DETERMINATION OF WATER, AMMONIUM NITRATE AND SODIUM NITRATE CONTENT IN 'WATER-IN-OIL' EMULSIONS USING TG AND DSC

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The main component of an emulsion explosive is a water-in-oil emulsion consisting of a supersaturated ammonium nitrate (AN) water phase, finely dispersed in an oil phase. Quantitative determination of nearly all the components in a W/O emulsion is possible using thermogravimetry (TG) and differential scanning calorimetry (DSC). Isothermal TG measurements enable determination of water content, while cycled DSC measurements allow the amount of ammonium nitrate to be determined. In the case that sodium nitrate (SN) is also added to AN as an oxidizing agent, it is necessary to quantitatively separate both salts from organic matter with diethyl ether. On the basis of the TG curve of the precipitated salts, the amount of AN can then be calculated, and that of SN is obtained from TG measurement of the original sample.

Introduction

Emulsion explosives, developed in 1962, are characterized by unusually high rates of detonation, which contribute to their ability to create fractures in rock, their good safety properties and low basic cost [1]. They consist of a water-in-oil emulsion and sensitizer ingredients. In the emulsion the components are an intimately mixed, all-liquid system, where a highly supersaturated water salt solution with a droplet size of 1 μm is finely dispersed in a small volume of hydrocarbon oil, which forms a thin film around the droplets [1]. The water phase generally contains ammonium nitrate (AN) and other salts, such as sodium (SN) and calcium nitrate, and is metastable due to supersaturation. Ammonium nitrate is the cheapest source of oxygen available in condensed form for commercial explosives. It is the major ingredient of the emulsion, about 70% of the overall composition. The dispersed aqueous phase, which constitutes over 90 mass% of the liquid fraction, is emulsified in 7 to 10% of oil phase. The emulsifier enables formation and stabilization of the emulsion comprising the two phases with very different polarity and also maintains the supercooled state.

The emulsion in not yet an explosive. An effective commercial explosive is obtained when glass or plastic microbubbles, which lower the density of the system, and aluminum powder (optionally) as high energy fuel, is added to such an emulsion. This can be done on site in a mobile unit before pumping the final emulsion into the drilled hole [2]. The type and distribution of the bubbles is critical in determining the detonation performance of the emulsion explosive. Water

proves to be an effective detonation inhibitor, and the desired sensitivities are achieved by controlling water levels in the formulation. Stability requirements are particularly demanding for these emulsions since crystallization, particle growth or emulsion breakdown causes the loss of the required explosive properties.

Thermal methods are often used in the analysis of explosive materials. Recently, Sućeska and Rajić [3] reviewed this topic in a comprehensive paper containing 54 references. According to them, thermal analysis is seldom applied for quantitative analysis of explosive materials. The sample heterogeneity and the associated problem of small sample size used for analysis on the one hand and, on the other, the dynamic character of events taking place during measurement, which is expressed through the influence of the mass of the sample and the heating rate on the outcoming signal, may all affect the precision of quantitative analysis. These factors explain why the derivation of truly quantitative data requires precise calibration, taking into account all the necessary corrections. According to our knowledge, there is no publication describing complex quantitative analysis of an emulsion sample using thermal methods of analysis.

The aim of our work was to introduce a quick method for quantitative determination of water, ammonium and sodium nitrate contents in an emulsion formulation, which would demand a minimum of analytical work, such as for instance separation of a single phase. Accurate and precise results are needed for quality control, and for determining the stability of the emulsion (water content, crystallization of AN) during its shelf-life.

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Experimental

Ammonium nitrate 99.999% (AN standard) from Sigma-Aldrich was used. Before each measurement it was dried for several hours at 150°C. Two commercial samples, used in the area of Slovenia, were analyzed. Both are W/O emulsions; in sample 1 AN is the sole oxidizing agent, whereas in sample 2 also some SN is added.

Thermogravimetric measurements were performed on a Mettler Toledo TG/SDTA 851[e] instrument in a dynamic air atmosphere with a flow rate of 100 mL min^{−1}. In dynamic measurements about 20–30 mg of the sample was weighed in a 150 μL alumina crucible and cover with a pierced lid. The heating rate was 5 K min^{−1} within the temperature range from 25 up to 850°C. The baseline was subtracted. The maximal resolution method (max res) was carried out over a temperature range from 25 up to 300°C. The parameters in the max res method were set as follows: maximal heating rate 2 K min^{−1}, minimal heating rate 0.5 K min^{−1}, high threshold 0.2 μg s^{−1}, and low threshold 0.05 μg s^{−1}. That means when the mass loss exceeded 0.2 μg s^{−1}, the heating rate was automatically lowered to 0.5 K min^{−1}. An aluminum crucible, covered with a 50 μL perforated lid, was used in this experiment. Since the temperature programme is not known before the max res measurement, a baseline could not be subtracted. Isothermal measurements at 100°C were performed in a 40 μL Al pan, covered with a 50 μm perforated lid. The furnace was heated at a heating rate of 5 K min^{−1} from 25 up to 100°C and then held at isothermal temperature for 6 h. The baseline was subtracted.

DSC analysis was carried out using a Mettler Toledo DSC 822[e] under the same atmosphere as TG measurements. Examined samples (mass around 4 mg) were weighed in a 40 μL Al pan. Several heating and cooling cycles within the temperature range from 25 to 135°C at a rate of 5 K min^{−1} were performed on the AN standard, and samples 1 and 2. In the repeated cycles sometimes open crucibles were used, or they were covered with a pierced lid, and in a third case with 50 μm perforated lid. As a reference an empty pan was used, covered in the same manner as the sample pan. The DSC analyzer was calibrated with high purity gallium, indium and zinc. Gallium was supplied by Physikalisch-Technische Bundesanstalt Braunschweig, whereas zinc and indium came from Mettler Toledo. DSC standards and all samples for DSC analysis were carefully weighed on a Mettler Toledo MX5 balance.

For sample 2 separation of AN and SN from the emulsion was made. An aliquot of the sample was mixed with diethyl ether by rotation. Both salts are insoluble in diethyl ether, while oil and emulsifier remained in solution. After precipitation the salts were filtered. The precipitate was dried at 70°C.
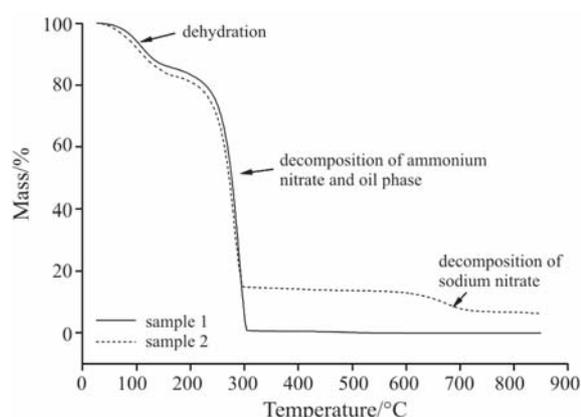
Fig. 1 Comparison of the TG curves of samples 1 and 2 in dyanmic air atmosphere

Results and discussion

Figure 1 shows a comparison of the TG curves of sample 1, which consists of water, AN, oil phase and emulsifier, and sample 2, which also contains a certain amount of SN. From room temperature up to around 150°C water is released from the samples. It is evident that there is no clear plateau between dehydration and thermal decomposition of AN and oil. Better resolution between these two processes could be obtained with a lower heating rate, but even at 0.4 K min^{−1} we could not clearly separate the first mass loss from the second. The total mass loss at 320°C is 100% for sample 1. Sample 2 displays another mass loss (onset temperature approximately 610°C) due to thermal decomposition of SN [4, 5]. Some authors claimed that thermal decomposition of SN is already finished at 800°C [6], but we always found a residue which, according to the residual mass, was probably Na_2O [5].

'Maxres' measurement of sample 1 (Fig. 2) shows that under the specific temperature programme (described in Experimental) it is possible to separate the dehydration process from the beginning of thermal decomposition of AN and the organic phase. Unfortunately, since the temperature program regulates itself within the preset parameters on the basis of a TG curve (the rate of mass loss), we could not subtract a blank curve and therefore the mass loss due to dehydration, as well for the decomposition process, is not accurate. However, this measurement helps us to determine the isothermal temperature at which probably all the water would leave the sample (100°C). The isothermal TG curves of both samples are shown in Fig. 3. The time needed for dehydration depends strongly on the mass of sample. In the case of sample 2 the signal stabilized after 180 min (mass
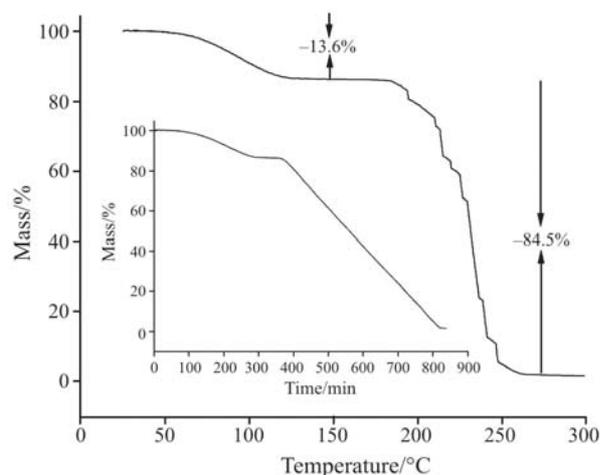
Fig. 2 TG curve of sample 1, in a 40 µL aluminum crucible, covered with 50 µm perforated lid. The inserted graph represents the mass dependence *vs*. time
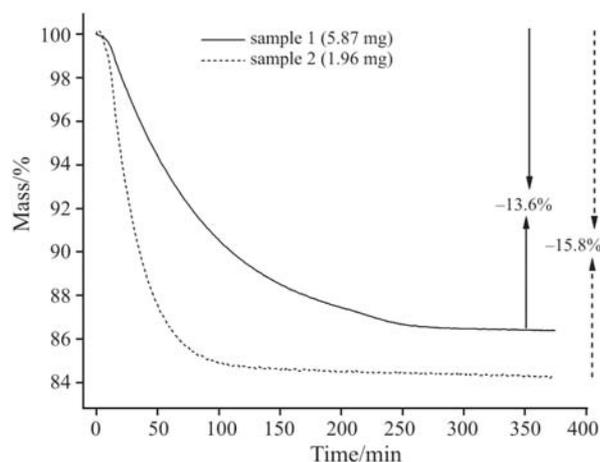
Fig. 3 Isothermal TG measurements at 100°C. The final temperature in the furnace was reached after 15 min

loss 15.5%), whereas for sample 1 after 5 h (13.5% mass loss). From the isothermal mass loss at 100°C the water content in both samples was determined.

After dehydration, decomposition of AN and oil takes place under further heating, according to the idealized reaction: $3nNH_4NO_3+(CH_2)_n \rightarrow nCO_2 + 7nH_2O+3nN_2$ [1]. From the difference of the mass loss at 310°C and water content, the sum of AN, oil content and emulsifier is obtained.

AN has been well studied since it undergoes at least two-phase transitions from room temperature until it melts at 169°C (Fig. 4) [7]. The transition temperatures, especially from the IV→III and IV→II state, depend on several factors [7–10]. Best known are the water content, the thermal history of the sample and the impurity content. The water content is recognized to be responsible for the phase transition IV→III, as well for the wide temperature range within which this transition occurs [7, 8]. The peak at 126°C
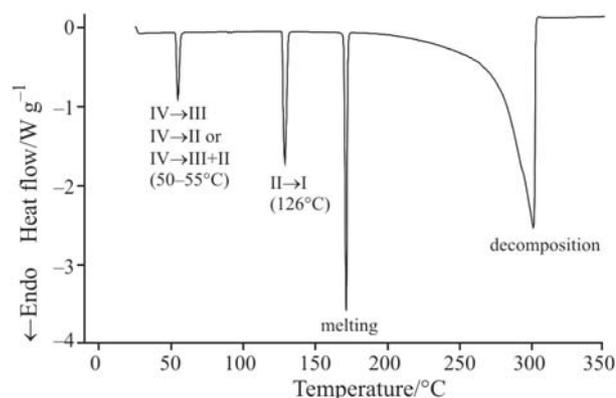
Fig. 4 DSC curve of dried AN

(II→I) is not affected by the conditions and is well reproducible as regards both, enthalpy and temperature [7]. Several values were published for the enthalpy of this phase transformation, ranging from 51.2 to 63 J g^{-1}.

We performed several cycling experiments on pure dried AN from 25 up to 135°C. The value obtained in the 1st cycle was smaller than in 2nd, in all cases regardless the measuring conditions (Table 1). Using a pierced lid, the value slowly started to decrease. From the 2nd to 5th cycle the value decreased by approximately 0.3%. This phenomenon was more distinct when we used opened pans, when the value from the 2nd to 5th cycle diminished by 3.0%. Therefore the corresponding TG measurements were performed (with the same temperature programme, same type of crucibles and lids) on the same sample. From Fig. 5 it is evident that the mass in the case of a pierced lid and without a lid decreases with time, which means that at that temperature AN has a considerable vapour pressure. From the 1st up to the 5th cycle the mass loss was 0.5% (pierced lid) or 3.8% when an open pan was used. Measured mass losses are in accordance with the observations made during DSC cycling experiments. In the case of a 50 µm perforated lid, the signal on the TG and DSC curve remained stable for several cycles, with ΔH=55.20±0.20 J g^{-1} (average value of ten cycling experiments; for each a mean value from the second to tenth heating scan was taken). This value is very

Table 1 Values of the enthalpies in J g^{-1} for the phase transition at 126°C of a pure AN in open pan, pan covered with a pierced lid or 50 µm perforated lid

Cycle no.	Open pan	Pierced lid	Perforated lid
1	54.83	54.80	55.16
2	54.88	54.87	55.21
3	54.32	54.83	55.19
4	53.76	54.78	55.22
5	53.21	54.69	55.20
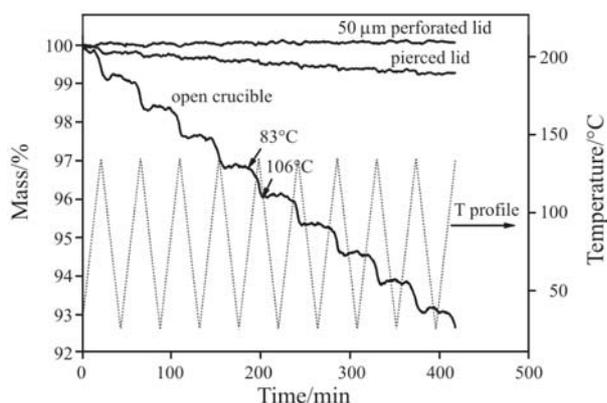
Fig. 5 TG cycling experiment (10 heating and cooling cycles) of dry AN in an open crucible, in a crucible covered with a manually pierced or 50 μm perforated lid

Table 2 Calculated content of AN in sample 1 [%] in differently covered pans. Values from the third cycle up to the tenth are given

Cycle no.	Open pan	Pierced lid	Perforated lid
3	73.1	75.6	59.5
4	71.9	77.8	74.1
5	70.6	78.4	78.2
6	68.8	78.1	79.2
7	67.5	77.8	79.3
8	66.2	77.4	79.5
9	64.9	77.0	79.5
10	63.8	76.7	79.5

close to the value published already in 1967 (ΔH=55.41±0.38 J g^{-1}) [11].

In the emulsion AN is present as an amorphous component. Cycling of the emulsion transforms amorphous AN to the crystallinic form (Fig. 6). In the 1st cycle no peaks are observed on heating. In the second the basic shapes of the peaks are formed. On heating the peak at 126°C reaches a stable value after several cycles, which is then used to calculate the amount of AN in the sample by simply dividing ΔH (sample)/ΔH (AN standard).The estimated error in this determination is ±0.7%.

As for pure AN, it is necessary to perform cycling in pans covered with perforated lids for the same reasons as already described in this article. We also observed that AN in emulsion form starts to crystallize only when water is released from the sample.

Fig. 7 TG cycling experiment (10 heating and cooling cycles) of sample 1. During the 8th cycle the ΔH value for the phase transition at 126°C reaches its maximum value on the DSC curve and then remains constant up to several tens of cycles. When the pan was covered with a pierced lid, the maximum was obtained in the 6th cycle, but ΔH was smaller and then continuously decreased (Table 2)

With the help of the corresponding TG experiments, performed under identical conditions, we found that dehydration must be complete, and after an additional four or five cycles AN completely crystallizes (Fig. 7, Table 2). Dehydration occurs earlier in the case of open pans or pans covered with a pierced lid. This means that the peak at 126°C reaches its maximum value within smaller numbers of cycles, but the value after that decreases because some AN has already evaporated. In hermetically sealed pans, no peaks are observed in the cycling experiment within this temperature range.

Using the DSC measurement described it was impossible to analyze sample 2, which contains AN and SN as oxidizing agents. Figure 8 shows a DSC curve of sample 2, which was previously 9 times cycled between 25 and 135°C. AN is already crystallized, but its content could not be determined, because in a mixture with SN an eutectic system is formed. The enthalpy of the phase transformation of AN around 50°C is not reproducible enough to allow the calculation of AN in sample 2.

Fig. 6 DSC cycling experiment of sample 1 (perforated lid). On repeated scans AN begins to crystallize
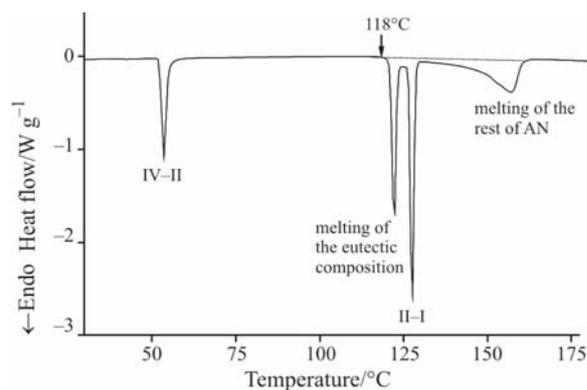
Fig. 8 DSC curve of sample 2, previously cycled 9 times from 25 to 135°C
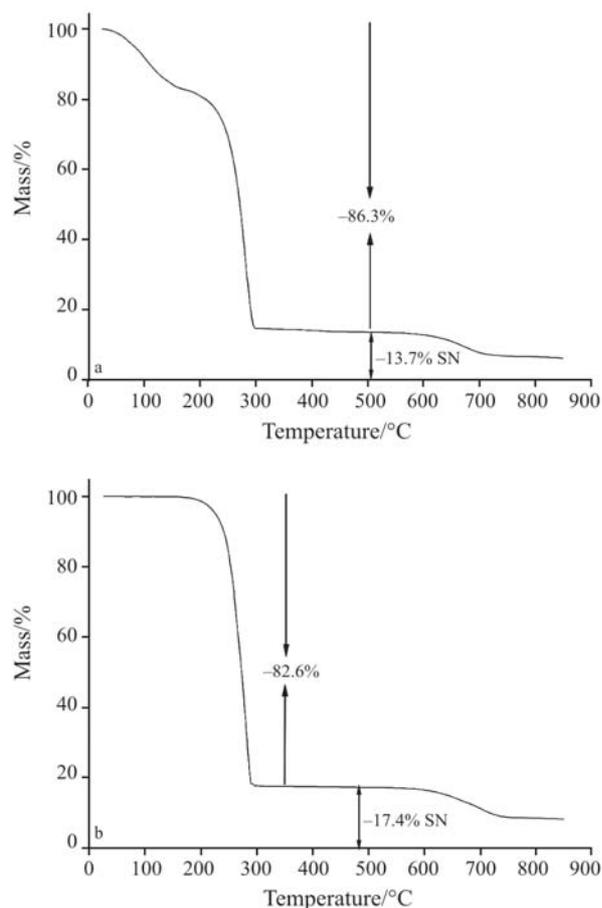
Fig. 9 TG measurement of a – sample 2 and b – after separation of AN and SN from the sample

Quantitative separation of both salts from organic matter in diethyl ether allow us to calculate the mass% of ammonium nitrate in sample 2 following the equation:

$$\frac{\omega(AN)_{sample}}{\omega(SN)_{sample}} = \frac{\omega(AN)_{separation}}{\omega(SN)_{separation}}$$

$$\omega(AN)_{sample} = \frac{82.6\% \cdot 13.7\%}{17.4\%} = 65.0\%$$

In sample 2 the whole mass that remains after dehydration and thermal decomposition of AN and organic components is attributed to the SN content (Fig. 9a). After separation the mass loss up to 500°C is smaller and is attributed only to thermal decomposition of AN (Fig. 9b).

The error in determination of the SN content can be very large. For instance, a 0.5% lower value for the amount of $\omega(NN)$ in sample 2 (13.2% – Fig. 9a) and a 0.5% lower value for AN content in the precipitate (82.1% – Fig. 9b) give as a result of 60.5% of AN in the sample (±4.5%). If both differences are 0.3%, the calculated result is 62.3% (±2.7%). To avoid such a large error, at least five measurements should be performed after making sure that no systematic error is present in the determination.

Conclusions

Thermal methods of analysis (TG and DSC) proved to be suitable methods to determine water content and the amount of AN, SN and organic phase in water in oil emulsions. Water content was determined by isothermal TG measurement at 100°C. In sample 1 the amount of AN was determined by performing ten heating and cooling DSC cycles between 25 and 135°C. During this experiment, water evaporated and AN began to crystallize. From the enthalpy of the phase transition at 126°C the amount of AN was calculated. The content of organic phase (oil+emulsifier) was calculated from the difference from 100%.

Amount of water, AN, SN and organic phase in samples 1 and 2 are as follows:

	Sample 1	Sample 2
Water	13.6%	15.8%
AN	79.5%	65.0%
SN	–	13.7%
Organic phase	6.9%	5.5%

In sample 2 the amount of SN corresponded to the mass remaining at 520°C in TG measurement. AN content was calculated on the basis of an equation which assumes that the ratio of AN and SN in sample 2 is equal to that in a quantitatively obtained salt precipitate from diethyl ether, where organic compounds remain in solution. Again, the difference from 100% is attributed to the sum of hydrocarbon oil and emulsifier.

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