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Assessment of the synthesis routes conditions for obtaining ammonium dinitramide by the FT-IR

Abstract: *Over the last two decades, many routes have been proposed to synthesize ammonium dinitramide (ADN). However, most of them lie in routes in which reactants are too expensive for large-scale production. In this sense, the use of ordinary reactants is of paramount importance in this case. The aim in this synthesis consists on nitrating a starting reactant in a reaction known as nitration. Both the nitrating agent and the starting reactant should preferably be ordinary, narrowing the possibility of having realistic options for them. The most ordinary nitrating agent consists of a mixture of sulfuric and fuming nitric acids. Therefore, the breakthrough must come from the suitable choice of the starting reactant. However, so far, the only viable reaction relies on the use of sulfamate salts. Even though the process with this kind of salt has been largely commercially developed, only few information are available in the literature to properly address issues emerged from it. In this study, an attempt is made to enlighten some effects on the product caused by modifications in the route conditions. Characterization of the resulting products was confirmed by FT-IR in the region of MIR and NIR. The characteristic bands employed to identify ADN in the region of middle infrared were: 3129 and 1384 cm^{-1} (NH_4^+); 1537, 1344, 1209, and 1177 cm^{-1} (NO_2); 1032, 954 cm^{-1} (N_3); 828, 762 and 732 cm^{-1}(NO_2). The near infrared analysis pointed out few bands at 5185 and 4672 cm^{-1} in NH combination bands region. The resulting middle infrared spectrum was compared to the reference found in the literature for this product. The results show excellent agreement with the expected product.*

Keywords: *Propellant, Oxidizer, Energetic material, ADN synthesis, Ammonium dinitramide, FT-IR, MIR, NIR.*

INTRODUCTION

Solid propellants are mainly composed of particulates of energetic materials. The study of these energetic materials is the way to optimize performance, burning behavior, stability, detonation properties, processing characteristics, and mainly their sensitivity (Teipel, 2005). Several compounds can take part in solid propellant composition, and although ammonium perchlorate (AP) is the most cited in the literature among the oxidizers, its downside, however, lies in the fact that it can release a large amount of chloride into the environment (Nagamachi *et al*., 2009).

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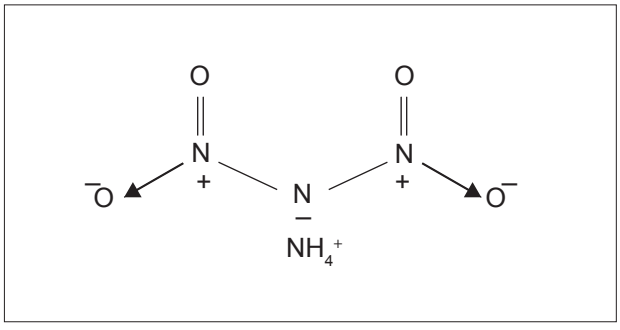
Based on the chemical structure, CL-20 or hexanitrohexaazaisowurtizitane (HNIW) and ammonium dinitramide (ADN) are potential components to be used in solid propellant formulation due to their special characteristics. Even though performance is the primarily criterion for the designer to define the convenience of any material, there are other practical considerations, including: availability and price; thermal and mechanical sensitivity (insensitive ammunitions – IM); processibility; compatibility; chemical and thermal stability; mechanical behavior temperature dependence; burning behavior; and pressure exponent (Teipel, 2005). It is also crucial to consider the oxidizing properties (including the oxygen positive balance) in the propellant development

process. ADN has positive oxygen balance of +25.8%, being a promising energetic material as a viable alternative to replace the ammonium perchlorate (AP) as an oxidizer in solid propellants. Its application can be found in civilian rockets and in smoke-low-emitting missiles (Teipel, 2005; Wingborg, 2010).

Monopropellant for micro-propulsion systems for space applications are almost based on hydrazine. This compound, however, is highly toxic, volatile, and carcinogenic. Therefore, it demands high costs in safety measures at the whole process. Hence, over the years, there has been a considerable interest in Europe and in the USA in finding possible substitutes for hydrazine. ADN liquid monopropellants seem to be also a potential substitute to replace it whether for being easier to handle or for its specific impulse, 10% higher than for hydrazine (Wingborg, 2005). ADN was cited for the first time by professor Tartakowsky at the Annual Conference (ICT), in 1993 (Nagamachi *et al.*, 2009).

Simultaneously, in the USA, it was presented as a new oxidizer for rocket-solid propellants by Pak (Teipel, 2005).

ADN has the chemical formula $NH_4N(NO_2)_2$ (Squeme 1), which is of primary interest in solid-rocket propellants as a potential substitute for AP for keeping high efficiency in systems that already employ AP. The use of ADN in combination with an energetic binder can enhance the specific impulse (I_{sp}) to reach values around 2,600 Ns/kg. If a metal fuel, such as Al or AlH_3, is also incorporated to this formulation, the specific impulse can reach even higher, around 2,700 to 2,800 Ns/kg (Teipel, 2005).



Squeme 1. Chemical structure of ADN (Shaw, 1993).

Among all the possible routes for this synthesis, in this paper, it was focused on the nitration of amidesulphonates. On one hand, the reaction can be carried out in the absence of organic solvents (Squeme 2). However, on the other hand, it must take place in a strong acid medium, which can also lead to

$$KO_3SNH_2+HNO_3 \rightarrow KHSO_4+NH_4N(NO_2)_2+H_2O$$

Squeme 2. Reaction involved in the route of ADN synthesis, by nitration of amidesulphonates (Teipel, 2005).

the decomposition of the dinitramide. This synthesis is completed by recovering ADN from the reaction medium followed by purification. This process was developed by FOI and Nexplo and now it has been used for commercial production (Teipel, 2005).

Several techniques are cited in the literature for characterization of ADN (Christe *et al.*, 1996; Santhosh *et al.*, 2002). Christe *et al.* (1996) have used Raman spectroscopy and infrared, in the middle infrared (MIR) region, to characterize ADN. The infrared (IR) bands attribution were: 1526 cm^{-1}, attributed to the unsymmetrical stretching (υ_a) in phase of group NO_2; 1344 cm^{-1} of symmetrical stretching (υ_s) in phase of group NO_2; and 1181 cm^{-1} (υ_s out of phase of group NO_2).

Santhosh *et al.* (2002) have used ultraviolet spectroscopy (UV), IR, and thermal methods and they have observed that the solution of ADN presents strong absorption with maximum at 284 nm under UV, and that IR spectra showed characteristic bands at 3136 cm^{-1} (υ N-H of NH_4^+), 1531 cm^{-1} (υ_a in phase of group NO_2), and 1344 cm^{-1} (symmetrical stretching (υ_s) in phase of group NO_2).

In this paper, ammonium sulfamate and sulfamic acid were used as starting materials for obtaining ADN in different route conditions for these syntheses. The proportion of reactants and purification methods were tested, and the resulting samples were analyzed in the MIR region. For the synthesis in which ammonium sulfamate was used as a starting reactant, the samples were also analyzed by near infrared (NIR) spectroscopy. Thus, it was expected to cover a more ample zone in the spectral region of IR, which is meant for a suitable characterization of the resulting products.

EXPERIMENTAL

Routes of synthesis for obtaining ADN

The routes applied in this study make use of sulfamic acid and ammonium sulfamate as starting reactants. The route conditions for these syntheses were adapted from Vörde and Skifs (2005) and Langlet, Ostmark and Wingborg (1997).

Synthesis route 1 (using sulfamic acid)

ADN 40F/20 (40 mL HNO_3 Fuming/20 mL H_2SO_4)

Nitration

For nitration of sulfamic acid, 40 mL of fuming nitric acid (96%) and 20 mL of sulfuric acid (95%) were mixed in a 500 mL 3-neck-round flask. The mixture was cooled down to -37ºC in a cryogenic bath (Ultra Termostato Criostato of Optherm, with controller HAAKE DC3). It was used 40% $CaCl_2$ in water as the refrigerant fluid. Sulfamic acid was added in small portions of 0.5 to 1.0 g (total=5 g) under strong agitation (250 rpm) with a mechanical stirrer, the mixture was left to react for 1.5 hour at the temperature ranging from -30 to -35ºC.

Neutralization

The reaction was conducted for 1.5 hour, then the whole mixture was transferred to a 1 L erlenmeyer, containing 85g small pieces of ice (deionized water) and equipped with magnetic stirrer. The erlenmeyer, was immersed and surrounded by pieces of ice inside a large flask. The aim of this procedure was to dilute the mixture before adding base, which can prevent it from reacting strongly with the acid mixture. Ammonium hydroxide was slowly dropped with a 200 mL burette, aiming at preventing the temperature inside the mixture from surpassing 0º C. The pH of solution was measured with litmus. Ammonium hydroxide was added until the solution became slightly alkaline. It was used 142.5mL of base for the neutralization.

Purification

The mixture provided from the neutralization step was transferred to a three-neck-round flask, and the liquid was left to vaporize in a bath at 35°C under vacuum (maximum capacity). After 80% of the liquid was vaporized, the round flask was removed and, with the aid of a spatula, the precipitated stuck on the flask was scratched out. This material was slightly ground and left inside the round flask. Acetone was added to promote dissolution of ADN. The round flask was manually shaken several times for 15 minutes. The content in the round flask was filtered with a paper-filter funnel, which was transferred to an erlenmeyer and newly cooled in cryostatic bath. White precipitated was formed again, which was finally analyzed by the IR. This cooling and filtering process was repeated for three times. Every filtered collected with acetone was placed in a warm bath and kept at nearly -33ºC under intense vacuum until the whole acetone was vaporized. The left liquid was a yellow solution highly concentrated. This solution was then transferred to a watch glass and left to vaporize at ambient temperature.

Synthesis route 2 (using ammonium sulfamate)

Nitration

Nitration has been conducted at temperatures ranging from -35 to -37º C in all the experiments. Concentration of acids, time of reaction, and mass of ammonium sulfamate have been varied, according to Table 1.

Neutralization

The resulting mixtures from the nitration were diluted and cooled with 100g of ice, except ADN 40F/20 (40mL HNO_3 Fum/20mL H_2SO_4) with "no dilution", in which this step was eliminated. The mixtures were neutralized with 70 to 140mL of ammonium hydroxide. The neutralization was carried out by dropping NH_4OH straight into the round flask, and immersed in a cryostatic bath at -35ºC.

Purification

For the synthesis of ADN 38/12 and ADN 30F/30, granular active coal (GAC) was used to extract the final product. It was previously boiled in acetone and it was dried inside an oven at 130°C for six hours. Adsorption of ADN was carried out by pouring the slightly alkaline mixture in a 500 mL florence flask with 20 or 11g of GAC, and shaken

Table 1. Data regarding the nitration – Syntheses routes 2.

Synthesis ADN	$NH_2SO_3NH_4$ (g)	HNO_3 (%)	H_2SO_4 (%)	Time (minutes)
38/12	17	65	98	60
30 F/30	5	95	98	90
40 F/20 no dilution	5	95	98	30
35 F/35 F	5	95	>100(SO_3)	90
40 F/20	5	95	98	90

manually for 10 or 45 minutes, respectively in each case. The mixture was filtered in a Buchner funnel and washed with approximately 300 mL of deionized water (Santhosh *et al.*, 2002). Desorption of ADN was carried out by re-circulating acetone through a Soxhlet, in which GAC was covered by a paper-filter. Vacuum and temperature were controlled in order to keep it at 60° or 50° C, respectively, in each case. The rest of the material inside the round flak was analyzed by IR.

For the synthesis of ADN 40F/20 with "no dilution", ADN 35F/35F and ADN 40F/20, the neutralized solution was filtered and the precipitated was washed with acetone. The resulting liquid turned out yellow. A large amount of precipitated lying on the filter was discarded. Water formed during the reaction and acetone in the filtered were removed at 40º C under vacuum. The purification process was repeated for three times, and the same yellow product was obtained each time. This product was left on a watch glass inside a desiccator under vacuum, and then it was analyzed by IR.

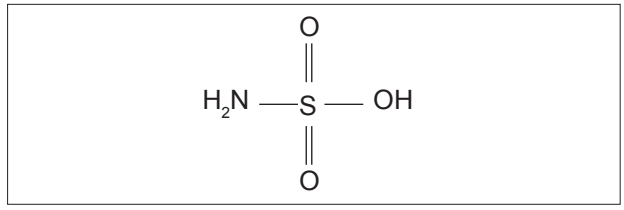
Analysis by IR

Spectrum one spectophotometer of PerkinElmer had been used in this paper, in the region ranging from 4000 to 400 cm^{-1}, resolution 4 cm^{-1} and gain 1. The samples were prepared according to the trasmission technique, with KBr pellets with concentrations around 0.5: 400 mg. For the NIR analysis, the samples were analyzed with the same equipment in the region ranging from 7800 to 4000 cm^{-1}, under the same conditions.

RESULTS AND DISCUSSION

MIR analysis of the starting material used in the route 1

Squeme 3 shows the chemical structure of the starting material used in the referred route of synthesis



Squeme 3. Sulfamic acid structure formula (NH_2SO_3H).

Figure 1 presents the sulfamic acid MIR spectrum, whose bands are at the same wave numbers found in the spectrum from the reference in the literature

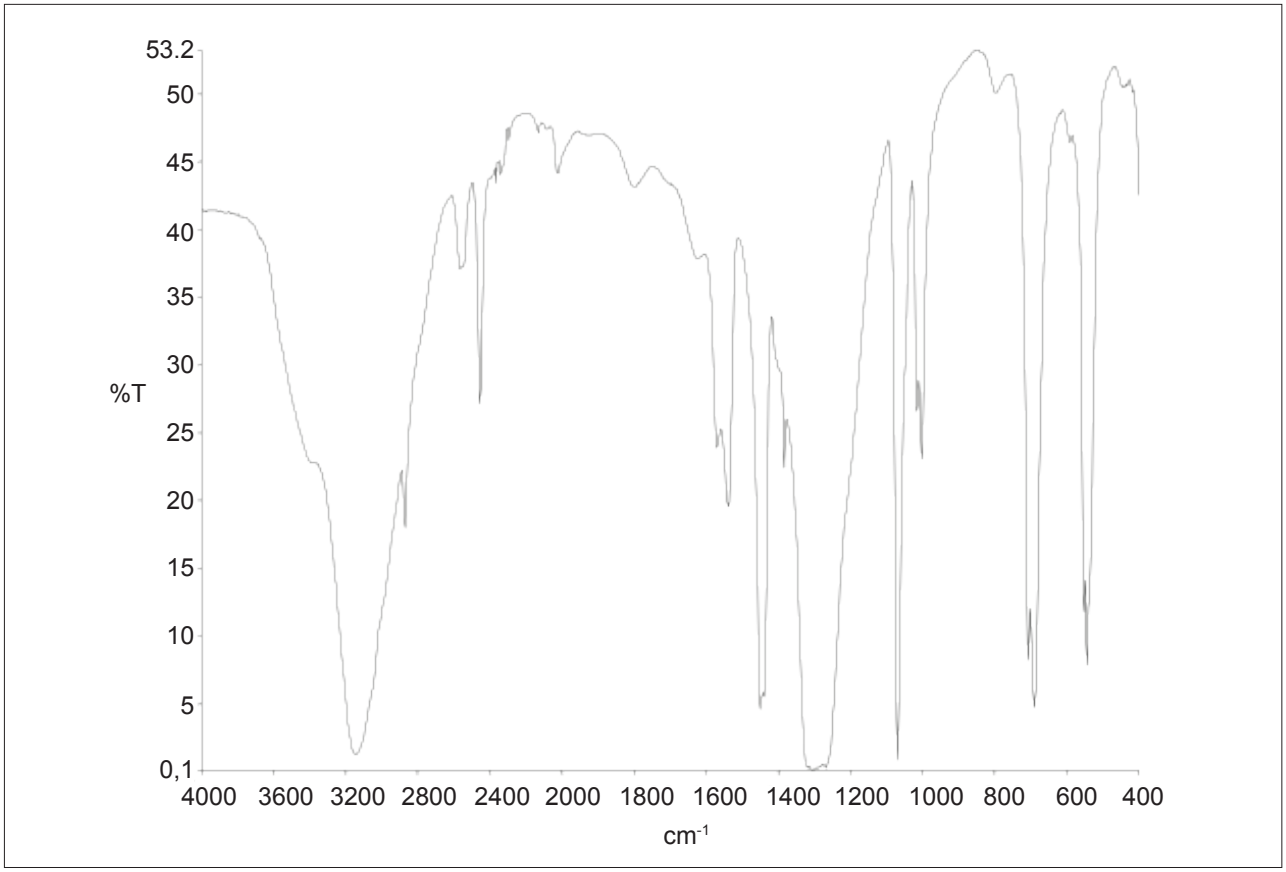


Figure 1. Sulfamic acid MIR spectrum.

(SciFinder®, 2011). The characteristic bands are likely attributed (Silverstein and Webster, 2000; Urbanski *et al.*, 1977; Smith, 1979) to their functional groups and they are situated at: 3151 cm^{-1} (NH); 2455 cm^{-1} (OH); and 1451, 1306, 1070 cm^{-1} (S=O). The absorption at 710 and 690 cm^{-1} can likely be associated with the group S-O.

MIR analysis of the resulting product in the route 1 (using sulfamic acid): ADN 40F/20 (40 mL HNO_3 Fuming/20 mL H_2SO_4)

The resulting sample was named ADN 40F/20 (40 mL HNO_3 Fuming/20 mL H_2SO_4) – sulfamic acid. Figure 2A shows the MIR bands of the sample. It has been observed more intense bands around 3420, 3130, 1710 and 1380 cm^{-1}.

According to Christe *et al.* (1996) and Santhosh *et al.* (2002), those bands are characteristics of ADN at: 3136 e 1380 cm^{-1} (NH_4^+); 1531, 1344, 1238 and 1181, 828 and 738 cm^{-1} (NO_2); 1025 and 954 cm^{-1} (N_3). However, in the MIR spectrum (Fig. 2A), only one band at 1380 cm^{-1} can be pointed out, which situates in the region characteristic of Group NH_4^+ of ADN. The MIR spectrum of the resulting sample is more similar to ammonium nitrate (Fig. 2B), indicating that, according to this route, this product is basically ammonium nitrate, which is likely obtained owing to the degradation during the purification process of the synthesis product.

MIR analysis of the starting material of route 2

Squeme 4 shows the chemical structure of the starting material used in this route.

Figure 3 shows the MIR spectrum of ammonium sulfamate, whose bands are at the same wave numbers found in the reference (SciFinder®, 2011). The characteristic bands attributed to their functional groups are situated at: 3288 cm^{-1} (NH); 3195 and

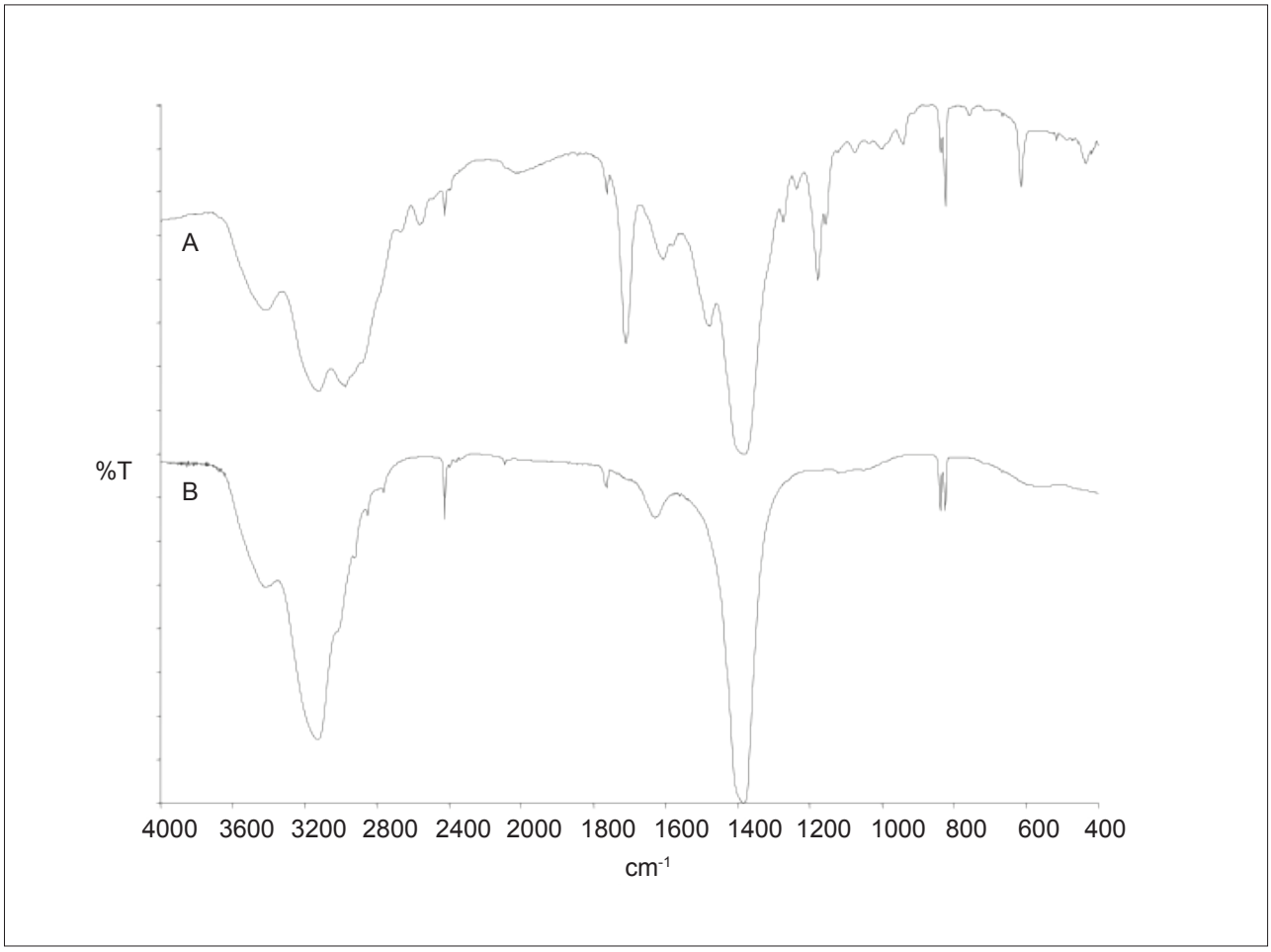
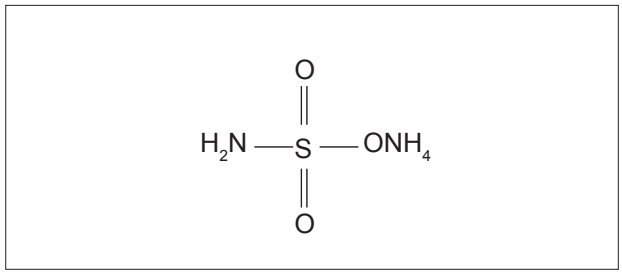


Figure 2. (A) MIR spectrum of the product obtained in synthesis 1 by using sulfamic acid: ADN 40F/20 (40 mL HNO_3 Fuming/20 mL H_2SO_4); (B) MIR spectrum of ammonium nitrate – Lot n. 171169 – B. Herzog.



Squeme 4. Ammonium sulfamate structural formula ($NH_2SO_3NH_4$).

1400 cm^{-1} (NH_4^+). The absorption ranges from 1260 to 1000 cm^{-1}, it is likely associated with the groups S=O e S-O.

MIR analysis of the resulting product in route 2 (using ammonium sulfamate): ADN 38/12 (38 mL HNO_3/12 mL H_2SO_4)

Like route 1, in route 2 any characteristic bands of ADN were found. Instead, only one band at 1380 cm^{-1}, characteristic of the group NH_4^+, was found. The spectrum of the resulting product was more similar to ammonium nitrate, which presents large bands.

MIR analysis of the resulting product in route 2 (using ammonium sulfamate): ADN 30F/30 (30 mL HNO_3 Fuming/30 mL H_2SO_4)

The resulting product presents bands at 3118 cm^{-1} (NH_4^+); 1377 cm^{-1} (NH_4^+); 1192 cm^{-1} (NO_2); 1028 cm^{-1} (N_3); 825 cm^{-1} (NO_2) and 763 cm^{-1} (NO_2), pointing out the presence of some characteristic absorptions of ADN, including contamination with ammonium nitrate, according to what was observed in the previously obtained products (Fig. 4).

MIR analysis of the resulting product in route 2 (using ammonium sulfamate): ADN 40F/20 (40 mL HNO_3 Fuming/20 mL H_2SO_4) "no dilution"

The resulting product presents bands at 3121 cm^{-1} (NH_4^+); 1384 cm^{-1} (NH_4^+); 1177 cm^{-1} (NO_2) and 825 cm^{-1} (NO_2), indicating the presence of few bands related to ADN besides contamination with other products (Fig. 5).

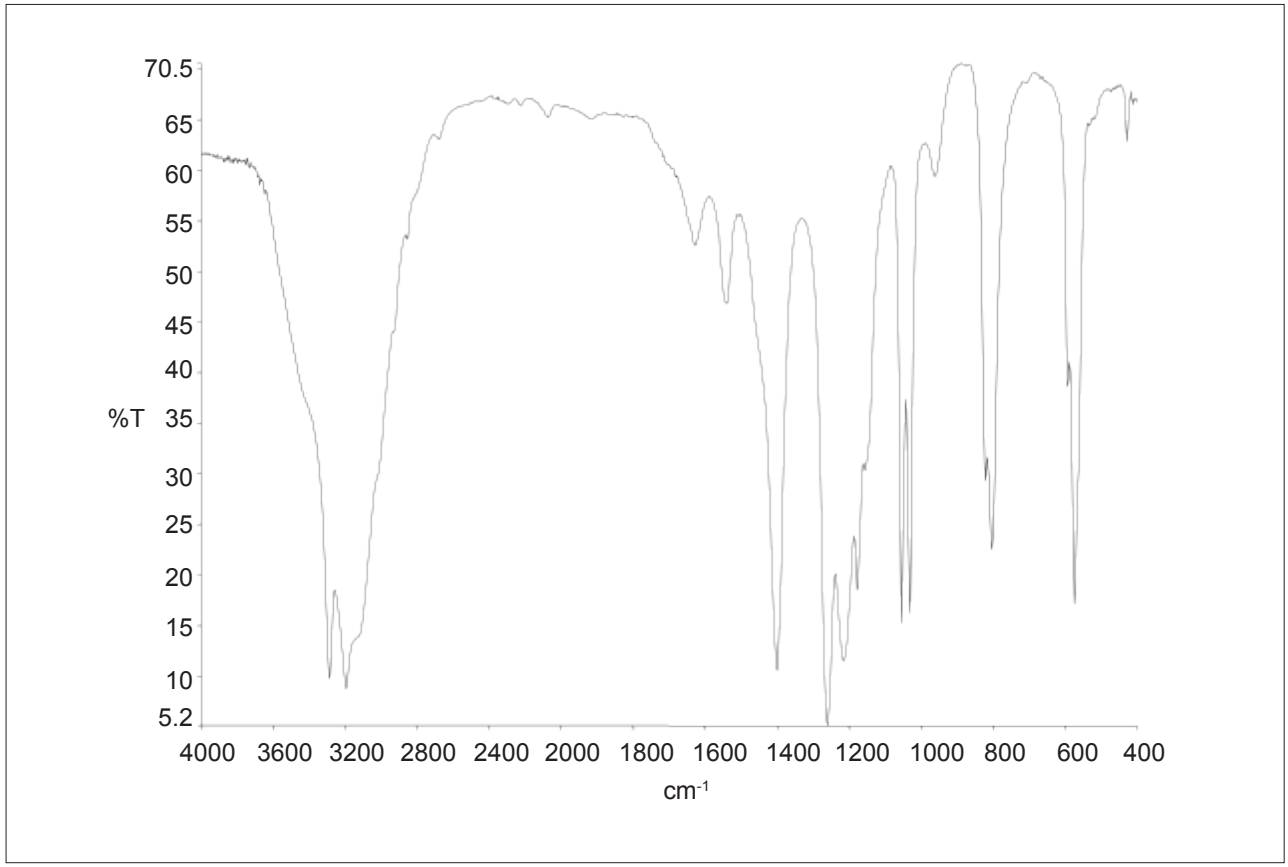


Figure 3. MIR spectrum of ammonium sulfamate.

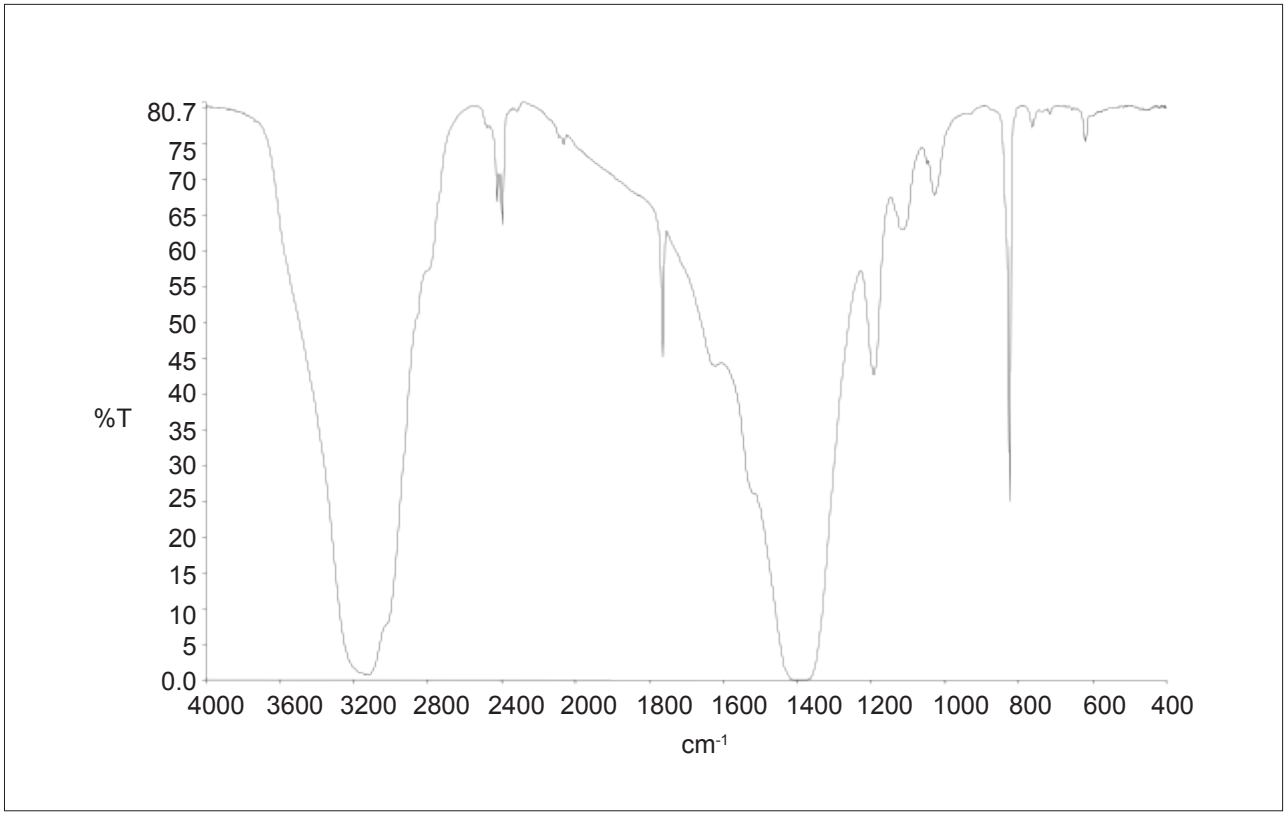


Figure 4. MIR spectrum of ADN 30F/30.

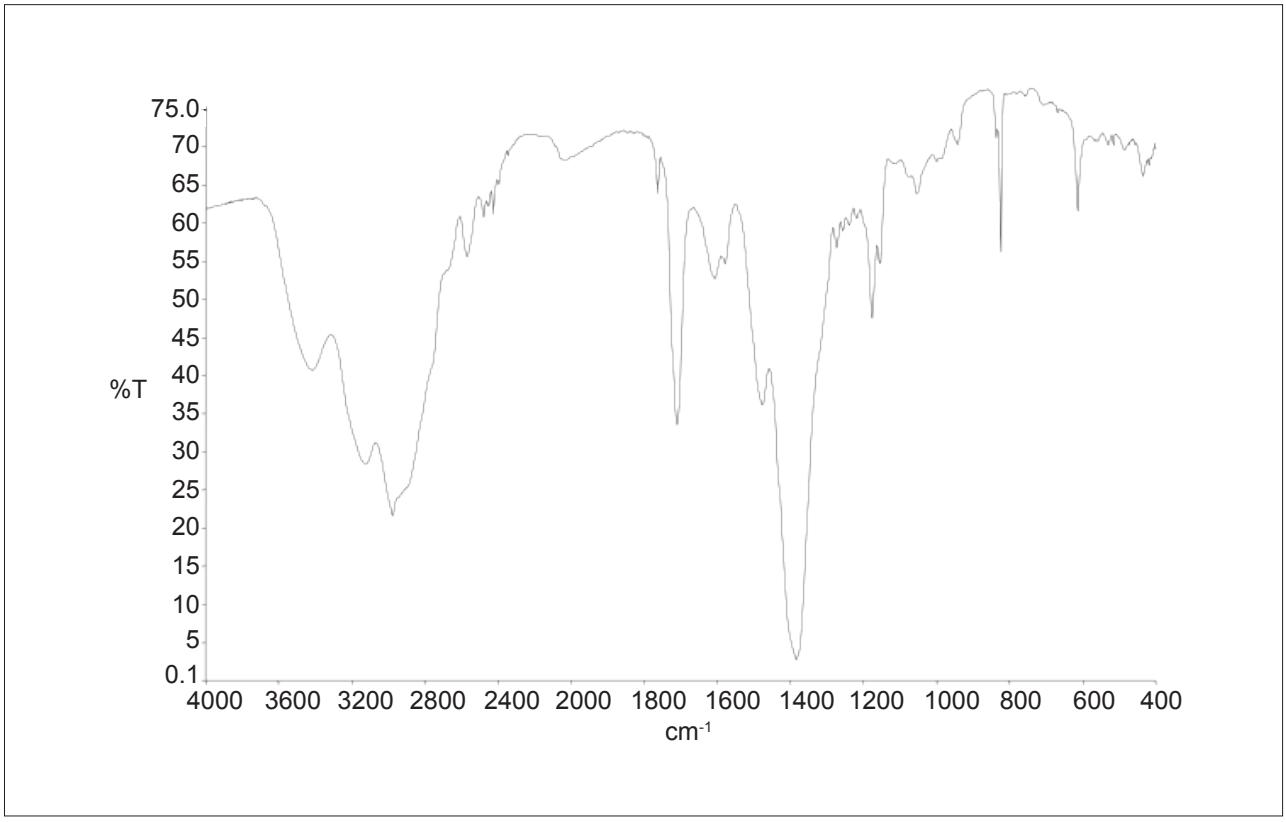


Figure 5. MIR spectrum of ADN 40F/20 “no dilution”.

MIR analysis of the resulting product in route 2 (using ammonium sulfamate): ADN 35F/35F (35 mL HNO_3 Fuming/35 mL H_2SO_4 Fuming)

The procedure applied for this synthesis did not provide any samples.

MIR and NIR analysis of the resulting product in route 2 (using ammonium sulfamate): ADN 40F/20 (40 mL HNO_3 Fuming/20 mL H_2SO_4)

Characteristic bands employed in this route to identify ADN in the MIR region were: 3129 cm^{-1} (NH_4^+); 1384 cm^{-1} (NH_4^+); 1537 cm^{-1} (NO_2); 1344 cm^{-1} (NO_2); 1209 and 1177 cm^{-1} (NO_2); 1032 cm^{-1} (N_3); 954 cm^{-1} (N_3); 828 cm^{-1} (NO_2); 762 cm^{-1} (NO_2); and 732 cm^{-1} (NO_2). The MIR spectrum was compared to one from the literature (Christe *et al.*, 1996) and shows good agreement (Fig. 6).

NIR analysis was conducted in this case since MIR characteristics bands of ADN were observed, which allows a more ample characterization of the resulting product (Fig. 7). Some number of bands at 5185 and 4672 cm^{-1} were seen. They were situated in the combination region of composed bands that present groups NH (Goddu, 1960).

CONCLUSION

Analysis conducted by FT-IR spectroscopy has proved a very effective way to characterize ADN, starting reactants, and sub-products. All characteristic bands for these compounds could be found, besides the resulting spectra, which also allow concluding that ADN 40F/20 (40 mL HNO_3 Fuming/20 mL H_2SO_4) route is the most promising to synthesize ADN among the alternatives tested in this paper. The result was only concluded based on IR spectroscopy. However, more researches must be done in order to learn about purity, yield, and how to deal with the large amount of sub-products.

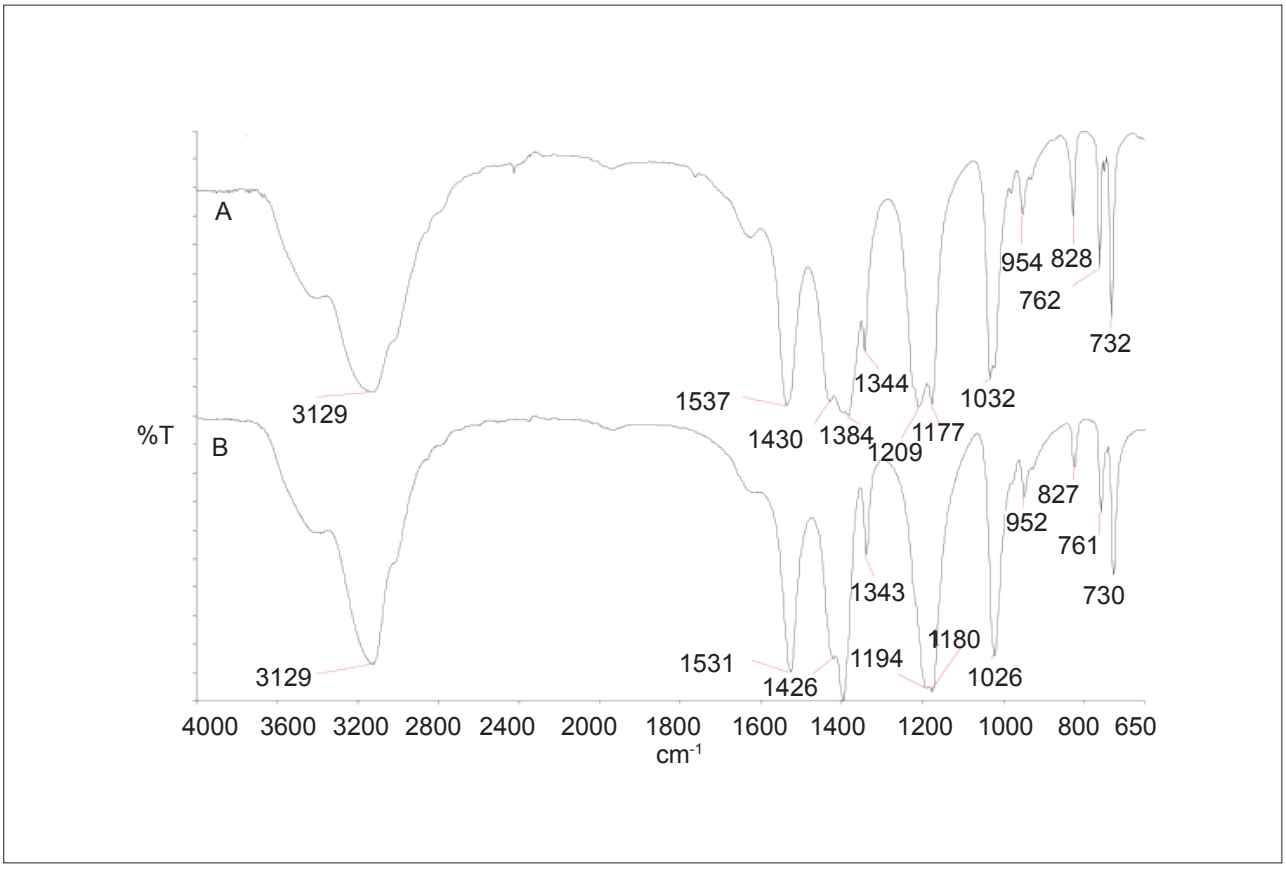


Figure 6. Comparison of IR (MIR) spectra. (A) ADN 40F/20 and (B) ADN reference.

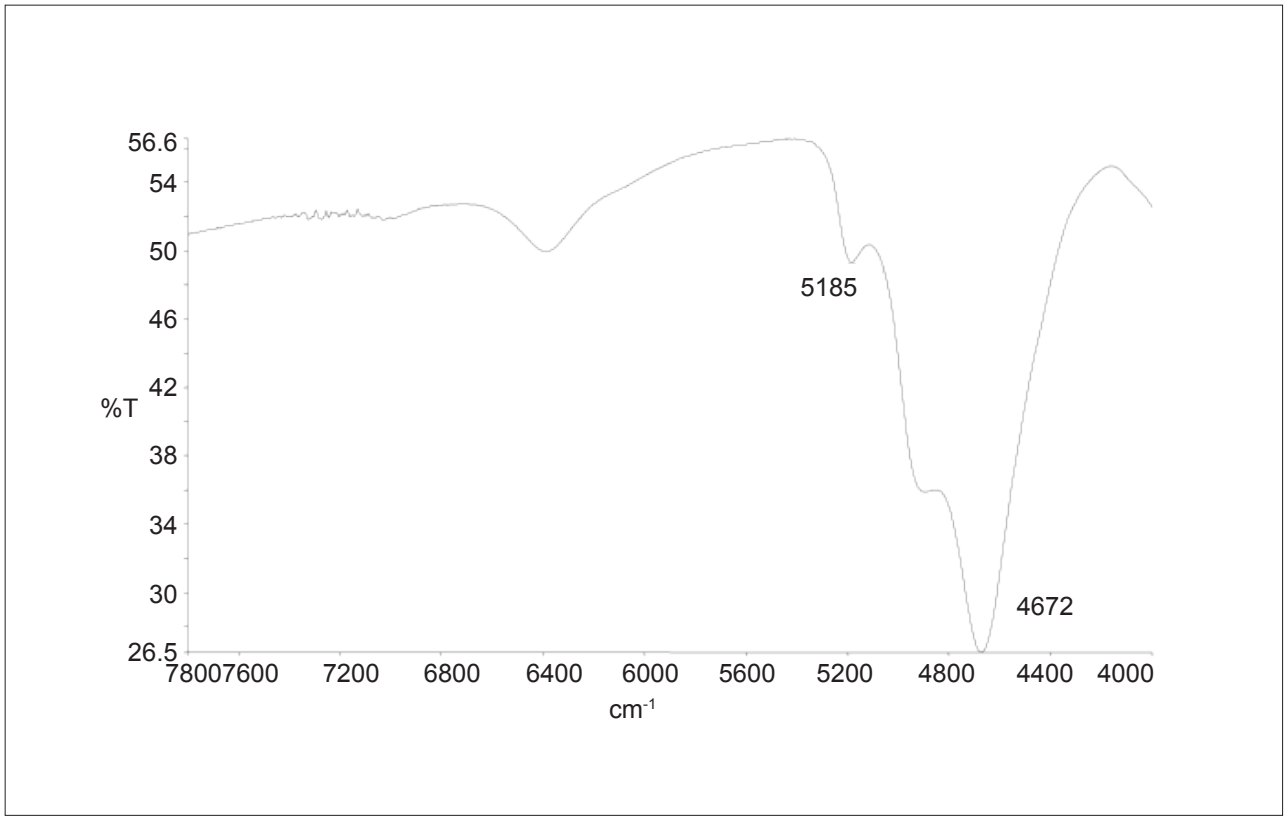


Figure 7. Partial NIR spectrum of ADN 40F/20.

REFERENCES

Christe, K. O. *et al.*, 1996, "The Dinitramide Anion, $N(NO_2)_2^-$", Phillips Laboratory, Propulsion Directorate, Edwards Air Force Base, California.

Goddu, R., 1960, "Near-Infrared Spectrophotometry", Advances Analytical Chemistry and Instrumentation, Vol. 1, p. 347-425.

Langlet, A., Ostmark, H., Wingborg, N., 1997, "Method of preparing dinitramidic acid and salts thereof", US Patent 5976483, FOI, Sweden.

Nagamachi, M. Y., Oliveira, J. I. S., Kawamoto, A. M., Dutra, R. C. L., 2009, "ADN – The new oxidizer around the corner for an environmentally friendly smokeless propellant", Journal of Aerospace Technology and Management, São Paulo, Vol. 01, No. 2, p. 153-160.

Santhosh, G. *et. al*., 2002, "Adsorption of ammonium dinitramide (ADN) from aqueous solutions: 1. Adsorption on powdered activated charcoal", Journal of Hazardous Materials, India, p. 117-126.

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Shaw, R. W., 1993, "Overviews of Recent Research on Energetic Materials – Advanced Series in Physical Chemistry", Singapore: World Scientific Publishung Co.

Silverstein, R. M., Webster, F.X., 2000, "Identificação Espectrométrica de Compostos Orgânicos", Rio de Janeiro: Livros Técnicos e Científicos S.A.

Smith, A.L., 1979, "Applied infrared spectroscopy", New York, John Wiley & Sons.

Teipel, U., 2005, "Energetic Materials. Particle Processing and Characterization", WILEY-VCH Verlag GmbH & Co., Weinheim.

Urbanski, J. *et al.*, 1977, "Handbook of Analysis of Synthetic Polymers and Plastics", John Wiley & Sons, New York.

Vörde, C., Skifs, H., 2005, "Method of producing salts of dinitramidic acid", WO/2005/070823, Sweden.

Wingborg, Niklas, *et al.*, 2005, "Characterization and Ignition of ADN-Based Liquid Monopropellants", Proceedings AIAA/ASME/SAE/ASEE Joint Propulsion, 41th Conference, Arizona.

Wingborg, N., *et al.*, 2010, "Development of ADN-based Minimum Smoke Propellants", Proceedings AIAA/ASME/SAE/ASEE Joint Propulsion, 46th Conference, Nashville.