Decomposition Studies: Solid and Liquid Phase Decomposition of ADN

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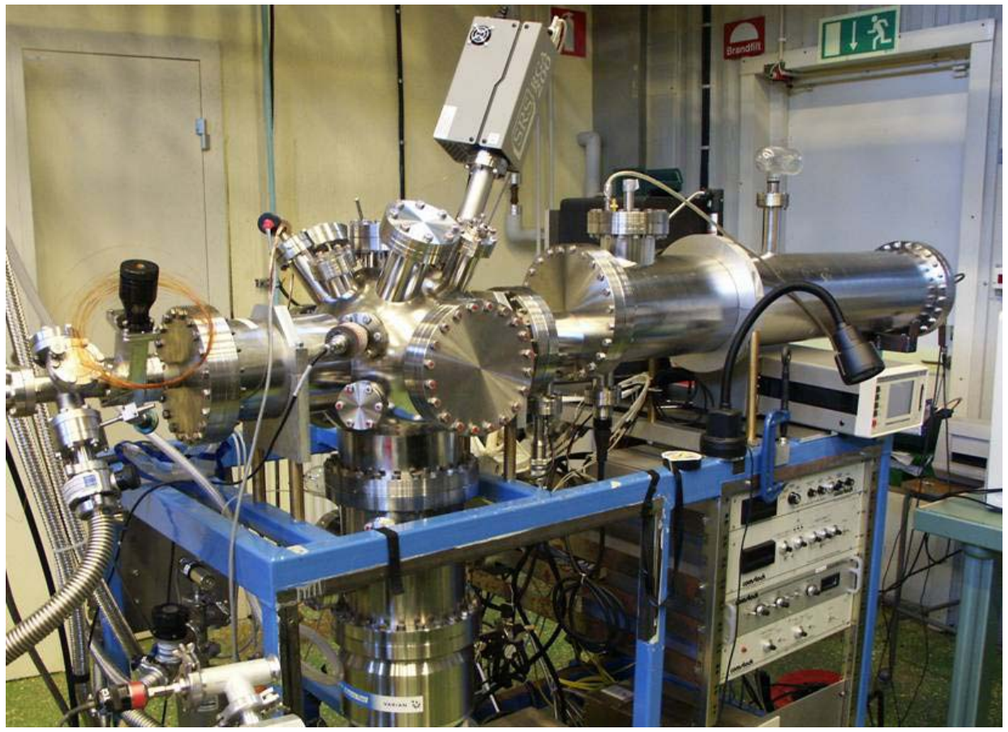

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Abstract
This report presents the results from the mass spectrometric studies of ADN moderate temperature decomposition. A decomposition mechanism for the anomalous 60-65ºC decomposition is proposed based on the experimental observations. Also presented are studies of ADN decomposition in the melt (100ºC), for two different batches of neat ADN, MgO stabilized neat ADN and prilled ADN.

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Sönderfallsstudier: ADNs sönderfall i fast och flytande fas

Sammanfattning
Denna rapport presenterar resultaten från masspektrometriska studier av ADNs sönderfall vid medelhöga temperaturer. En sönderfallsmekanism för det anomala sönderfallet vid 60-65ºC föreslås utifrån de experimentella observationerna. Även resultat från en studie rörande smält ADN (100ºC) presenteras, studien innefattar ADN från två olika batcher, ADN stabiliserad med MgO samt prillad ADN.

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Sammanfattning

Ammoniumdinitramid, ADN, är ett energetiskt salt som har stor potential inom områden som framdrivning, pyroteknik och explosivämnen. Beståndsdelarna utgörs av väte, syre och kväve som bildar rena, icke-korrosiva och osynliga gaser vid användandet. Fördelarna är bl a lägre flygsignatur för missiler, mindre risk för upptäckt av avfyrningsposition och större säkerhet för manskap.

Den här rapporten är en uppföljning på den tidigare påbörjade masspektrometriska studien om ADNs sönderfallsmekanismer i fastfas, ”Decomposition Studies - New Methods Applied on ADN and RDX”. Särskilt intresse har fästs vid den s k anomalin, dvs det sönderfall som förekommer hos mycket torrt ADN vid 60-65ºC. Det är viktigt att förstå den kemiska mekanism som ligger bakom sönderfallet eftersom det aktuella temperaturintervallet ligger nära operativa temperaturförhållanden.

De data som erhållits visar på att sönderfallsmekanismen vid 60-65ºC är en direkt omvandling av ammoniumdinitramid till mer stabilt ammoniumnitrat och icke-reaktiv lustgas (N_2O) enligt:

$$NH_4N(NO_2)_2\ (s) \rightarrow N_2O(g) + NH_4\ NO_3\ (s)$$

Reaktionen är dessutom avklingande och omfattar endast en delmängd av ADN-provet. Tillsammans gör detta att det anomala sönderfallet inte utgör någon säkerhetsrisk då det används i verkliga applikationer. Vissa problem med gasbildning och därpå följande sprickbildning kan möjligen uppstå. Tilläggas i sammanhanget bör att det anomala sönderfallet observeras enbart för finkristallint och mycket torrt ADN.

Sönderfallsmekanismer för ADN i smält form har också studerats, både vid konstant temperatur av 100ºC och i form av en temperaturstegning. I det senare fallet höjdes temperaturen med 5ºC var 20:e minut. Resultaten tyder på att en reaktionsväg är densamma som den som förekommer vid lägre temperatur, dvs det direkta sönderfallet till ammoniumnitrat och N_2O. Utöver denna existerar åtminstone ytterligare en mekanism som ger upphov till produkter som vatten (H_2O), kvävgas (N_2) och kvävedioxid (NO_2). För att komma vidare med den senare mekansimen behövs sannolikt kompletterande studier med andra metoder.

De ADN-prov som studerats uppvisar alla rester av isopropanol. Detta är inte helt överraskande eftersom isopropanol ofta används i produktionen av ADN. Vid en approximativ jämförelse av isopropanolinnehållet mellan den vid 65ºC stabilare batchen F1010 och NSA001 7034 befanns den senare innehålla större mängd isopropanol. Detta utgör inte något bevis för isopropanols inverkan

på anomaliskt sönderfall, men det möjliggör heller inte ett direkt avfärdande. Eftersom isopropanolinnehåll i ADN inte tidigare har rapporterats eller undersökts i detta sammanhang är det önskvärt att utifrån fortsatta studier säkerställa att någon påverkan inte finns.

ADN prillad med sprayteknik studerades också i vätskefas. Prillad ADN innehöll endast mycket små mängder isopropanol. Detta var ett förväntat resultat, eftersom prills framställs från ADN i smälta, och isopropanols kokpunkt ligger under ADNs smältpunkt. Prillad ADN uppvisade också ett fördröjt sönderfallsförlopp jämfört med finkritsallint ADN. Hur stabilt prillat ADN är vid temperaturer associerade med anomalt sönderfall är ännu inte utrett.

Det är allmänt vedertaget att ADN bör stabiliseras vid smältgjutning för att undvika långsamt sönderfall. Magnesiumoxid (MgO) har testats som stabilisator för ADN med gott resultat. Vid en mikrokalorimetriupptagning vid 95ºC fanns ADN stabiliserat med 1% MgO ge en tydlig fördröjning av sönderfallet. Analys av sönderfallsprodukterna tyder på att MgO hämmar eller fördröjer framförallt den mekanism som ger ammoniumnitrat och lustgas som produkt.

Experimentella data tyder på att den skillnad som finns mellan batchers sönderfallsbenägenhet vid lägre temperaturer (60-65ºC) återspeglas även för reaktioner i smälta. Denna omständighet bör undersökas vidare för att öka förståelsen för sönderfallsmekanismer i flytande ADN.

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Background

Ammonium dinitramide (ADN) is useful as an oxidizer for highly energetic materials, such as propellants, pyrotechnics, explosives, etc. It comprises nitrogen, hydrogen and oxygen that will provide a clean exhaust gas, composed of invisible, non-corrosive gases such as nitrogen and water vapour. For this reason, in a tactical military scenario, ADN produces a reduced smoke exhaust compared to ammonium perchlorate (AP), allowing better protection from discovery of the launch site. The clean exhaust also results in greater occupational safety for crews in confined launch areas, as well as less missile signature during flight. The molecular structure of ADN is seen in Figure 1.

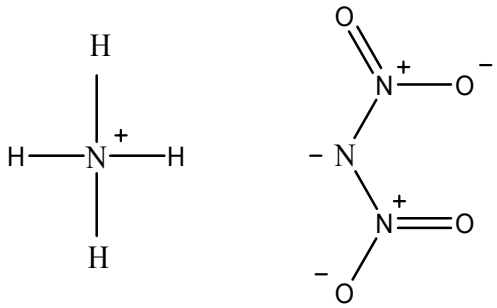

Figure 1 ***The molecular structure of the energetic salt ADN.***

Common ground is that ADN needs to be stabilized in order to be useful in explosives and propellant systems. Studies investigating how to stabilize ADN in both liquid and solid state have been made [1-6]. However, only a few studies have focused on the stability of ADN at temperatures well below its melting temperature (92-94°C) [3, 4, 7]. From an application point of view, it is of interest to investigate the stability closer to storage and service temperatures. Hence it is of importance to understand the anomalous decomposition mechanism of solid ADN found at 60°C-65°C. Work directed towards understanding the anomalous decomposition has been pursued also by other research labs [4-6, 8, 9]

Concerning ADN decomposition in general, several decomposition products have been reported [3, 5, 8, 10-12], including ammonium nitrate (NH_4NO_3), nitrous oxide (N_2O), water (H_2O), nitrogen dioxide (NO_2), nitrogen monoxide (NO), ammonia (NH_3), nitrogen (N_2), oxygen (O_2), nitric acid (HNO_3), HONO and HNO_2.

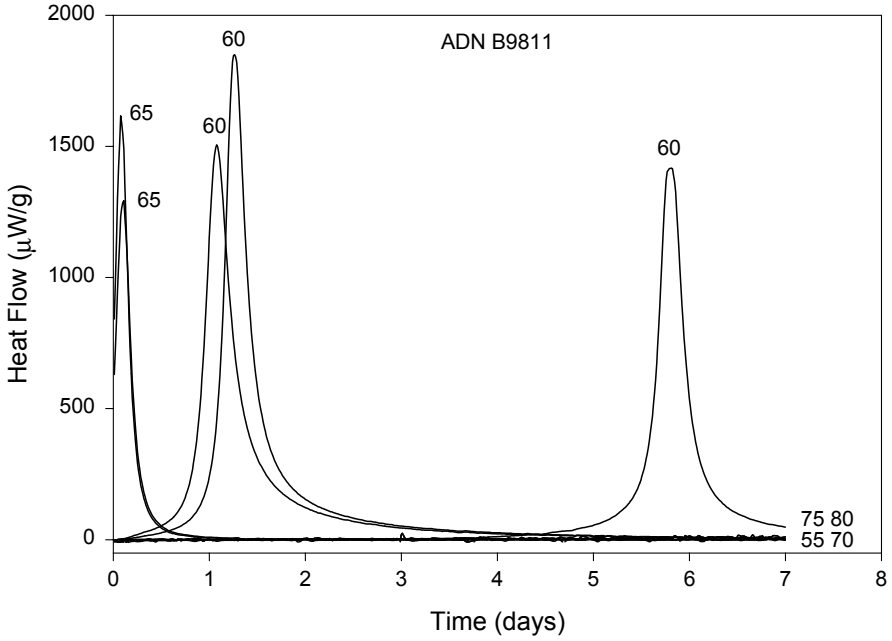

Figure 2: *Thermal stability of ADN batch no B9811 at different temperatures. Heat flow calorimetric measurements of dry ADN (0.01-0.05 % moisture content) show evidence of decomposition reactions at both 60ºC and 65ºC [13]. ADN is considerably more stable at both lower and higher temperatures (55ºC, 70ºC, 75ºC, 80ºC). This is often referred to as the anomalous behaviour of ADN.*

Results from previous mass spectrometric study

The preliminary results from mass spectrometric studies of the 60-65ºC ADN anomaly is presented in a previous report [14]. In conclusion, the interpretation of the mass spectrometric data, as presented in that report, is summarized in Table 1:

m/z	14	16	28	30	32	44	45
Corresponding fragment	N	O	N_2	NO	O_2	N_2O	(HNNO?)

Table 1 *m/z of fragments and their suggested interpretations – from earlier study [14]* .

The main decomposition product is identified as being N_2O (*m/z* 44, 30, 28, 16 and 14). Another observation is that solid ADN contains some air that is released during heating. This is supported by the findings of masses 28 and 32 originating from N_2 and O_2 in combination with the m/z 40 ion. The origin of *m/z* 40 is likely to be Ar, which has the occurrence in air of approximately 1%. One possibility would then be that air, being trapped in the sample or in the crystals, is released from the sample upon heating. Worth noting is also the absence of NH_3 and water in the decomposition products. The assignment of the m/z 45 ion (HNNO) was uncertain, and the ion has later been reassigned, as is reported below.

Introduction

In order to compare the solid state and liquid state decomposition mechanisms more closely, and to verify the presence of additional decomposition mechanisms in the liquid state, further mass spectrometric studies have been undertaken. The basis for the experiments is the assumption that a difference in decomposition mechanisms is likely to yield at least a subset of differing gaseous decomposition products that can be detected under the current experimental circumstances. Mass spectrometric (MS) measurements on ADN were therefore performed at 65ºC and 100ºC.

Experimental setup

For MS measurements on ADN decomposition, a time-of-flight mass spectrometer (TOF-MS) with a capillary column inlet is used, see Figure 3. The method of using a capillary column to transport decomposition products into an MS has previously been used with good results, leading to the identification of stable fragments as well as some relatively unstable intermediates [15]. Radicals that are produced in the reaction will most probably not survive the transport through the capillary column and have to be studied by other means.

An external sample vessel, which can be kept at constant, elevated temperatures within the ambient to 200ºC regime, is connected to the MS via the capillary column. MS data can be collected during a relatively long time span, typically a few hours. If data collection is needed for even longer periods, a residual gas analyzer (SRS RGA200) placed on the TOF-MS ionization chamber can be used. When running in pressure versus time mode, the RGA logs the partial pressure history of up to 10 selected ions. The constant heating and the long data collection periods make it possible to closely study the products formed in the relatively slow decomposition of solid and liquid ADN. Monitoring was done both at 65ºC (solid phase) and at 100ºC (liquid phase).

The experimental setup was described in detail in a previous report [14].

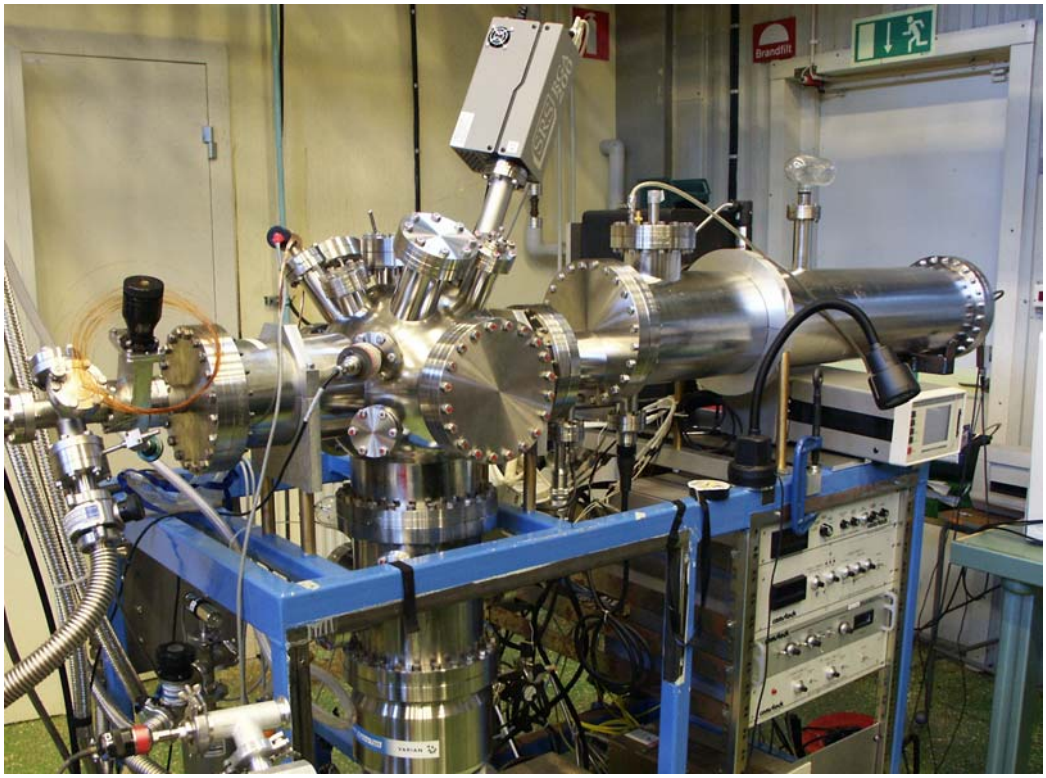

Figure 3 *The TOF-MS has been equipped with a capillary column feed through. The capillary terminates in the ionization chamber.*

The TOF-MS was run in positive detection mode, using an electron impact (EI) energy of 70 eV. The ADN samples were in most cases taken from batch NSA001 lot 2002-7034, the same batch that was used in the previous study. Exceptions are the sample from the FOI prepared batch F1010 that was included for batch difference comparisons, and FOI produced prilled ADN that was prepared from the NSA001 batch, lot 2002-7034, using a narrow zone spray technique with a pressure of 8.5 bar. The amount of ADN constituting the samples ranged from 250-300 mg.

The low temperature samples were dried over silica gel in a heating oven kept at a constant temperature of 40ºC for 7 days. After that, they were placed in the stainless steel sample vessel and connected to the high vacuum system via the capillary column. The sample vessel was pumped via the capillary column for at least one day prior to measurement. The main purpose for this was to reach a good vacuum in the mass spectrometers ionization chamber, thereby minimizing the spectral background signal arising from oxygen and nitrogen in air.

Decomposition Studies

Liquid ADN

ADN was heated to 100ºC and kept at constant temperature and mass spectra were recorded during several hours. The earlier reported m/z 45 ion that could not be given a certain interpretation was identified as belonging to isopropanol (C_3H_8O). Isopropanol constitutes a major part of the mass spectrum during the first hour of heating, with the peak intensity reached after approximately 20 minutes. Its molecular ion can be found at m/z 60, but the highest abundance ion is m/z 45. Isopropanol is present for the first ~3 hours of heating. The finding of isopropanol in ADN is not surprising, since it is commonly used in the crystallization of ADN. The spectrum presented in Figure 4 is a recording of sample no 6, which was placed directly in the sample vessel without preceding drying. A reference spectrum of isopropanol is presented in Figure 5 for comparison.

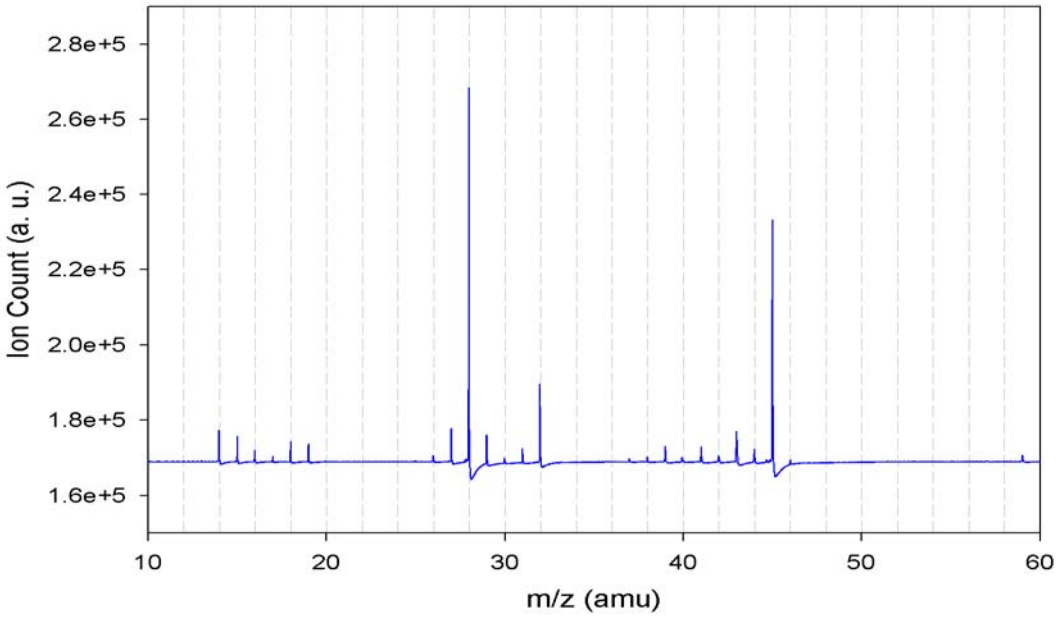

Figure 4 *A spectrum averaged over a five minute period, starting at 25 minutes and ending at 30 minutes into the 100ºC heating. The spectrum exhibits a very clear isopropanol fingerprint where m/z 45 is the highest abundance fragment ion of isopropanol. Other peaks originating from isopropanol are m/z 60, 59, 46, 44, 43, 42, 41, 40, 39, 38, 37, 31, 30, 29, 28, 27, 26, 19, 15 and 14. Also present in the spectrum are m/z 32, and 16, and overlapping signals from m/z 28 and 14, from molecular and atomic oxygen and nitrogen respectively. Water is also present with m/z 18 and 17. Recordings from sample no 6.*

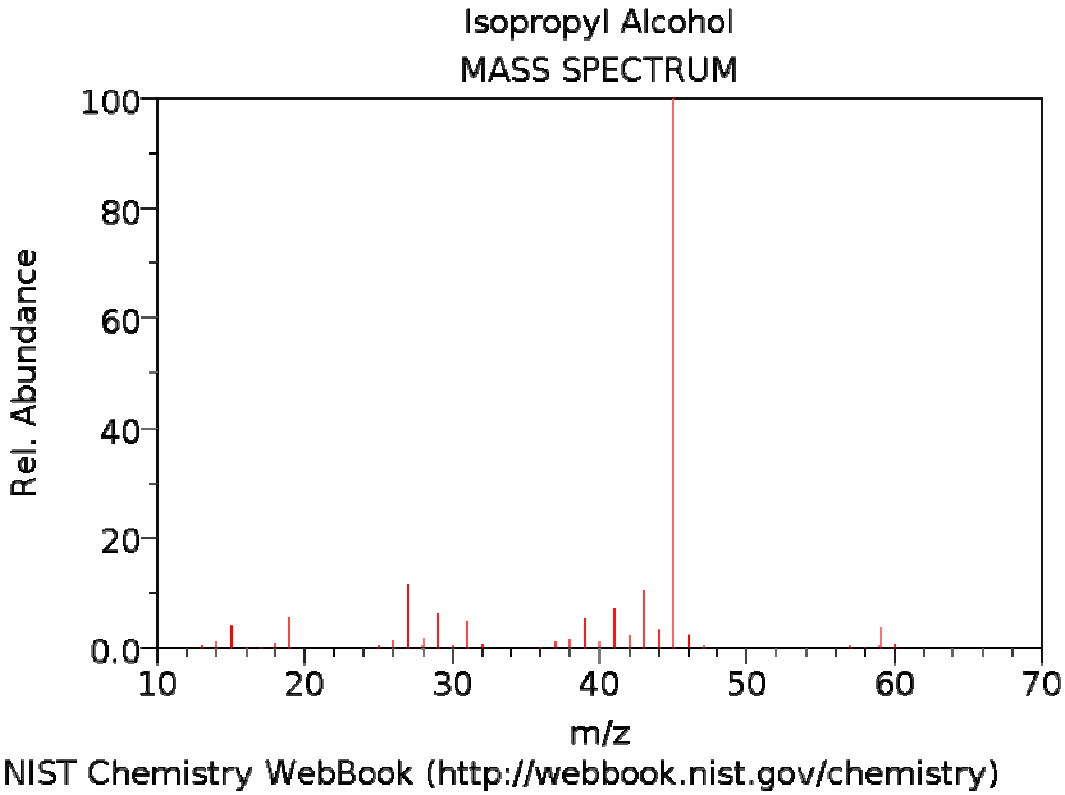

Figure 5 *A typical isopropanol mass spectrum from NIST chemistry web book, presented for comparison. Ionization method is EI (electron impact) at a voltage of 70 eV.*

Figure 6 shows the resulting mass spectrum after 21 hours at a constant temperature of 100ºC. As in the low temperature measurements, the spectrum reveals formation of N_2O (m/z 44, 30, 28, 16 and 14). However, the intensity of the m/z 28 peak is too high to originate only from N_2O. Thus, there is an additional formation of N_2, (m/z 28, 14). There is also a considerable amount of H_2O (m/z 18, 17) in the spectrum. Because the m/z 15 ion is missing, there is no evidence for the formation of NH_3 (m/z 17, 16, 15, 14). A small peak at m/z 46 is identified as NO_2. The presence of m/z 32 (O_2) in the high temperature spectra, primarily during the first hours of measuring, originates from air background.

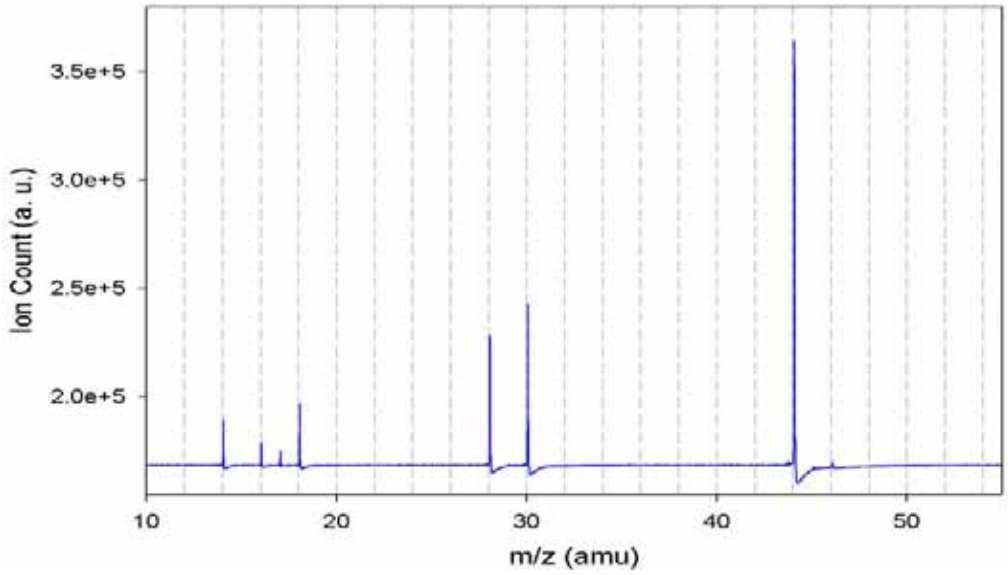

Figure 6 *Sample no 6, spectrum taken after 21 hours at 100ºC. The spectrum reveals formation of N_2O, N_2, H_2O and a small amount of NO_2.*

The fact that water is produced becomes even more evident when looking at the recording of sample no 9. This sample was exposed to 36 hours of heating at 100ºC plus a temperature ramping (100ºC - 120ºC) occurring during hours 15-18 followed by slow cooling down to 100ºC again. The spectrum thereafter recorded is presented in Figure 7. As can be noted, H_2O with m/z 18 and 17 is the dominating species in this spectrum.

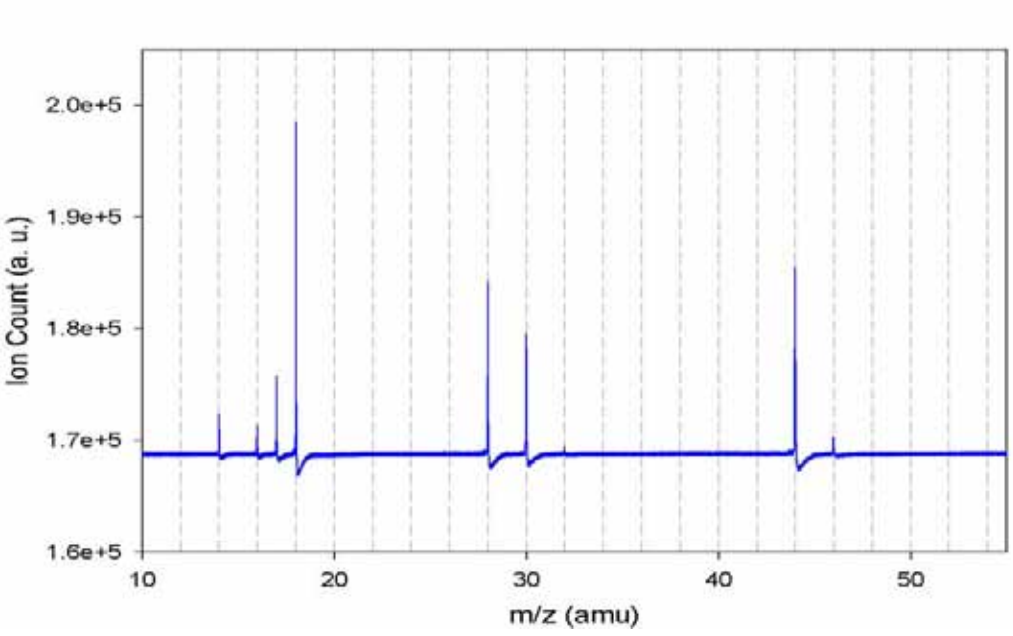

Figure 7 *Sample no 9 after prolonged heating and temperature ramping. Water is the dominating species in this spectrum, leading to the conclusion that water is formed in the decomposition of liquid ADN.*

One of the samples, no 6, was kept at constant temperature at 100ºC for approximately 21 hours. It was then removed from the sample vessel for several days before the heating procedure was repeated. The partial pressure as a function of time was recorded during the second heating (hours 3-21) of sample no 6. The resulting diagram can be viewed in Figure 8 and Figure 9.

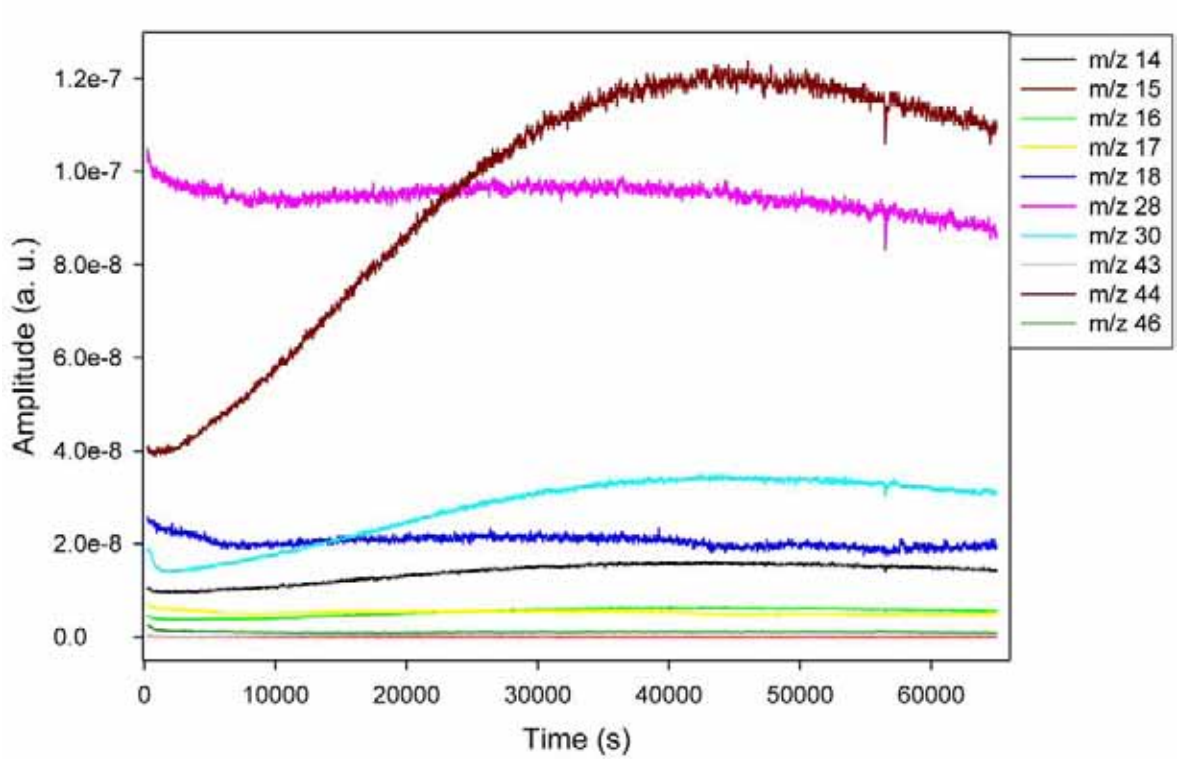

Figure 8 *A diagram of sample no 6, showing how the partial pressure of different ions vary respectively with time. As expected, m/z 44 and 30 (NO-fragment of N_2O) show a similar pressure variation over time. Interesting to notice is the differing behaviour of m/z 28 and 18 (N_2 and H_2O) as compared to m/z 44. The spectrum is recorded during hours 3-21 of the second heating to 100ºC.*

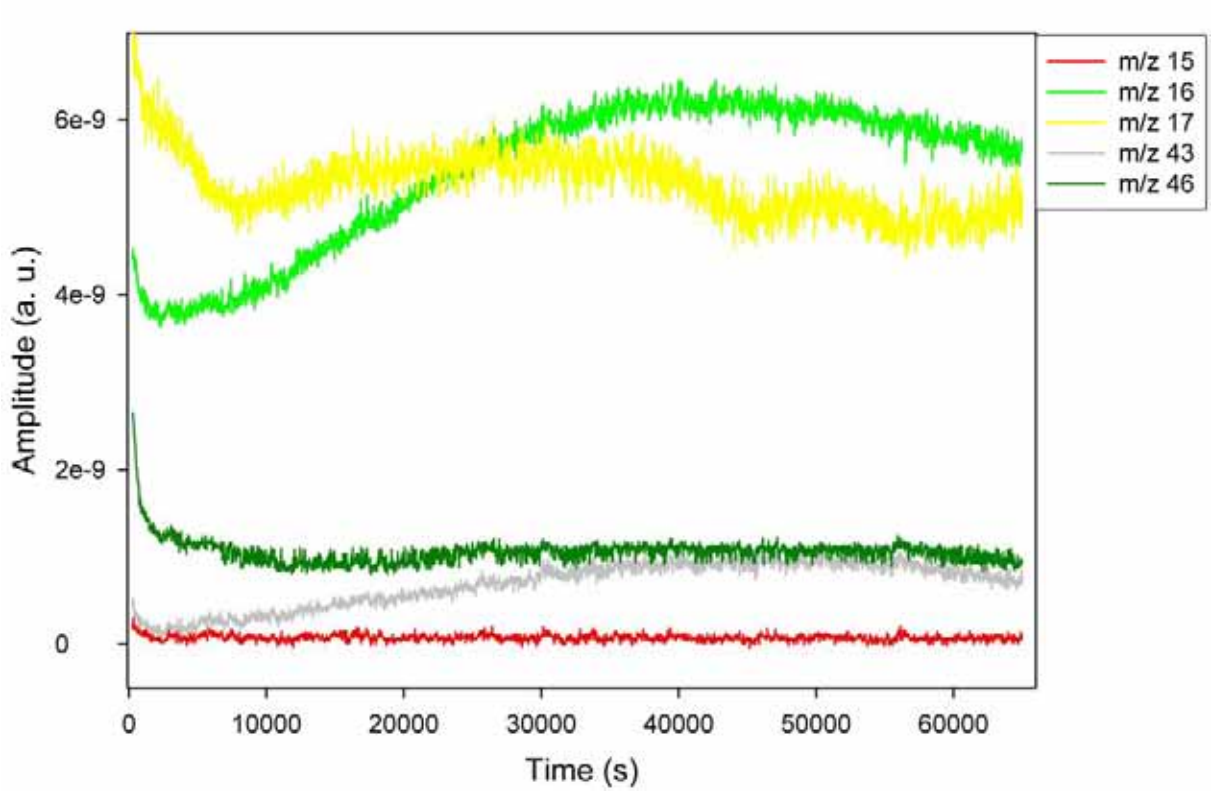

Figure 9 *A subpart of the ions shown in the diagram above. It can be noted that the lower abundance ion m/z 46 (NO_2) follows the partial pressure variation of N_2 and H_2O, whereas the ion m/z 43 (not assigned) has a partial pressure variation concordant to that of N_2O.*

Figure 8 and Figure 9 show the partial pressure variation of product ions during a time span of 18 hours (100ºC). Interesting to notice is that the observed ion counts follow two different partial pressure variation profiles:

The formation of N_2O (major peaks at m/z 44 and 30) and an ion of m/z 43 follows the same partial pressure variation pattern. Thus it is likely that they originate from the same decomposition pathway. The assignment of the m/z 43 ion is not certain, but it is likely to be from a contamination of the NSA001 2002-7034 batch of ADN. Isopropanol, which could be a source of the m/z 43 ion, is not present in the sample after this prolonged heating. If it is produced directly from the ADN decomposition, the interpretation would be N_3H. This has not been suggested in any published decomposition mechanisms.

Following another partial pressure variation profile are ions from N_2 (m/z 28,14), H_2O (m/z 18, 17) and NO_2 (m/z 46, 30, 16, 14).

From the above described observations, it is suggested that there are at least two different reaction pathways occurring under the stated experimental circumstances. The first is proposed to be:

$$NH_4N(NO_2)_2 \rightarrow N_2O + NH_4\,NO_3$$

The lack of NH_3 formation in the early stages of ADN decomposition has also been observed in [16], where the decomposition is suggested to follow two parallel reaction pathways, one being the reaction suggested above, the other the formation of NO_2 and NH_4 NNO_2 (mononitramide). The mechanism producing N_2O and NH_4 NO_3 has also been considered in [11] for a condensed phase reaction.

Calculations also suggest that in gas phase below 160ºC, the ionic decomposition scheme for direct formation of ammonium nitrate may be occurring [11] as one out of several possible decomposition mechanisms.

The other reaction mechanism or mechanisms would involve the formation of N_2, H_2O and NO_2 and could take place in several steps. The details of how these products are formed will not be resolved without complementing efforts using other analytical and experimental methods.

The findings of N_2O, N_2 and H_2O as the main gaseous products from thermal decomposition of liquid ADN together with minor amounts of NO and NO_2 has been reported earlier in [5] The authors also noted that the ratio between formation of N_2O and N_2 varied strongly over time.

The m/z 30 ion (NO) found in the spectra has been assigned to the electron impact ionization (EI) MS fragmentation of N_2O. The m/z 30 fragment ion count typically constitutes 32% of the m/z 44 ion count in EI mass spectra. It is possible that because of the large formation of N_2O, a minor (direct) formation of NO would be masked.

The relatively small amounts of H_2O and NO_2 found in the mass spectrometric recordings may be a result of their high solubility in liquid ADN.

Solid ADN

Measurement of the low temperature (65ºC) decomposition was repeated for verification purposes. Figure 10 shows a mass spectrum of sample no 8 recorded after 2 hours and 45 minutes at a temperature of 65ºC. The spectrum, which is averaged over 200 seconds, reveals formation of N_2O (m/z 44, 30, 28, 16, 14) and the presence of air (m/z 32, 28, 16, 14). There is a distinct m/z 45 ion, likely originating from isopropanol residues, but no evidence of H_2O being produced in the reaction can be found, nor can the formation of NH_3 be verified. Furthermore, the ions m/z 43 and 46 have not been observed in the solid state decomposition.

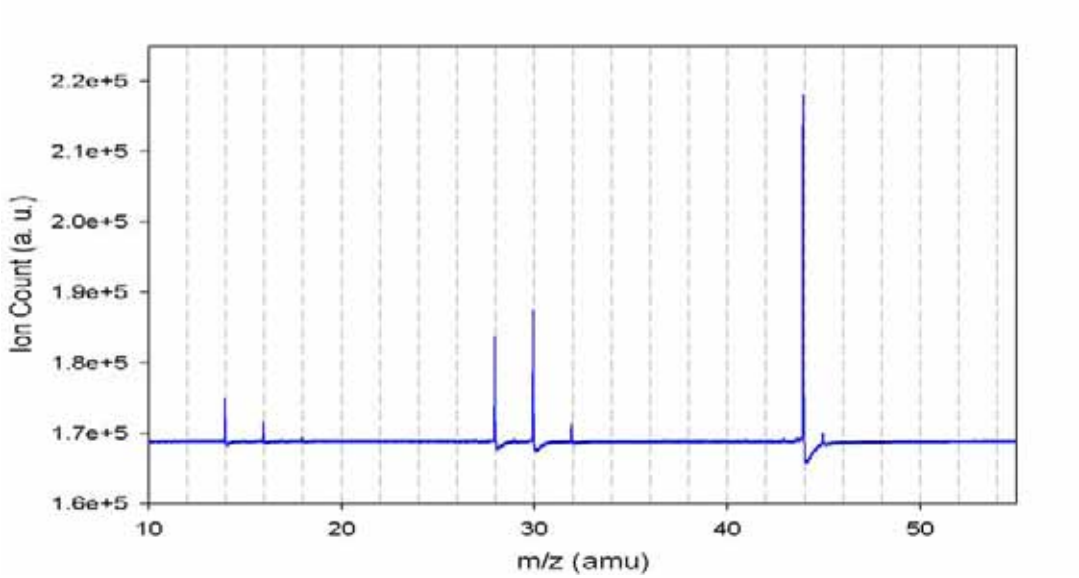

Figure 10 *Sample no 8 after 2 hours and 45 minutes at 65ºC. The peaks can be referred to N_2O, air (N_2, O_2) and isopropanol.*

The findings are in agreement with the suggestion that ADN in solid phase, under the experimental conditions described above, decomposes directly to ammonium nitrate and N_2O:

$$NH_4N(NO_2)_2\ (s)\ \rightarrow N_2O(g) + NH_4\ NO_3\ (s)$$

The proposed mechanism [11] where the initial steps in ADN decomposition are the transfer of a proton to form ammonia and dinitramidic acid, and a subsequent formation of nitric acid, HNO_3 and N_2O, is thus not probable to take place:

$$NH_4N(NO_2)_2 \leftrightarrows NH_3 + HN(NO_2)_2$$

$$HN(NO_2)_2 \rightarrow HNO_3 + N_2O$$

Instead it has been suggested from theoretical studies [17] in [18] that the direct formation of N_2O and ammonium nitrate is facilitated by a proton transfer caused rearrangement of the dinitramide group. The proton transfer in turn is facilitated by the N ─ H···O hydrogen bonds in ADN crystals. According to [5], the anomalous decay of dinitramide salts is related to the nonsymmetrical geometric and electronic structure of the $N_3O_4^-$ anion in the crystal state. The presence of water molecules decreases polarization, smoothens the electronic asymmetry and thereby prevents the intramolecular rearrangement responsible for the anomalous decomposition.

That solid ADN decomposes to the more thermally stable ammonium nitrate and to a non-reactive gas, N_2O, is good from an application point of view. Furthermore, the reaction is decaying at the stated experimental conditions and involves a limited fraction of the ADN sample. The

observation that the reaction is decaying is supported by the experimental results in [4], where ammonium nitrate and N_2O concentrations are found to reach asymptotic limits after prolonged heating at temperatures below 80ºC. The decaying properties of the anomalous decomposition are interesting, since this means that there is no safety hazard related to the anomalous decomposition phenomenon. The gas evolution can possibly cause some problems with cracking.

The decaying property of the anomalous decomposition is illustrated by the partial pressure versus time spectrum of ADN in Figure 11. The sample was heated to 65ºC for three hours before starting the pressure vs. time- recording. The formation of N_2O decreases rapidly and leaves the spectrum dominated by N_2 and O_2. These in turn, when appearing with such low amplitudes, are likely to arise from air leaks within the high vacuum MS-instrument.

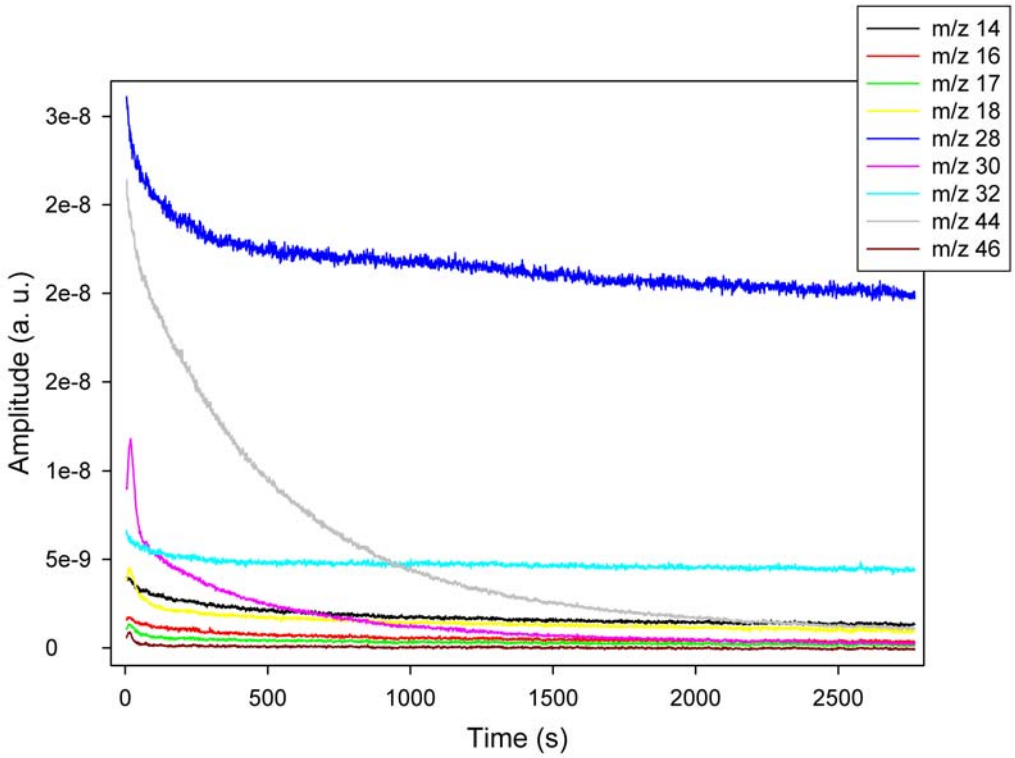

Figure 11 *Pressure vs. time - recording of decomposition products after a few hours of heating the sample at 65ºC. N_2O formation (m/z 44) rapidly decreases, leaving the spectrum dominated by air background (m/z 28 and 32 from N_2, O_2). Sample no 7.*

Isopropanol and stability variance

To investigate the possibility of isopropanol content influencing the lower temperature stability of ADN, a comparison between two different batches was carried out. The comparison is based on earlier Heat Flow Calorimetric data comparing the NEXPLO batch NSA001 2002-7034 with an FOI produced batch - F1010. The data shows that the F1010 batch takes longer time to react and does not produce as much heat during the reaction. The Heat Flow data can be seen in Figure 12.

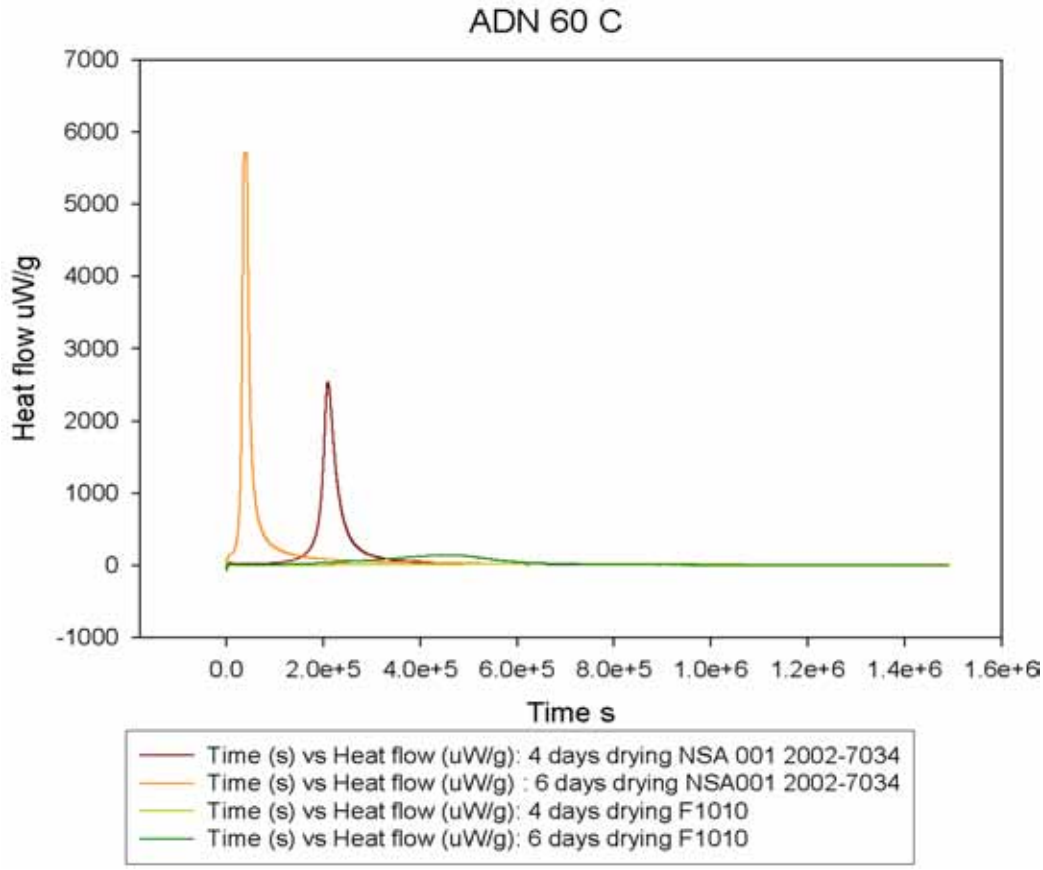

Figure 12 *Heat Flow Calorimetric data on two different ADN batches. The temperature was 60 ºC and samples were dried over silica gel for 4 or 6 days respectively.*

The thermal decomposition behavior at 100ºC was compared for one sample from each batch. At this temperature, isopropanol will evaporate within a few hours, reaching a maximum in mass spectrometric reading after approximately 20 minutes of heating. Sample 6 from NSA001 2002-7034 was compared with an F1010 sample in order to investigate if any difference in isopropanol content could be detected. The spectra were compared at their maximum ion count of m/z 45, the highest abundance ion in the isopropanol EI spectra, and the ion count of m/z 45 for the F1010 batch was found to be 45% of the NSA001 batch, as can be seen in Figure 13. Figure 14 illustrates the ion count variation over time for the m/z 45 ion among others. To give further support for the observed difference in isopropanol content, a very crude integration (by geometric area calculation) of ion count over the entire period of isopropanol presence was performed for both batches. The integrated ion count for F1010 was found to be 29% of the integrated ion count for NSA001, giving further support for a difference in isopropanol content between batches. However, caution must be given that the mass spectrometric method applied in these studies is not intended for quantitative measurements, indications of a difference in isopropanol content must be more closely verified with another method, e. g. gas chromatography.

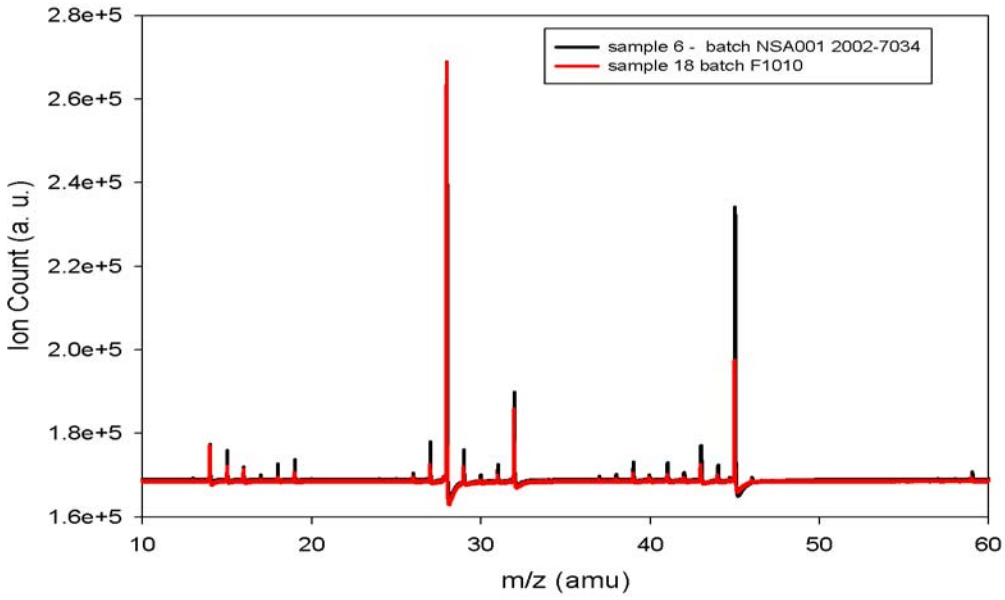

Figure 13 *Mass spectra taken from two different batches – NSA001 2002-7034 and F1010. The highest abundance ion of isopropanol is m/z 45. The ion count for m/z 45 for the F1010 batch (sample no 6, 304 mg ADN) is 45% of the NSA001 m/z 45 ion (sample no 18, 283 mg ADN). The measurements are not quantitative, but are indications of difference in isopropanol content between the batches.*

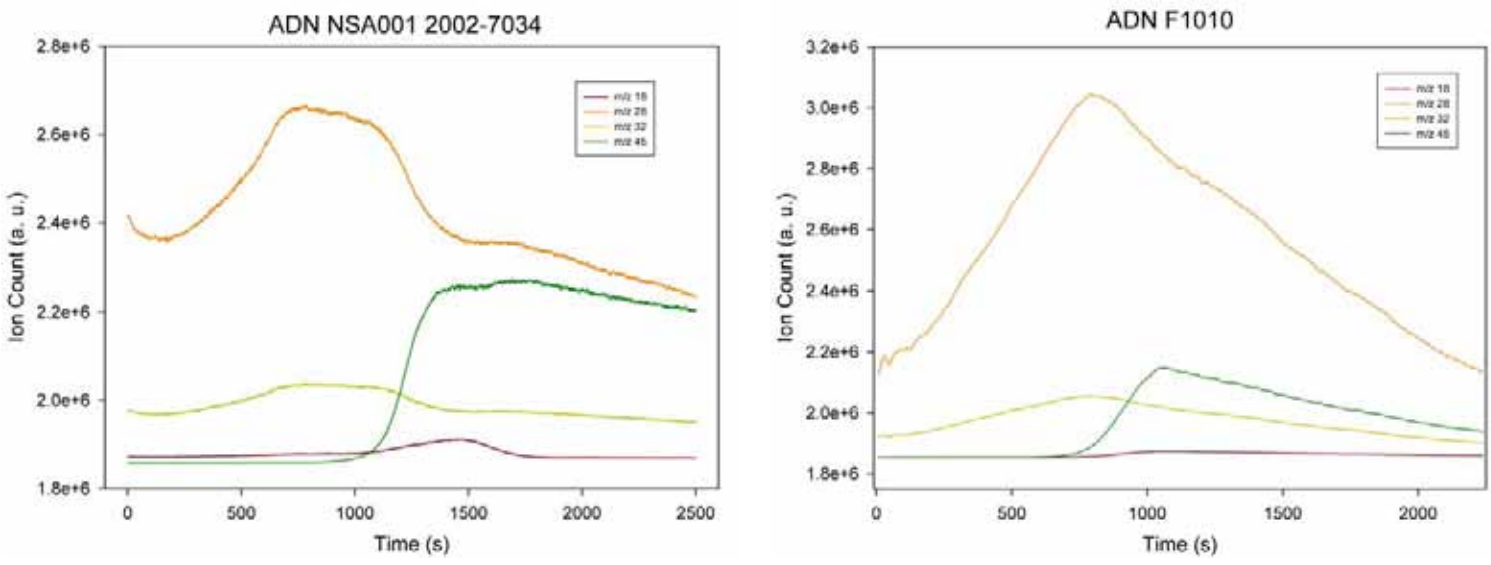

Figure 14 *Ion count for ions m/z 18, 28, 32 and 45 plotted as a function of time for the two different batches. m/z 45 represents isopropanol's major fragment ion. Samples no 6 and 18.*

The observed difference in anomalous decomposition rate between batches has not been correlated to isopropanol content. However, since isopropanol is detected also in the solid phase decomposition mass spectra, and since its presence has not been reported previously, the results may call for further investigations regarding possible correlations between low temperature

stability and isopropanol residues in ADN. There may be other factors that have not been considered here that can explain the observed differences, one being the difference in ammonium nitrate content between batches. A comparison of ammonium nitrate (NH_4NO_3) content may therefore be considered.

Comparison of chemical stability for different batches in the melt

The two batches NSA001 2002-7034, sample no 9, and F1010, sample no 18, were compared also in a temperature ramping measurement. Sample no 9 was kept at 100ºC for 14.5 hours prior to temperature ramping, sample no 18 was kept at 100ºC for 24 hours before the ramping experiment. The relative intensity of the total ion count was comparable at 100ºC. The temperature was thereafter raised by 5ºC every 40 minutes. The experiment was terminated when the pressure in the MS flight tube was nearing the damage threshold for the detectors – $1 \cdot 10^{-6}$ torr. For sample no 9, this pressure was reached at 110ºC, for sample no 18 at 120ºC. The resulting ion count intensity variation over time for the last temperature setting can be viewed in Figure 15.

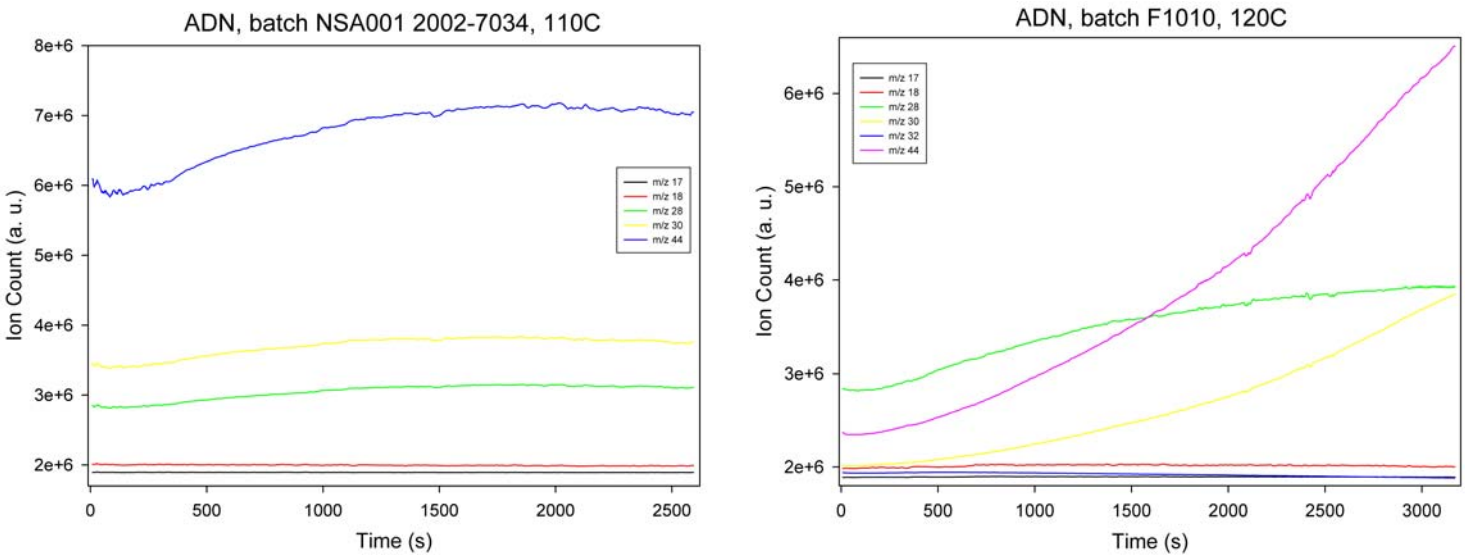

Figure 15 *Ion count intensity variation over time for selected product ions at finishing ramping temperature. The finishing temperature was defined by the MS detectors damage threshold pressure. Samples 9 and 18.*

The reaction patterns differ between the two batches. The NSA001 2002-7034 batch releases a greater amount of decomposition products earlier in the temperature ramping and shows a steady increase of product formation, reaching the finishing temperature at 110ºC. The dominating ion signal from the start of the temperature ramping is m/z 44 (N_2O), this is the dominating species up to the termination of the measurement. The F1010 batch does not reveal a dominant N_2O formation to start with, instead the dominating ion is m/z 28 (N_2). When reaching the finishing temperature at 120ºC, there is a pronounced increase in the formation of N_2O leading to the

pressure reaching the MS damage threshold.

This observation leads to the conclusion that it may be possible to gain information about mechanisms resulting from differences in stability between ADN batches by monitoring the relative rates of evolution of decomposition gases. The comparison of temperature ramping experiments point towards batch related differences not only in the solid phase but also in the liquid phase decomposition.

MgO stabilized ADN in liquid phase

A temperature ramping of MgO stabilized material was conducted on sample no 22 stabilized by 1% MgO (by weight). The sample was held at 100ºC for 1 hour and 40 minutes prior to starting the ramping. The measurement was terminated at 130ºC, without the pressure reaching the detector threshold. Instead, the termination was due to extensive clogging of the capillary from sample material. In Figure 16, the intensity variation over time for 130ºC is shown.

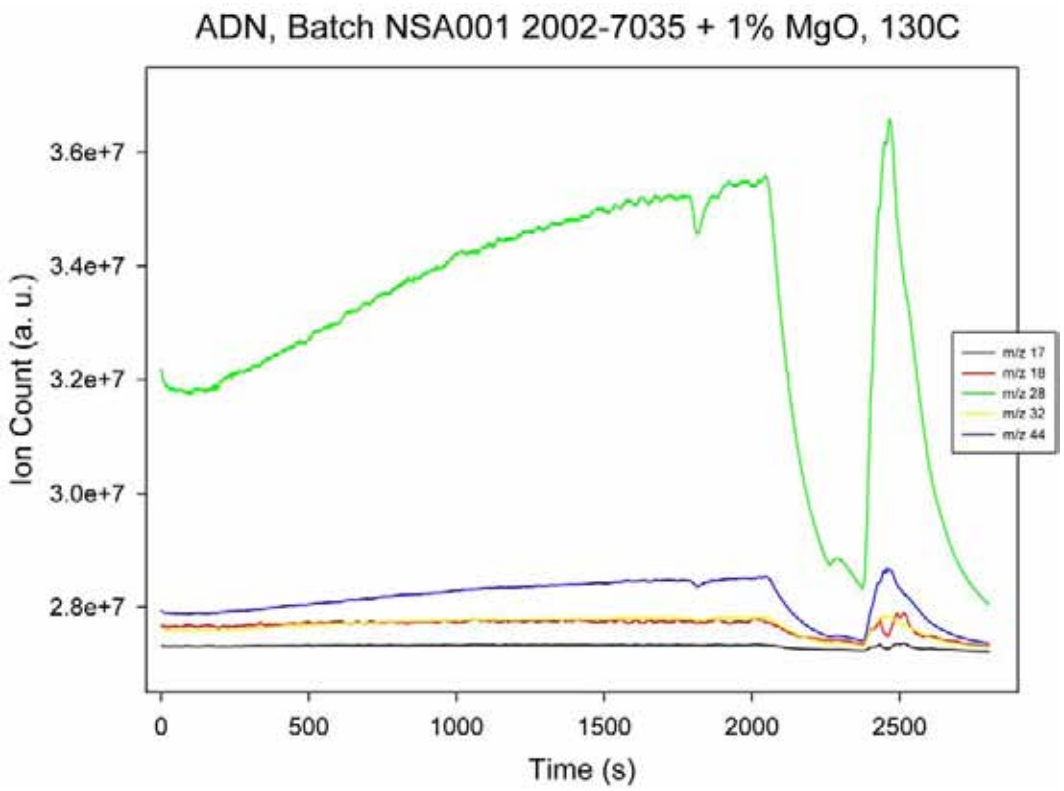

Figure 16 *Ion count intensity variation over time for selected product ions at finishing ramping temperature. In difference to the intensity variation diagrams of unstabilized ADN (see previous page), the ion with highest peak intensity is N_2 and not N_2O. The sudden drop in ion count intensity is caused by temporary clogging of the capillary column.*

As can be seen from Figure 16, the additive hampers specifically the formation of N_2O, whereas the formation of N_2 is not affected to a noticeable extent. This implies that the stabilization is

effective only or mainly for the mechanism producing N_2O and ammonium nitrate directly from ADN.

The comparison of unstabilized and MgO stabilized ADN was also done by means of Heat flow calorimetric measurements at 95ºC. The results show that ADN with 1% MgO postpones the autocatalytic reaction by several days, as seen in Figure 17.

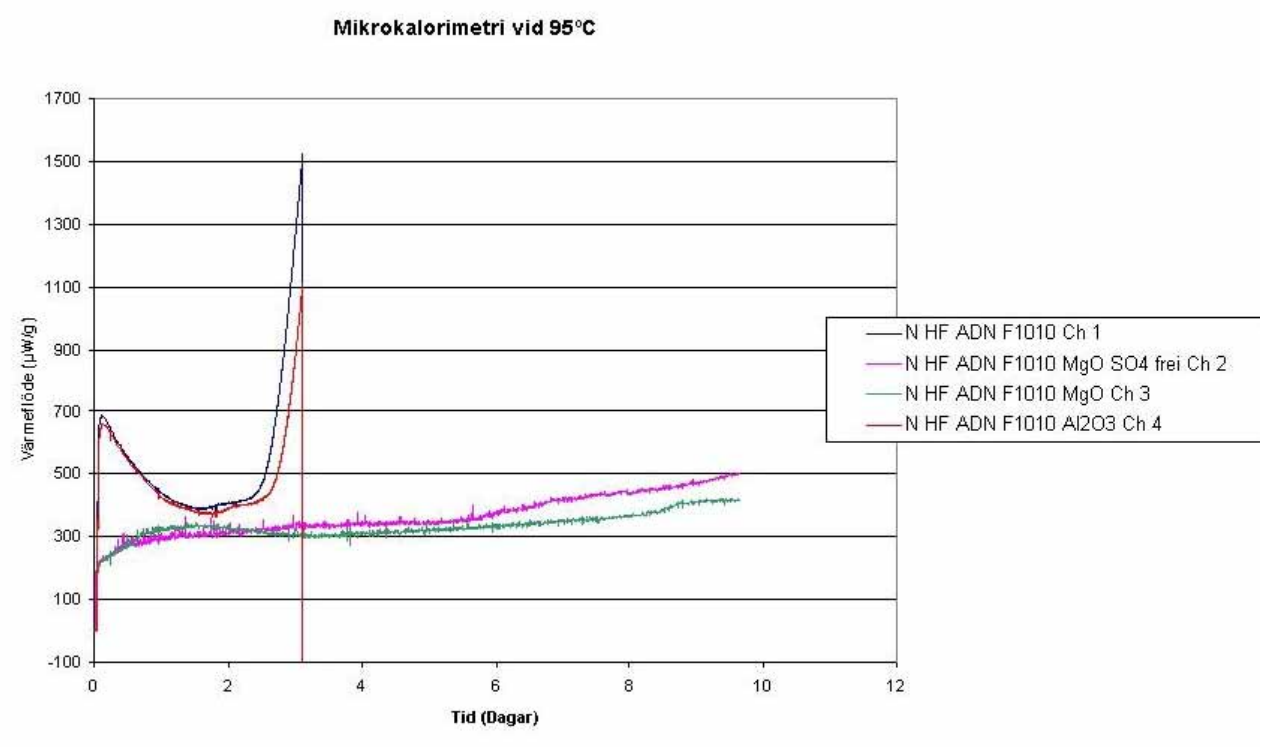

Figure 17 *Heat flow calorimetric data for ADN F1010 with and without the addition of 1% MgO. The additive is effective in stabilizing ADN and postpones the autocatalytic reaction by several days.*

Prilled ADN in liquid phase

A mass spectrometric study of prilled ADN in the melt (100ºC) was also performed. Prilling was made from the NSA001 2002-7034 batch by using spraying technique at a pressure of 8.5 bar. Prilling is expected to give less contamination from isopropanol, since it is done from ADN in the melt, and the boiling point of isopropanol (82ºC) is below the melting point of ADN. This expectation was verified by the collected MS data. There are still some traces that can be detected from the highest abundance ion from isopropanol, m/z 45, but the amount is significantly reduced as compared to neat ADN. The peak intensity of isopropanol ion and fragments appears after approximately 20 minutes, as was also the case with the other ADN samples. The resulting spectrum can be seen in Figure 18. Also worth noting is the very low amount of N_2O formation. The spectrum is dominated by air.

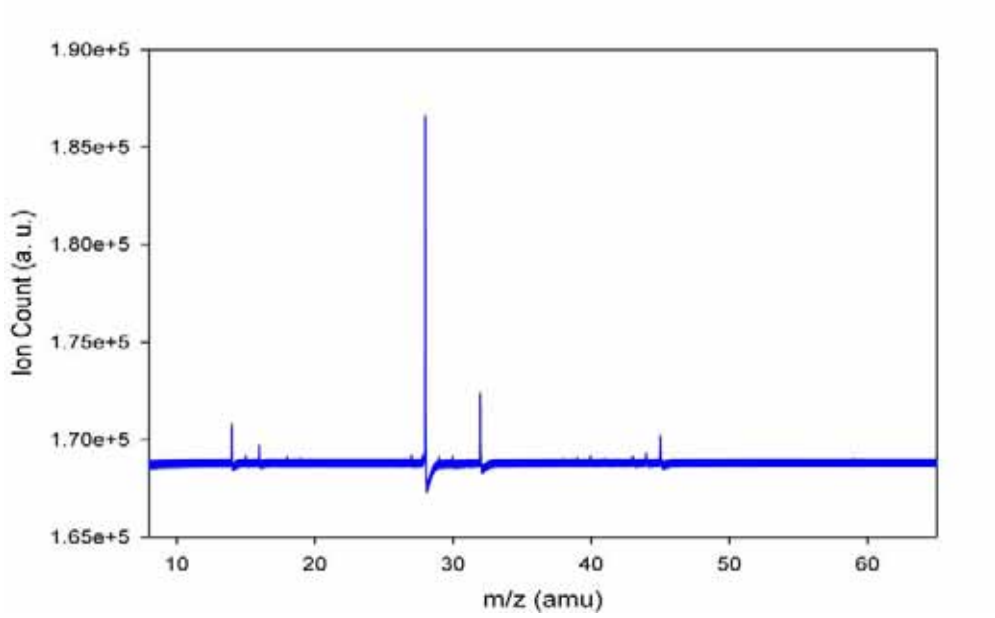

Figure 18 *The maximum intensity of the m/z 45 ion, origination from isopropanol, is reached after approximately 20 minutes. The spectrum is an average of the interval 2400-2500s.*

The onset of N_2O formation is late in comparison to neat ADN (Figure 19), which typically shows a detectable formation of N_2O when the measurement/heating begins, given that the sample is dry. The prilled sample was stored in Ar atmosphere from the point of production until being placed in the sample vessel. That the prilled sample also is dry can be concluded from a lack of water in the 100ºC spectra.

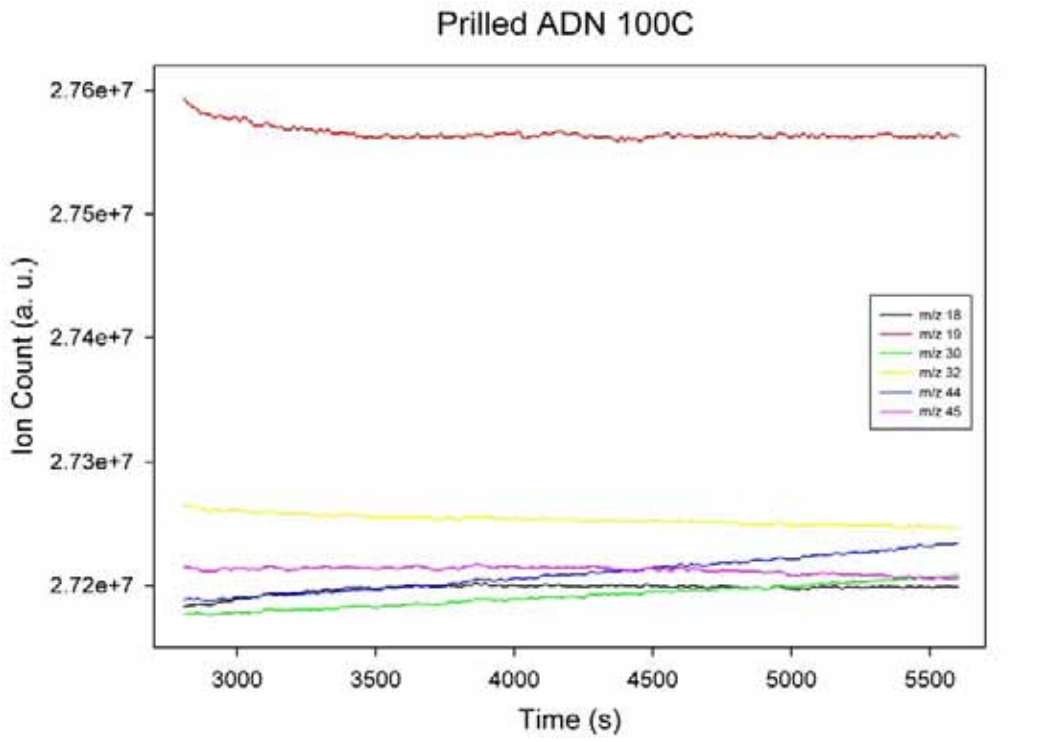

Figure 19 *The peak intensity of the m/z 45 ion (isopropanol) dominates over m/z 44 (N_2O and isopropanol) after 70 minutes at 100ºC. The timeframe for the above diagram is 46-93 minutes.*

The prilled ADN sample was also exposed to a temperature ramping experiment. As with the MgO stabilized sample, the experiment was interrupted at 120 ºC because of clogging of the capillary from sample material, and not because of reaching the detector damage threshold. In line with the results from the neat ADN samples, the dominating decomposition product at the terminating temperature is N_2O. This is shown in Figure 20.

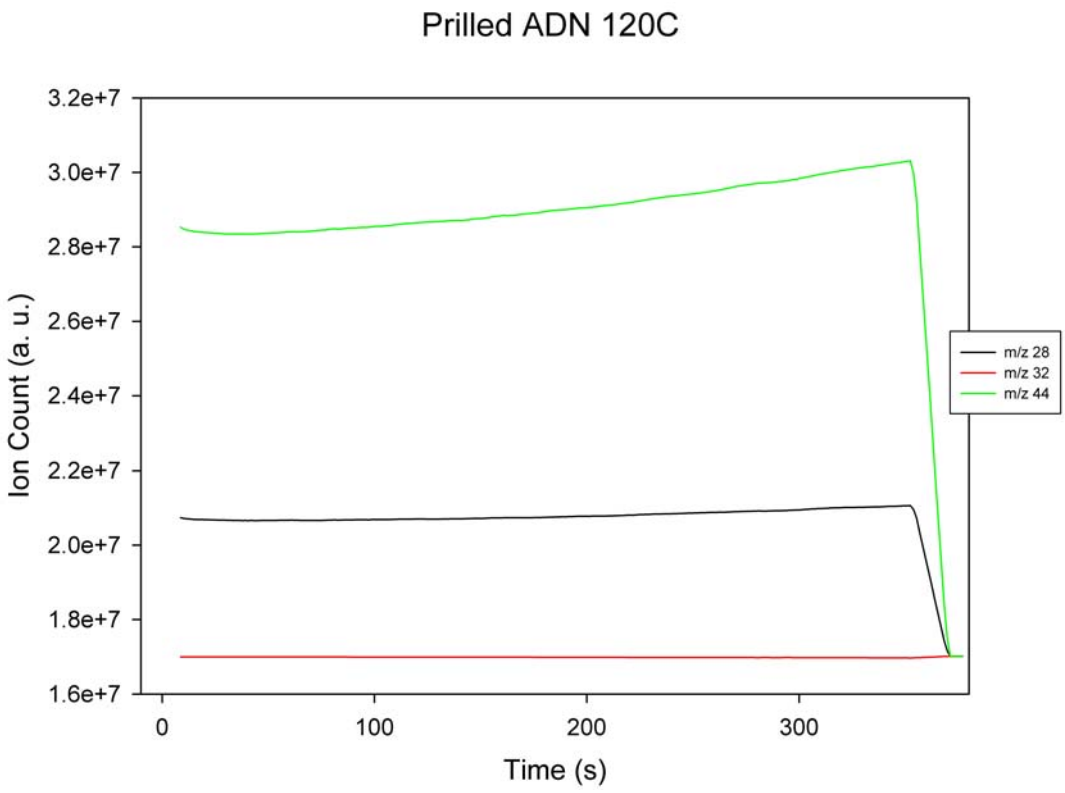

Figure 20 *N_2O is the dominating decomposition product for the prilled ADN sample. The temperature ramping experiment was terminated at a temperature of 120ºC because of clogging of the capillary column. Time span in the diagram is approximately 6 minutes.*

Conclusions

A mass spectrometric investigation of ADN decomposition has been undertaken. The experimental equipment used was a time of flight mass spectrometer that was connected to a sample vessel via a capillary column. This allowed for studying the thermal decomposition products evolving during several hours of ADN at a constant, elevated temperature.

The anomalous decomposition mechanism occurring at 60-65°C was studied. The spectra revealed the presence of air (released upon heating and from background) and considerable formation of N_2O. Because the 65°C decomposition spectra lacks evidence for formation of NH_3, H_2O and NO_2, or any additional products, the conclusion is that ADN decomposes directly to ammonium nitrate (HN_4NO_3) and N_2O in the solid phase under dry conditions at 65°C.

$$NH_4N(NO_2)_2\ (s)\ \rightarrow N_2O(g) + NH_4\ NO_3\ (s)$$

That solid ADN decomposes to the more thermally stable ammonium nitrate and to a non-reactive gas, N_2O, is good in an application point of view. Furthermore, the reaction is of decaying nature and involves a limited fraction of the ADN sample, which means that there is no safety hazard related to the anomalous decomposition phenomenon. The gas evolution can possibly cause some problems with cracking.

A study of decomposition products from ADN in the melt was also performed. This was done both at a constant temperature of 100°C and by temperature ramping experiments. In the latter, the temperature was raised by 5°C every ~20 minutes.

Judging by the differing partial pressure changes of the decomposition products over time, ADN in the melted state at 100°C exhibits at least two different decomposition mechanisms. One is the direct decomposition to ammonium nitrate (HN_4NO_3) and N_2O observed also at lower temperatures. The other mechanism, or mechanisms, leading to the formation of H_2O, N_2 and small amounts of NO_2, has not yet been understood and needs further attention to be resolved.

Data showed good stabilization effects from an additive of 1% MgO by weigth to ADN. MgO is therefore a good candidate for stabilizing meltcasted ADN. Data suggest that it effects the mechanism responsible for the formation of N_2O and ammonium nitrate, resulting in an observable delay or reduction in N_2O formation. Further investigations into this possible effect should be considered.

During the liquid phase decomposition studies, it was discovered that all samples of ADN used contain isopropanol residue. Isopropanol is commonly used in the production of ADN. A lesser

content of isopropanol was indicated in the more stable (65ºC) F1010 batch than in the NSA001-7034 batch. This might be a coincidence and does not prove that isopropanol residue plays a role in the anomalous decay, but on the other hand it does not give grounds for discarding this possibility. Since this matter has not been the subject of attention in any study, the possibility of isopropanol affecting the low temperature stability should be further considered.

Prilled ADN, produced from the NSA001-7034 batch using spray technique, contained only very small amounts of isopropanol. This is not surprising since prilling is done from liquid ADN and isopropanol has a boiling point of 82ºC, which is below the melting point of ADN. Prilled ADN also had a slower decomposition onset at 100°C than any of the neat ADN samples. Still an open question is the stability of prilled ADN at temperatures related to anomalous decomposition.

According to the experimental data, ADN batches with differing low temperature stability (60-65ºC) also exhibits differences in partial pressure variation over time for decomposition products at moderate temperatures (above ADN melting point). This is a circumstance that could be further explored in order to undertand the decomposition mechanisms in liquid ADN.

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Appendix 1

Compillation of sample data from ”Decomposition Studies: Solid and Liquid Phase Decomposition of ADN”.

Sample (no.)	Batch designation	Days in heating oven (no.)	Days in sample vessel (no.)	Meassuring temperature (ºC)	Meassuring temperature at reheating (ºC)	Weight (mg)
1	NSA001 2002-7034	0	1	100	-	302
2	NSA001 2002-7034	7	2	65	-	303
4	NSA001 2002-7034	9	3	100	-	304
6	NSA001 2002-7034	6	1	100	100	304
7	NSA001 2002-7034	7	1	65	-	288
8	NSA001 2002-7034	7	1	65	-	282
9	NSA001 2002-7034	7	1	100	100 →	275
18	F1010	0	1	100 →	-	283
21	Prilled NSA001 2002-7034	0	1	100 →	-	~300
22	NSA001 2002-7034 +1% MgO	0	1	100 →	-	296