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# Burning Rate Modifiers to Tailor Combustion of ADN/AN-Based Solid Propellants

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**This paper presents a study, carried out in the framework of the H2020 european project GRAIL, on thermal and catalytic decomposition of a solid ADN/AN mixture. Decomposition pathways of the mixture are proposed thanks to thermal analyses coupled with mass spectrometry. Thirty-four burning rate modifiers have been investigated using thermal analyses. This led to the selection of five candidates considered as promising additives: nano-CuO, CuO, Cr<sub>2</sub>Cu<sub>2</sub>O<sub>5</sub>, ZnO and ferrocene. Finally, a bicatalytic system with nano-CuO and ferrocene was considered for possible improvement of the decomposition. It prove to display a much attractive behavior towards the decomposition of this oxidizer mixture.**

## Nomenclature

ADN	= Ammonium dinitramide
AN	= Ammonium nitrate
BRM	= Burning rate modifier
DTA	= Differential thermal analysis
MS	= Mass spectrometry
TGA	= Thermogravimetric analysis

## I. Introduction

Ammonium perchlorate (AP) is widely used as an oxidizer in the formulation of solid propellants for launcher boosters. However, its decomposition leads to the formation of hydrochloric acid which is toxic and may cause environmental issues such as ozone depletion. The latter could lead in the future to a regulation of the space transportation [1]. Thus, the European H2020 project GRAIL aims to replace this oxidizer by a green component. A mixture of ammonium dinitramide (ADN) and ammonium nitrate (AN) allowing at least equivalent performance to those obtained with AP was selected as a green alternative. The replacement of this component implies to redesign the global composition of the propellant and more particularly to find adapted burning rate modifiers (BRM) in order to tailor the combustion [2].

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AN has been widely studied as an oxidizer for rocket propellant [3, 4]. Further, it is environmentally friendly and low cost. However, it displays some drawbacks such as phase transition near room temperature, high hygroscopicity; it has a low burning rate and releases low amounts of energy. The latter can be correlated in part to the endothermic step frequently observed during its thermal decomposition. It is a well-known phenomenon which corresponds to the proton transfer between ammonium cation and nitrate anion of the oxidant.

Contrarily to AN, few studies on BRM dedicated to ADN-based propellant can be found in the literature. Fujisato et al. [5] studied the effect of different additives: Al, Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, NiO, Cu(OH)NO<sub>3</sub>, CuO, nano-CuO and nano-Al (Alex). Decomposition temperature is lowered with nickel oxide and copper oxide as well as with borocarbonitride materials. In addition, and as expected, the use of nano-CuO instead of CuO leads to a higher 20 °C decrease of the onset temperature with a loading of 2 parts (corresponding to 2 % of additive in mass). CuO also demonstrated an enhancement of the burning rate especially at low pressure (20 mm s<sup>-1</sup> below 1 MPa) which makes it the most effective additive among those tested in the study. It is explained by catalyzed decomposition in the condensed phases. Copper oxide has recently been studied by Matsunaga et al. [6] in order to tentatively elucidate the role of the catalyst in the decomposition mechanism. This study was carried out using TG-DTA-MS, TG-DTA-IR, DSC (with sealed cells) and a hot stage equipped with a microscope for visual inspection during the reaction (phase change, color etc.). They highlighted that catalytic reaction begins essentially with ADN melting. Finally, Li and Yang [7] showed that carbon nanotubes (CNT), iron oxide supported on carbon nanotubes (Fe<sub>2</sub>O<sub>3</sub>/CNT), as well as iron and copper supported on carbon nanotubes (Fe-Cu/CNT) have a catalytic effect and lower the decomposition temperature by 18.3, 12.1 and 11.6 °C, respectively, when 1 wt.-% of catalyst is added. They also showed that the addition of 3 wt.-% of catalyst leads for the nanotubes alone, the supported iron oxide and the supported bimetallic, to a pressure exponent decrease from 0.81 to 0.36, 0.67 and 0.75 while the burning rate of ADN at 4 MPa increases from 30.5 to 50.6, 39.7 and 38.8 mm s<sup>-1</sup>, respectively.

In this study, both thermal and catalytic decomposition of ADN/AN were investigated. Several inorganic and organic metal salts, metal oxides as well as nano-metal oxides were evaluated as burning rate modifier candidates of an ADN/AN mixture displaying ratio close to the targeted final formulation. For this, DTA-TGA analysis was chosen as an adapted preliminary evaluation tool which allows comparison of the ADN/AN/BRM behaviors compared to that of pure ADN/AN mixture. The selection of BRM was based on three criteria: lower the decomposition temperature, promote an exothermic decomposition and accelerate the decomposition rate of ADN/AN mixture. Among the BRM tested, five of them (nano-copper, copper, copper-chromite, zinc and ferrocene) have shown promising behavior towards the decomposition of this oxidant mixture.

## II. Materials and methods

Samples are prepared using AN (Yara AB), 99 % non-prilled ADN (EURENCO AB) or 99 % prilled ADN (EURENCO) and different BRM which are listed in Table 1. Mixtures were prepared by mechanical mixing of 59.4 wt.% ADN, 34.0 wt.% AN, and 6.6 wt.% of BRM, respectively, using a rotating platform. Targeted masses to prepare the ternary mixtures ADN/AN/BRM with the aforementioned mass compositions are 63.6, 36.4 and 7.1 mg, respectively. Prior to mixing, ADN, AN and BRM are ground in an agate mortar and sieved to retrieve particles with a diameter between 40 µm and 100 µm. If needed, components are then stored separately in a ventilated oven at 50 °C for 4 h. Mixtures are prepared manually in a glove box. Powders are then introduced in glass vials (volume = 4 mL) along with 3 glass spheres (~ 1 mm of diameter) to get better mixing and disaggregation of aggregates. The vials are then removed out of the glove box and placed onto a rotating platform, directed 30 ° downwards for 30 min and directed upwards for another 30 min relatively to the axis of the engine, so that the pill container is rotated 600 times.

**Table 1. Burning rate modifiers suppliers**

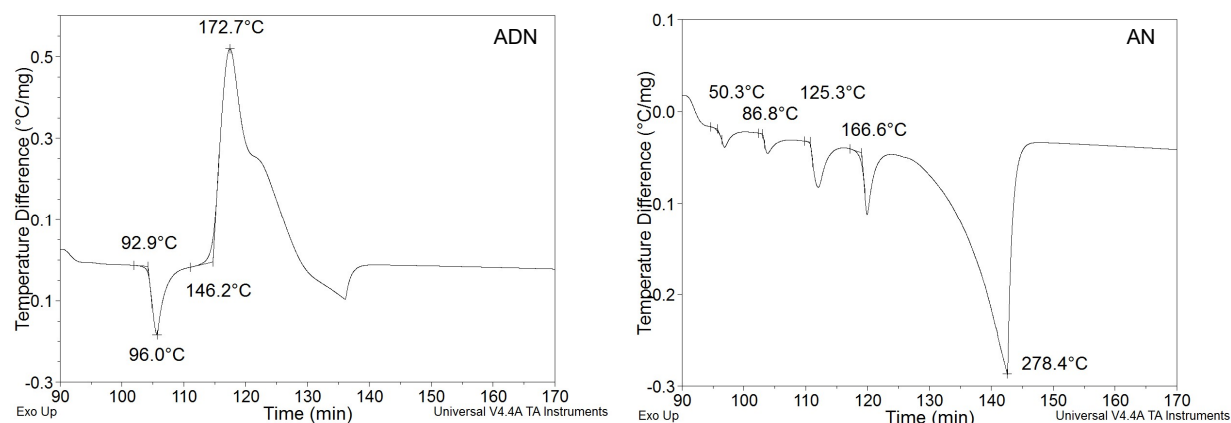
BRM	Supplier (purity)	Ballistic modifier	Supplier (purity)
nano-Fe <sub>3</sub> O <sub>4</sub>	Sigma-Aldrich	nano-ZnO	-
Fe <sub>3</sub> O <sub>4</sub>	-	ZnO	Prolabo (99%)
Fe <sub>2</sub> O <sub>3</sub> (AVIO)	Avio	Zn(C <sub>5</sub> H <sub>7</sub> O <sub>2</sub> ) <sub>2</sub>	Carlo Erba(99.5%)
FeC <sub>2</sub> O <sub>4</sub> ·2H <sub>2</sub> O	Labosi	Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	
Fe <sub>2</sub> (C <sub>4</sub> H <sub>4</sub> O <sub>6</sub> ) <sub>3</sub>	Sigma-Aldrich	Al <sub>2</sub> O <sub>3</sub>	Alfa Aesar
Fe(C <sub>5</sub> H <sub>7</sub> O <sub>2</sub> ) <sub>3</sub>	Fluka (97%)	Al(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	Aldrich (>98%)
Fe <sub>2</sub> (C <sub>4</sub> H <sub>4</sub> O <sub>6</sub> ) <sub>3</sub>	Sigma-Aldrich	2.5 %Cu/Al <sub>2</sub> O <sub>3</sub>	IC2MP
C <sub>10</sub> H <sub>10</sub> Fe	Alfa Aesar	Co(C <sub>5</sub> H <sub>7</sub> O <sub>2</sub> ) <sub>2</sub>	Aldrich (>98%)
Fe(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	Fisher (98%)	Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	Aldrich (>98%)
nano-CuO	-	K <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ·H <sub>2</sub> O	Prolabo
CuO	Prolabo	KNO <sub>3</sub>	Prolabo (99.5%)
Cu(HCO <sub>2</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	Alfa Aesar	V <sub>6</sub> Mo <sub>15</sub> O <sub>60</sub>	ICT
Cu(MeCO <sub>2</sub> ) <sub>2</sub> ·H <sub>2</sub> O	-	MnO <sub>2</sub>	-
CuC <sub>4</sub> H <sub>4</sub> O <sub>6</sub> ·xH <sub>2</sub> O	Sigma-Aldrich	MgO	-
Cu(C <sub>5</sub> H <sub>7</sub> O <sub>2</sub> ) <sub>2</sub>	Lancaster (99%)	Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	Aldrich
Cu(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	Fisher (95%)	Cr <sub>2</sub> Cu <sub>2</sub> O <sub>5</sub>	Aldrich
		Nano-FeCuZnO <sub>x</sub>	Sigma-Aldrich

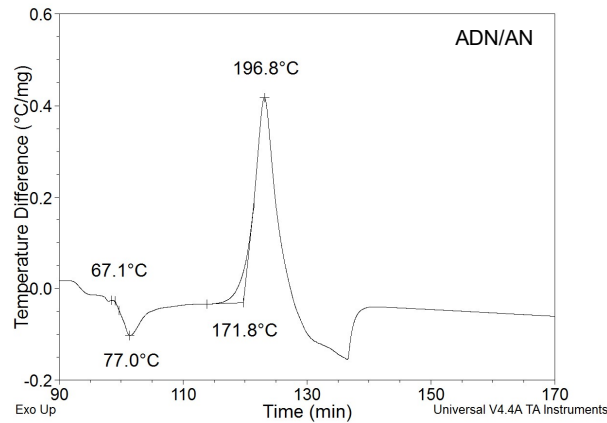
DTA-TGA apparatus was a SDT Q600 from TA instrumentations and the MS (model QGA) was supplied by HIDEN Analytical. DTA-TGA and DTA-TGA-MS (in scan mode) were performed from ambient temperature (step of 1 h 30 min) to 350 °C and 450 °C respectively with a slope of 5 °C min<sup>-1</sup> under an argon flow of 100 mL min<sup>-1</sup>. DTA-TGA-MS were also performed under an argon flow of 100 mL min<sup>-1</sup> from ambient temperature (step of 1 h 30 min) to 100 °C with a ramp of 5 °C min<sup>-1</sup>, then a step of 2 min is kept at 100 °C (the record of the defined m/z starts from the beginning of this step), finally the temperature is increased until 350 °C with a ramp of 1 °C min<sup>-1</sup> (stop of the MS record at 280 °C).

### III. Results and discussion

#### A. Thermal decomposition of ADN, AN and ADN/AN mixture

First, thermal decomposition of non-prilled ADN, AN and non-prilled ADN/AN were followed by TDA-TGA-MS.

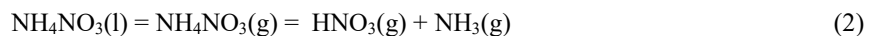
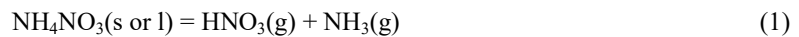




**Figure 1. DTA analysis of non-prilled ADN, AN and non-prilled ADN/AN mixture (ramp: 5 °C min<sup>-1</sup>)**

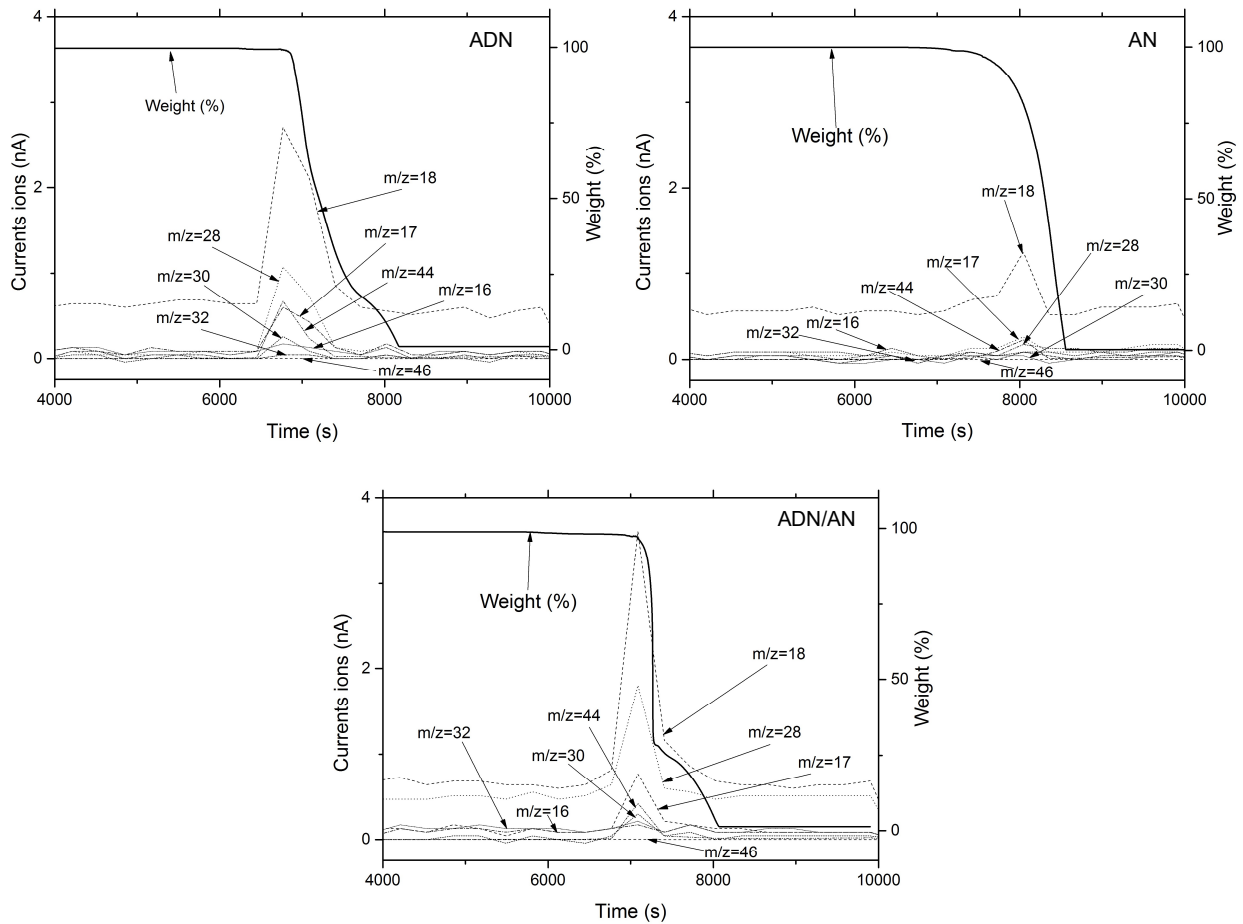
Temperature difference evolution vs. time as depicted in Figure 1 shows that for pure ADN, the fusion onset temperature is equal to 92.9 °C. Previous studies showed that decomposition of ADN alone in closed conditions proceeds in two steps. The first one consists in the decomposition of ADN followed by a second exothermic peak due to the subsequent decomposition of AN [3,8]. The endotherm could be attributed either to the vaporization of water [9] or to the one of AN.

As expected [3], solid phase transitions are visible for pure AN. The IV → II crystalline phase transition at 50.3 °C, III → II at 86.8 °C, II → I at 125.3 °C. AN melting starts at 166.6 °C. Then, a wide endothermic peak is observed. This event could be attributed to the hydrogen transfer from the ammonium cation to the nitrate anion of AN, thus leading to the formation of ammonia and nitric acid and their subsequent evaporation which is characterized by an endothermic event (Eq. 1) or to the evaporation of NH<sub>4</sub>NO<sub>3</sub>(l) (Eq. 2) which can be accompanied by the hydrogen transfer in the gas phase. Recent works have demonstrated, via the study of NH<sub>4</sub>NO<sub>3</sub> sublimation, the presence of stable NH<sub>4</sub>NO<sub>3</sub>(g) molecules [10,11]. In addition, the second step of the latter pathway (Eq. 2), corresponds to an enthalpy variation of 98 ± 9 kJ mol<sup>-1</sup> [10].



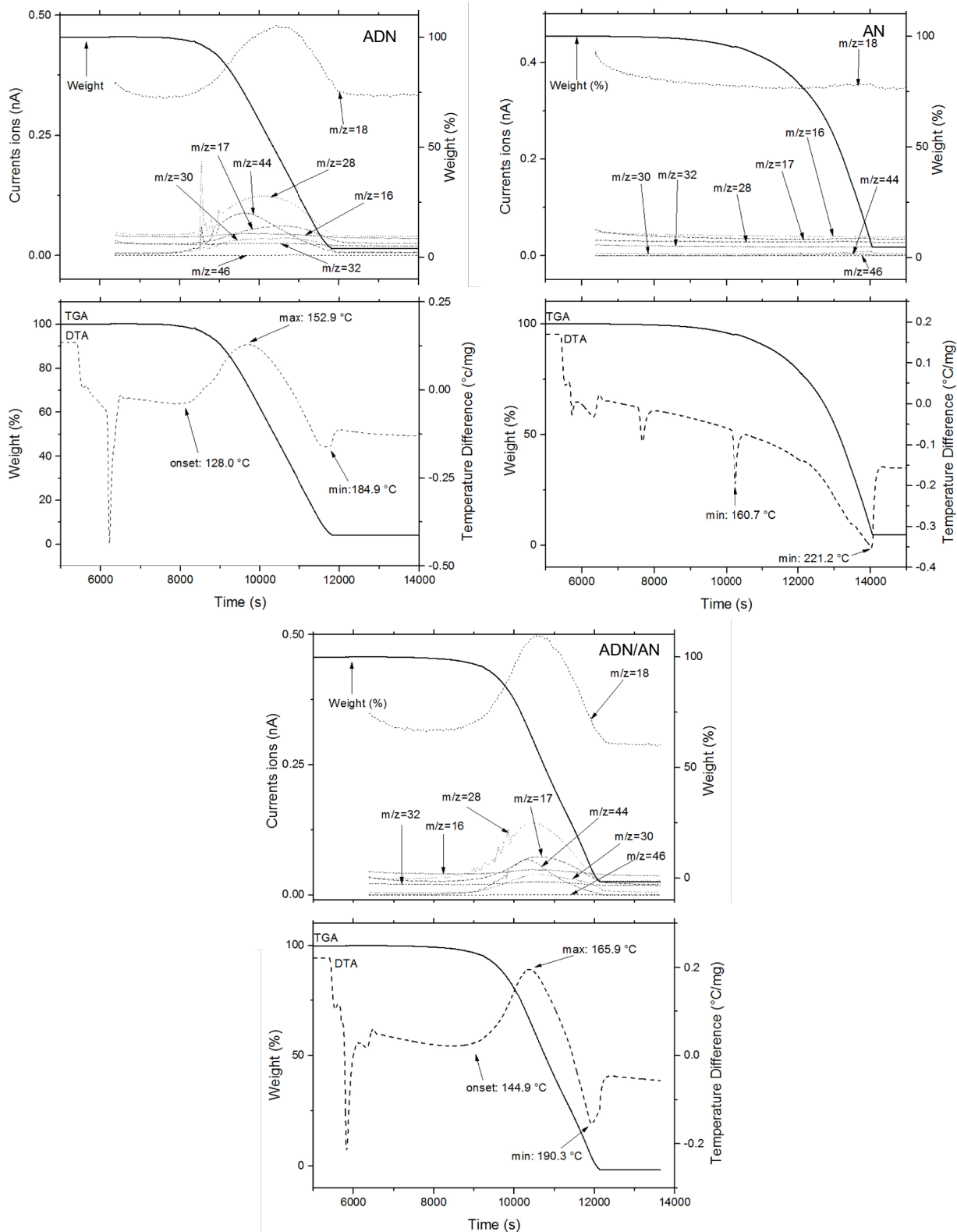
The thermal decomposition profile of the ADN/AN mixture is close to the ADN alone. The oxidizer mixture shows, after an endothermic peak due to the IV → II phase transition of AN at 55.3 °C followed by a second endothermic peak at 67.1 °C related to the eutectic melting, that the decomposition of the mixture occurs in an at least two-step process from 171.8 °C. Results show that the second exothermic peak almost disappeared and that the area of the entire exothermic event seems to decrease. This phenomena could be due to the presence of AN in the mixture in quite a high proportion. Thus, the proportion of AN evaporating or sublimating (hydrogen transfer from the ammonium cation to the nitrate anion of AN followed by the evaporation of the nitric acid and ammonia formed) compared to the one decomposing could increase.

MS analyses have been performed by scanning the mass to charge ratios from 1 to 200 during thermal analyses (Figure 2). The variation of ion parents and fragments (detected or supposed to be detected) m/z = 16, 17, 18, 28, 30, 32, 44, 46 intensities along with mass loss are drawn vs. temperature in Figure 2. Results highlight the release of three products during non-prilled ADN, AN and non-prilled ADN/AN mixture decomposition, namely: H<sub>2</sub>O, N<sub>2</sub> and N<sub>2</sub>O. Ion parents and mass fragments assigned to H<sub>2</sub>O (m/z = 17 and 18), N<sub>2</sub> (m/z = 28) and N<sub>2</sub>O (m/z = 30, 44) are monitored for the oxidizers alone and for the mixture. However, NO<sub>2</sub> (m/z = 30, 46) was not observed contrarily to the results obtained using the same technique to characterize the decomposition of pure ADN [6].



**Figure 2. MS analysis of non-prilled ADN, AN and non-prilled ADN/AN mixture (ramp:  $5\text{ }^{\circ}\text{C min}^{-1}$ )**

The analyses of the pure components and of their mixture was then performed at a lower ramp of  $1\text{ }^{\circ}\text{C min}^{-1}$  during the decomposition event with recording of the signals from fragments 16, 17, 18, 28, 30, 32, 44 and 46 only, in order to obtain a better accuracy of the measurement (by increasing of the analysis frequency). Results are presented in Figure 3.



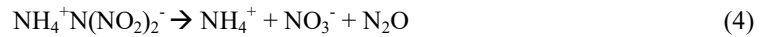
**Figure 3.** DTA-TGA-MS analysis of prilled ADN, AN and prilled ADN/AN mixture (ramp:  $1^\circ\text{C min}^{-1}$ )

The analyses of the samples using a lower heating ramp confirm the presence of the products observed before. For AN, very few amounts of decomposition products are detected showing that evaporation is favored when decreasing the temperature slope. However, the expected ammonia, following Eq. 1, is observed only as traces. This fact supports the involvement of the first equilibrium proposed in Eq. 2 between  $\text{NH}_4\text{NO}_3(\text{l})$  and  $\text{NH}_4\text{NO}_3(\text{g})$ . Thus, the main reaction occurring for AN in such conditions seems to be as followed:



Another explanation could be that, the supposed total recombination of ammonia and nitric acid occurred before their detection and should be facilitated and explained thanks to the release of gaseous  $\text{NH}_3$  and  $\text{HNO}_3$ , not as separate gases but as a probable complex  $\text{H}_3\text{N} \cdots \text{HNO}_3(\text{g})$ . This intermediate equilibrium is proposed by Zhu *et al.* [12] for ammonium salts, and calculated with an ammonium chloride system.

Both prilled ADN and prilled ADN/AN shows perturbation in the first period of the decomposition. The first products to be observed correspond to  $\text{N}_2\text{O}$  ( $m/z = 44$ ) followed by  $\text{N}_2$  ( $m/z = 28$ ) and  $\text{H}_2\text{O}$  ( $m/z = 18$ ).  $\text{NH}_3$  seems to be present as traces ( $m/z = 17$ ). This observation supports the observations made by Oxley *et al.* [9] and Vyazovkin and Wight [13] related to a decomposition mechanism involving mainly direct formation of  $\text{N}_2\text{O}$  without formation of dinitramic acid in the condensed phase. This should follow, in agreement with the authors cited above, this ionic pathway:



This first step is followed by the formation of  $\text{N}_2$  and  $\text{H}_2\text{O}$  which should originate from ammonium nitrate. Oxley *et al.* [9], stated that the  $\text{N}_2/\text{N}_2\text{O}$  ratio produced is lowered when decreasing the temperature during ammonium nitrate decomposition and suggest that at low temperature the decomposition of the latter leads mainly to  $\text{N}_2$ .

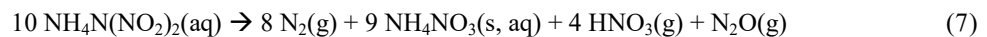


This route differs from most of mechanisms proposed that all passes through, first, ammonia and dinitramic acid formation ([14]). Then, the dinitramic acid could decompose into nitric acid and nitrous oxide, and finally the recombination of nitric acid and ammonia recombine into ammonium nitrate. It can be noticed that, in the gas phase, this first step involving the hydrogen transfer should actually take place [9].

The decrease of the ion parent  $m/z = 44$  signal is not followed by a proportional decrease of the one of fragment 30 indicating that NO is formed undeniably. The fragment 30 is also common to  $\text{NO}_2$ , however no evidence of the presence of this compound can be noted as: no peak at  $m/z = 46$  can be detected. Thus, NO is formed after  $\text{N}_2\text{O}$  and seems to come from the decomposition of AN. This result is in agreement with the mechanism proposed in the literature [3]:



Other products like nitric acid could be also formed during decomposition, as it was observed by Farhat *et al.* for ADN diluted in water [15], however it was not observed by MS analysis.



The addition of AN leads to a pronounced increase of the onset temperature along with a slight increase of the end temperature decomposition. As a consequence, a narrowing of the thermal decomposition process is observed.

## B. ADN/AN catalytic decomposition

Considering that ADN decomposes before AN and that AN is an intermediate product of ADN decomposition, it was assumed that ADN could facilitate the decomposition of AN. Thus, the selection of BRM able to catalyze the decomposition of ADN and consequently of the mixture was mainly focused on ADN decomposition. In addition, new active species and typical BRM used for AN-based propellants were also studied. Thus, thirty BRM were tested (inorganic and organic metal salts, metal oxides and nanometal



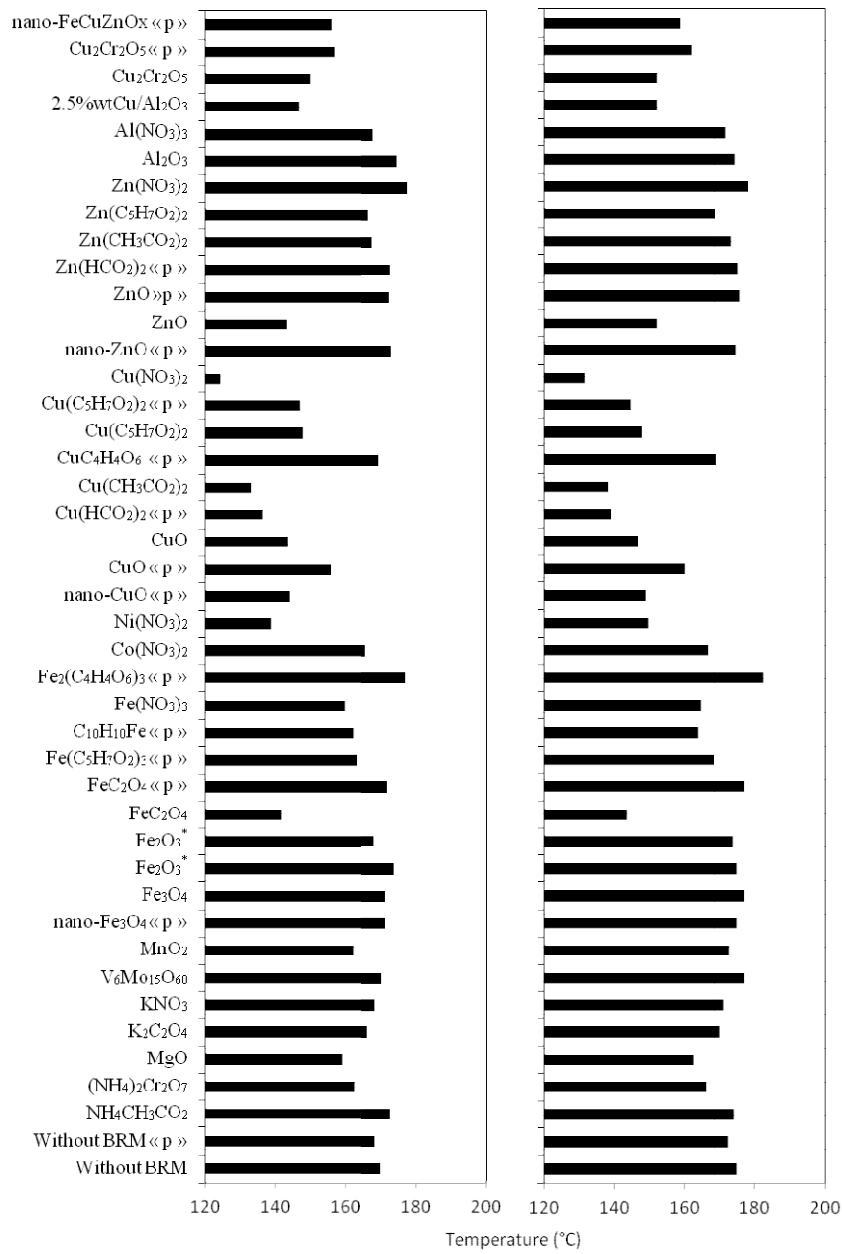
oxides) with non-prilled ADN/AN mixtures or/and prilled ADN/AN mixtures. Regarding the specificities of the mixture alone, the selection of potential BRM candidates has been based upon following criteria:

- Lower the decomposition temperature of ADN/AN mixture
- Accelerate the decomposition rate of ADN/AN mixture
- Promote an exothermic decomposition of ADN/AN mixture

Figure 4 and

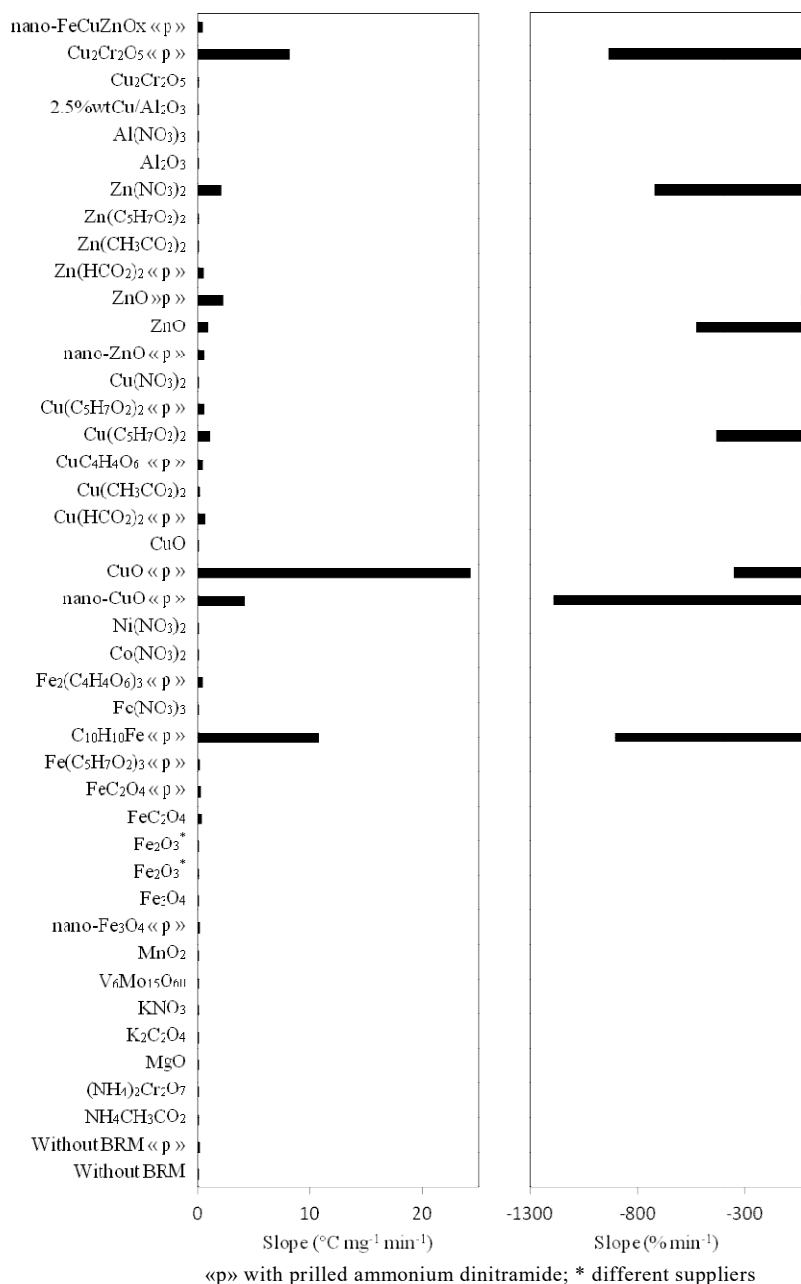
«p» with prilled ammonium dinitramide; \* different suppliers

Figure 5 depict ADN/AN decomposition temperature and decomposition rate observed in the presence of the BRM investigated, respectively. The decomposition temperature is assigned to the ignition temperature, in other word to the temperature at which the first exothermic event starts. The decomposition rate is evaluated using the slope of the TGA and DTA signals related also to the first main exothermic event.



«p» with prilled ammonium dinitramide; \* different suppliers

Figure 4. ADN/AN decomposition onset temperatures for various BRM deduced from DTA (left) and TGA (right).

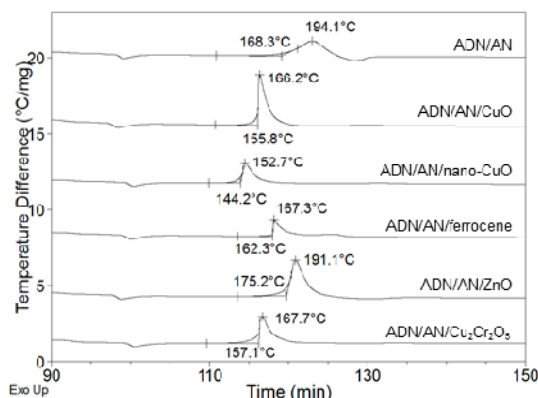


**Figure 5. Slope of the first main ADN/AN decomposition exothermic peak for various BRM deduced from DTA (right) and TGA (left).**

Most of the copper-based materials allowed to decrease the decomposition temperature: CuO, nano-CuO, Cu(HCO<sub>2</sub>)<sub>2</sub>, Cu(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>, Cu(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>2</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>, 2,5%Cu/Al<sub>2</sub>O<sub>3</sub>, Cu<sub>2</sub>Cr<sub>2</sub>O<sub>5</sub> and nano-FeCuZnO<sub>x</sub>. Results show that zinc- (especially ZnO, nano-ZnO and Zn(NO<sub>3</sub>)<sub>2</sub>) and copper-based materials (CuO, nano-CuO, Cu<sub>2</sub>Cr<sub>2</sub>O<sub>5</sub> and Cu(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>2</sub>) display good performances when considering the reaction rate.

Overall, the oxide seems to present a better activity. The only exception is for ferrocene which also seems to be very active toward the decomposition of these oxidants. Reference BRM for AN, namely Fe<sub>2</sub>O<sub>3</sub> do not show interesting properties and thus seems to be inhibited by the presence of ADN or by some of its decomposition products. However, no evident correlation can be established on the burning behavior concerning the effect of the anion for a specified cation.

Nano-copper oxide, copper oxide, copper-chromite and ferrocene have demonstrated their capabilities to fulfill two of the three aforementioned criteria with “prilled ADN”/AN mixtures. This makes them potential candidates as BRM for such oxidizer couple. DTA traces obtained when decomposing prilled ADN/AN mixture in the presence of the candidates are plotted in **Erreur ! Source du renvoi introuvable.**



**Figure 6. DTA of prilled ADN/AN mixture alone and with nano-CuO, CuO, Cr<sub>2</sub>Cr<sub>2</sub>O<sub>5</sub>, ZnO, ferrocene. Ramp: 5 °C min<sup>-1</sup>.**

Nano-CuO, CuO, Cr<sub>2</sub>Cr<sub>2</sub>O<sub>5</sub> and ferrocene allow starting the mixture decomposition at 144.2, 155.8, 157.1 and 162.3 °C, respectively, vs. 168.3 °C for the pure oxidizer mixture. ZnO did not show a lowering of the ignition but displays interesting behaviors since a significant improvement of the decomposition is observed along with an exothermic decomposition as it is the case for copper, copper-chromite and iron-based materials.

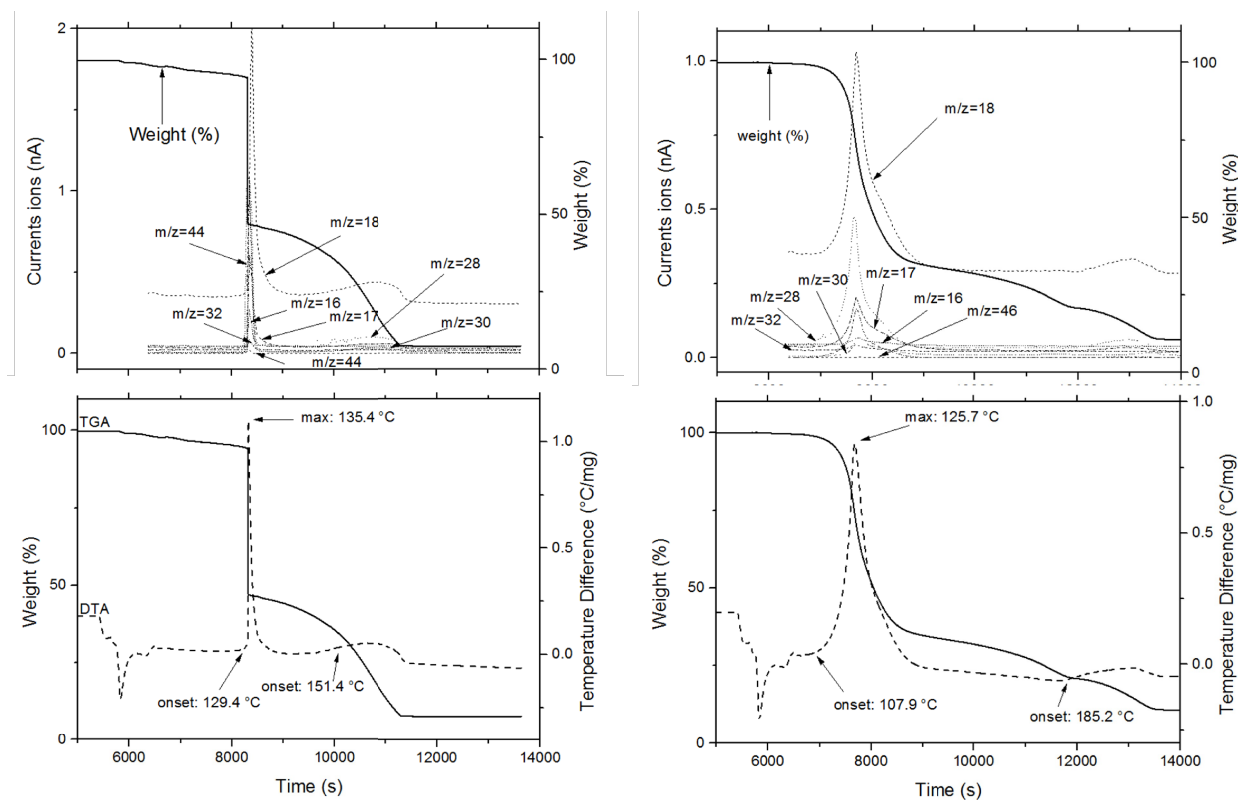
However, selected catalysts allowing high decrease of the decomposition temperature, lead to a broadening of the decomposition process and generally to an increase of the end decomposition temperature. As the oxidizer blend is composed of two components with two distinguishable decomposition temperatures, a bicatalytic systems such as nano-CuO/ferrocene could be considered. The nano-CuO would trigger the decomposition of ADN at low temperature while ferrocene would permit to decrease the final decomposition temperature.

### C. ADN/AN catalytic decomposition with ferrocene and nano-CuO

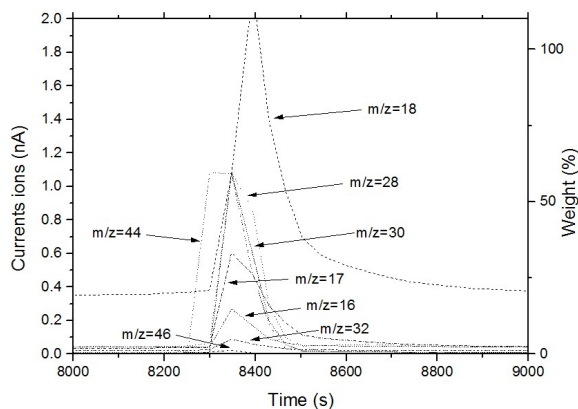
DTA-TGA-MS is used as a starting point to address the decomposition mechanism of ADN/AN mixtures in the presence of these two catalysts alone and in combination.

The results obtained with ferrocene are presented in Figure 7 and **Erreur ! Source du renvoi introuvable.** Ferrocene promotes the formation of N<sub>2</sub>O followed by the release of H<sub>2</sub>O and N<sub>2</sub> in high quantities as it was observed during the thermal decomposition. However, O<sub>2</sub> (m/z = 32), NO<sub>2</sub> (m/z = 46) and NH<sub>3</sub> (presence confirmed from the higher surface area of m/z = 16 peak than m/z = 32 one) are also observed demonstrating that the mechanism should, in part, passes through the hydrogen transfer to form NH<sub>3</sub> and dinitramidic acid as the first step of decomposition. The weak shoulder observed most probably accounts for AN decomposition. Finally, the temperature increase leads to the decomposition of AN into H<sub>2</sub>O, N<sub>2</sub> and NO.

Experimental results obtained with nano-CuO are presented in Figure 7.



**Figure 7. DTA-TGA-MS of prilled ADN/AN mixture with ferrocene (left) and nano-CuO (right). Ramp:  $1\text{ }^{\circ}\text{C min}^{-1}$ .**

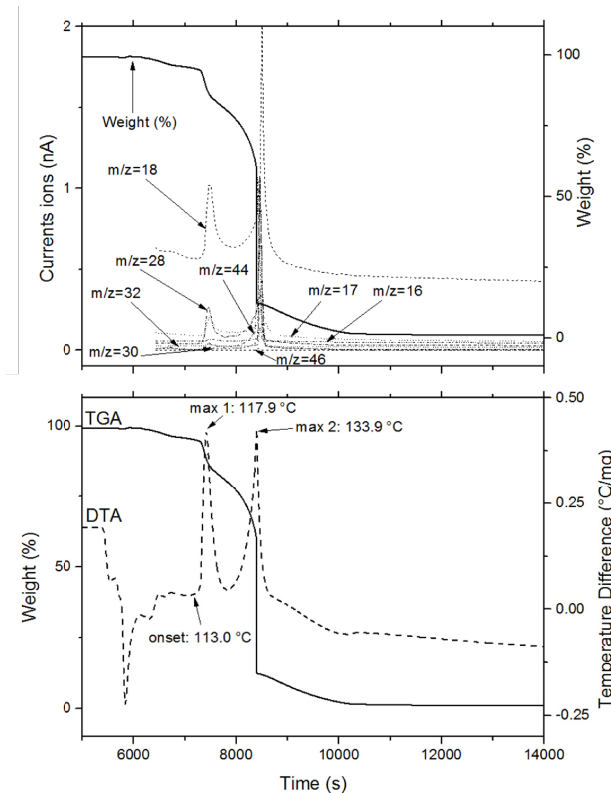


**Figure 8. Enlargement of MS signals of prilled ADN/AN mixture with ferrocene.**

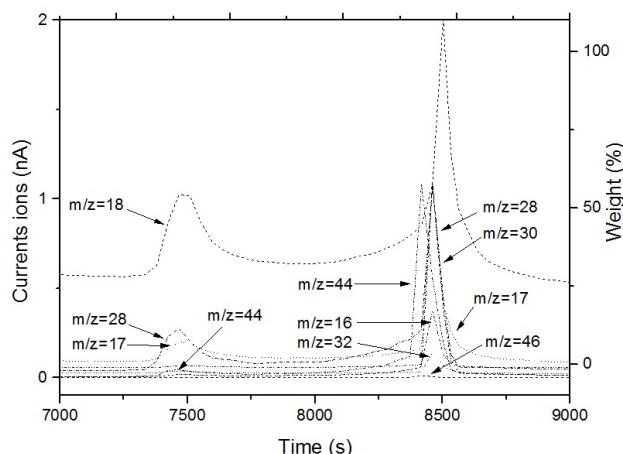
Observation of ion parent or fragment of  $m/z = 32$  and  $m/z = 16$  can be noticed, which gives the evidence of the probable presence of little amount of both  $\text{O}_2$  and  $\text{NH}_3$  (since  $m/z = 32$  peak surface area is close to  $m/z = 16$  one).  $\text{NO}_2$  seems also to be detected in very few quantities. The use of a catalyst highlights the multiple stages of the first exothermic event between 6800 and 9200 s, with firstly the decomposition of ADN into  $\text{N}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{O}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{NO}_2$ , and then, the decomposition of AN leading to  $\text{H}_2\text{O}$ ,  $\text{N}_2$  and  $\text{NO}$  and characterized by a shoulder observed on the signals. The release of  $\text{N}_2$  first,  $\text{O}_2$ ,  $\text{NO}_2$ , and of kinetic products like  $\text{NH}_3$  seems to show that, as for ferrocene, a different decomposition pathway is followed, compared to the thermal decomposition pathway which was proposed earlier. This is supported by the formation of a product difficult

to decompose observed from 12000 s. Between these two decompositions region, the partial evaporation or sublimation of AN is observed.

The use of a bicatalytic system consisting of 4,7 wt. % ferrocene + 2 wt. % nano-CuO was considered and investigated. DTA, TGA and MS traces thus obtained are shown in Figure 9 and a focus on the MS signals during the decomposition event is depicted in **Erreur ! Source du renvoi introuvable.**. An exothermic profile with two well-defined peaks are observed on the DTA profile. The first one should originate from the decomposition reaction catalyzed by nano-CuO and the second one by ferrocene. Products observed with the bicatalytic system are comparable to those obtained previously. The use of this catalytic system allows keeping a low temperature, though not as much as nano-CuO actually did, and significantly contribute to decrease the temperature at the end of the decomposition. It seems that a synergy effect is observed since the end decomposition temperature decreases drastically along with a significant narrowing of the decomposition process: about twice less than with the mixture alone and about one third less than with ferrocene.



**Figure 9. DTA-TGA-MS of prilled ADN/AN mixture with the bicatalytic system: ferrocene/nano-CuO (4,7 + 2 wt %). Ramp: 1 °C min<sup>-1</sup>.**



**Figure 10. Enlargement of MS analysis of prilled ADN/AN mixture with ferrocene(4,7 wt %)/nano-CuO (2 wt %).**

#### IV. Conclusion

Thirty-three preselected additives have been incorporated in non-prilled ADN/AN mixture or/and prilled ADN/AN mixtures. Thermal analyses (DTA-TGA) have been performed to evaluate their capabilities to control the burning rate. Five of them, namely nano-CuO, CuO,  $\text{Cr}_2\text{Cu}_2\text{O}_5$ , ZnO and ferrocene, have demonstrated interesting behaviors which make them potential candidates as BRM for such oxidizer mixtures. A bicatalytic system was tested in order to tentatively get an exothermic decomposition, decrease the onset temperature, accelerate the reaction rate while reducing the temperature range during which the decomposition takes place. Nano-CuO/ferrocene successfully met these requirements. Stand burner tests should be carried out with the aim to confirm the potential of these catalysts to tailor the combustion of an ADN/AN mixture. Finally, the first step of non-catalyzed ADN/AN mixture decomposition, under low temperature increase, seems to proceed via the direct formation of  $\text{N}_2\text{O}$  while catalytic mechanism seems to go, in part, through the hydrogen transfer to form  $\text{NH}_3$  and  $\text{HN}(\text{NO}_2)_2$ . Catalytic and thermal AN decomposition led mainly to the formation of  $\text{H}_2\text{O}$ ,  $\text{N}_2$  and NO. The main decomposition products of the mixture are  $\text{N}_2\text{O}$ ,  $\text{N}_2$ ,  $\text{H}_2\text{O}$  along with lower amount of NO and, when decomposed in the presence of a catalyst, of  $\text{NH}_3$  and  $\text{NO}_2$ .

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