and DN^- anion is not commercially available. Hence, the synthesized and fully characterized GUDN is assumed as standard for future analysis of GUDN. Figure 8 (a) shows the cation in KDN and while 8 (b) shows the ion chromatogram of dinitramide ion in standard sample. These ions show Rt of 6 and 5 minute respectively. Figure 9 (a) and 9 (b) show ion chromatogram of ADN. The K^+ and DN^- ions in KDN show Rt of 6 and 3.1 minute which indicates the presence of both the ions. The chromatogram does not show the presence of guanylurea cation present in GUDN which indicates the complete conversion of GUDN to KDN. Figure 9 (a) and 9 (b) shows the ion chromatogram of cations and anions in KDN respectively which shows the presence of NH_4 ions (Rt = 5 minute) and it do not show the presence of potassium ions which indicates the complete conversion of KDN to ADN.

Further, the quantification of ammonium and potassium ions is also carried out. The standard solutions of ammonium and potassium have concentration of 5 ppm each are injected. The resulting ion chromatogram shows well defined peaks. The area under the curve is the function of their concentration from which a calibration curve is generated. Similarly, the diluted solutions of KDN and ADN are injected which directly gives the concentration in terms of parts per million (ppm) from the calibration curve. The result indicates that the percentage

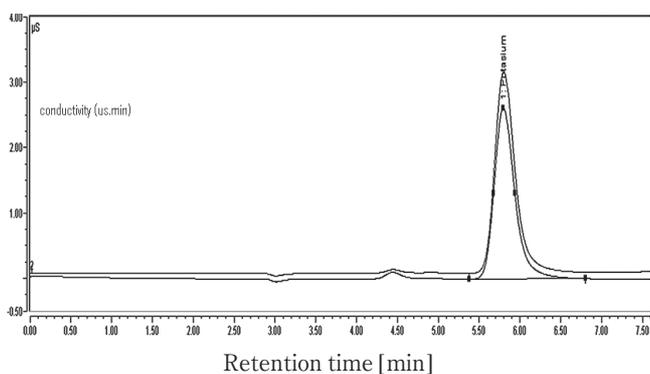


Figure 8(a) Ion chromatogram of cation for KDN.

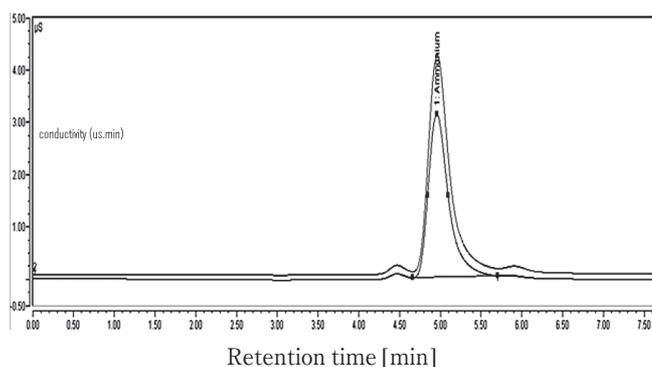


Figure 9(a) Ion chromatogram of cation for ADN.

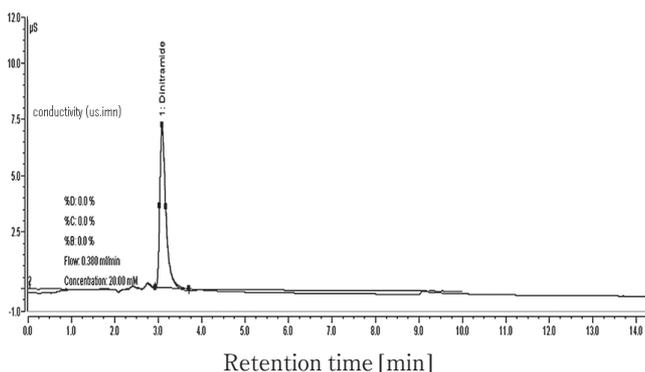


Figure 8(b) Ion chromatogram of an anion for KDN.

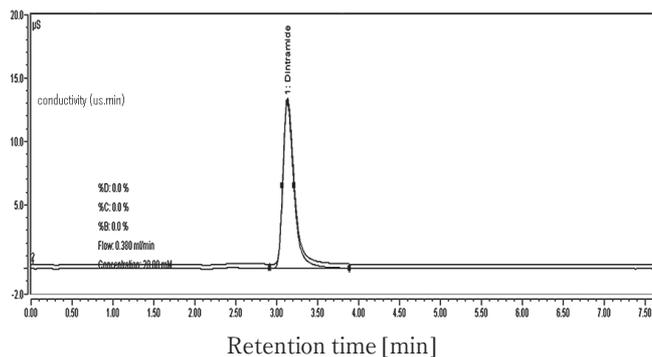


Figure 9(b) Ion chromatogram of an anion for ADN.

of these ions is in close agreement with the theoretical values i.e. 14.5% and 27% respectively. The retention time of DN⁻ ions in KDN and ADN is identical to that in standard GUDN which shows that the DN⁻ entity remains unaffected as desired during the synthetic conversion of GUDN to KDN and subsequently to ADN.

3.3 Purity determination of ammonium dinitramide (ADN)

The percentage of ammonium nitrate (AN) present in the ammonium dinitramide (ADN) sample was determined by the amount of ammonium nitrate present in the sample which was subtracted from assuming that 100% of ADN for different batches. So, we have determined the different percentage of AN present in ADN. In general, the amount of AN present in ADN was up to 0.5-1.5%. Therefore the purity of the ADN was up to 98.5%.

3.4 Purity Determination by Ion chromatography (IC) and atomic absorption spectrometry (AAS)

The performance of ADN as an oxidizer in propellant compositions mainly depends on its authenticity/purity. The presence of undesired impurities would be detrimental to its performance. Further, the overall yield of the product depends on the purity of the precursors. Hence, it becomes essential to analyze both the precursors and the final product using a suitable analytical technique prior to its application in propellant compositions^{13, 14}. The analytical technique should be suitable for qualitative and quantitative analysis. ADN and its precursors are

ionizable into their respective cations and anions in aqueous medium and exhibit electrical conductivity which is a function of their concentration in the analyte. The retention time (Rt) of the ions is a clear signature of their existence which helps in qualitative analysis.

In the present work the analysis of dinitramide ion is very important moiety since the anionic counterpart plays a major role in imparting the explosive properties to an oxidizer. UV spectroscopy and thermal analysis have been employed previously for this purpose but their applications are limited. On the other hand, Ion chromatography is a suitable choice which offers both qualitative as well as quantitative estimates of anions and cations even at ppb level. Hence we have employed Ion chromatography for the analysis of ADN and its precursors.

The IC system (Model No. ICS 3000) used is from Dionex (I) Pvt. Ltd. This system uses a suppressor viz. ASRS 300 (2mm) and CSRS 300 (2mm) for anion and cations respectively. The suppressor reduces the ground conductivity of the eluent ions chemically by using deionized water as regenerant yielding a greater usable detection range which is desired. The IC system used is equipped with a dual pump with parallel IC columns namely AS11 HC for anions and CS12A for cations.

Electrical conductivity detector (ECD) is employed to measure the conductivity of the ions eluted which is the measure of their concentration. The eluent used is 20 mM potassium hydroxide (KOH) and 20 mM methane sulphonic acid for anions and cations respectively and the flow rate was optimized at 0.38 mL·min⁻¹ for Anions and 0.25 mL·min⁻¹ for cations to obtain moderate retention and

sharp response. Sodium hydroxide has also been used previously as a eluent in place of KOH. However, the former exhibit very high elution time and require higher flow rates as compared to those required for the latter. This is attributed to higher basicity of KOH in comparison to NaOH. Hence, KOH was used in place of NaOH which eventually saves time and the quantity of eluent. The standard solutions of ammonium and potassium ions both have concentration of 5 ppm. Such low concentrations of the standard solution are advisable to obtain high degree of precision in the measurements. The standard solutions of ammonium and potassium were injected respectively for ADN and KDN analysis and their electrical conductivity is recorded. The entire process of injection and data acquisition is controlled by CHROMELEON software. Similarly, the aqueous solutions of KDN and ADN appropriately diluted were injected and their conductivity is recorded from which their concentration in percentage is computed using the calibration curve.

The applications of KDN in pyrotechnic compositions are well known. The performance of KDN as an oxidizer can be realized only after its analysis for its purity. Therefore we have also employed Atomic Absorption Spectrometry along with IC for the confirmation of the purity of KDN. In AAS, the analyte ions are converted to atomic state due to high temperature of the flame. The atoms are excited to higher energy state by absorption of electromagnetic radiation from a hollow cathode lamp which emits radiation of a specific wavelength. The excited atoms get deexcited to ground state by emitting energy in the form of radiation which is detected. The absorbance is the function of the concentration of the analyte atoms according to Lambert's law. In the present work the potassium content in KDN have been estimated quantitatively using 769.9 nm line which is best suitable and the results are compared with those of IC. The standard solutions of ammonium and potassium of 1000 ppm concentration from Merck (I) Pvt. Ltd. have been used for analysis. These standards were diluted appropriately as per the requirement. The standard solution of potassium (4 ppm) is aspirated in the flame and the absorbance is recorded. Further, the aqueous solution of KDN is aspirated in the flame and similarly the absorbance is recorded from which the concentration of potassium ions in KDN is computed. Previously analyzed and authenticated GUDN was used as standard for comparison of IC chromatograms with those of synthesized GUDN.

4. Conclusion

The present work describes the synthesis, characterization and purity determination of ADN and its precursors such as GUDN and KDN. The synthesized ADN and its precursors were characterized using UV, FTIR and thermal techniques such as DSC. Ion

chromatography and atomic absorption spectrometry were also used to estimate their purity. The paper describes the suitable ion chromatographic method for the direct analysis of anions and cations involved in energetic dinitramides. The reported method for the synthesis of energetic dinitramides involves the separate and different starting compound. These methods were not amenable to scale up further synthesis of ADN. These methods were not specified and operational since the yield of ADN is not appreciable. In order to overcome the limitations of the reported method, in present study we have attempted the synthesis of ADN using GUDN as a starting compound. The synthesis of GUDN has been carried out using nitration of ammonium sulphamate at -40°C . Ammonium sulphamate is the starting material in reported method for ADN synthesis but this resulted in low yield of the product.

In present study, the yield of ADN via GUDN and further synthesis of KDN is appreciable and at the same time the proposed method is amenable to scale up. The literature says that the dinitramide was characterized by using UV, IR, and DSC. These technique does not quantify the percent purity of the ADN. We have established a suitable ion chromatographic method to estimate the purity of each ions involved during synthesis of ADN, KDN and GUDN.

References

- 1) D. M. Badgujar, M. B. Talawar, S. N. Asthana, P. P. Mahulikar, *J. Haz. Mat.*, 151, 289–305 (2008).
- 2) J. C. Bottaro, R. J. Schmitt, P. E. Penwell, D. S. Ross, *PCT Int. Appl. WO 91/19669*; *US Appl. 540020*; *C.A.*, 116: 217513 (1991).
- 3) A. Langlet, Guanylurea dinitramide an explosive, propellant rocket motor charge and gas generator, *US patent, US*, 6, 291, 711, B2, (2001).
- 4) G. da Silva, S. C. Rufino, K. Iha, *J. Aerosp. Technol. Manag.*, 5 (2), 139–144 (2013).
- 5) H R Blomquist, Gas generating compositions comprising Guanylurea dinitramide, *US Patent*, 6,117, 255 (2000).
- 6) J. C. Bottaro, *Chem. Ind.* 10, 249–252 (1996).
- 7) H. Matsunaga, S. Yoshino, M. Kumasaki, H. Habu, A. Miyake, *Sci. Tech. Energetic Materials*, 72, 131–135 (2011).
- 8) Y. Sugie A. Miyake, *Sci. Tech. Energetic Materials*, 76, 57–61 (2015).
- 9) J. C. Bottaro, R. J. Schmitt, P. Penwell, S. Ross, *U. S. Patent 5254324*, 1993, SRI International, USA (1993).
- 10) H. Ostmark, U. Bemm, H. Bergman, A. Langlet, *Thermochim. Acta.*, 384, 253–259 (2002).
- 11) F. Zhao, P. Chen, H. Yuan, S. Gao, R. Hu., *Chinese Journal of Chemistry*, 22, 136–141 (2004).
- 12) A. Langlet, H. Ostmark, N. Wingborg, *U. S. Patent 5976 483*, (1999), Forsvarets Forskningsanstalt, Sweden.
- 13) G. Bunte, H. Neumann, J. Antes, and H. H. Krause, *Prop. Explos. Pyrotech.*, 27, 119–124 (2002).
- 14) S. A. Oehrle, *J. Energ. Mat.*, 14, 27–36 (1996).