Rapid Screening Device - RSD™
Technical Application Note 19
Phase Transitions in Ammonium Nitrate

Introduction

The use of the Rapid Screening Device (RSD) for the study of exothermic decompositions has been well documented in previous application notes. In this study we detail the use of the RSD for the measurement of endothermic transitions.

Ammonium Nitrate (AN) is commonly used in both the explosives and agrochemical markets where it is used as a source of oxygen and nitrogen respectively. Several significant industrial accidents have occurred where large quantities of ammonium nitrate have detonated - the most recent example being the Toulouse explosion in 2001.

Ammonium Nitrate Fertilizer

As has been shown in the literature the stability of the material is highly dependent on purity, pH, particle size and density. Solid AN generally exhibits several phase transitions before both the melting and decomposition exotherms and these can be used to characterise the overall stability of the material.

Experimental

These experiments were conducted on a sample of explosive grade Ammonium Nitrate Prill supplied by ExChem Explosives (UK). To ensure that the grain size was not a contributory factor in the experiment one of the samples was carefully crushed to a powder using a pestle and mortar.

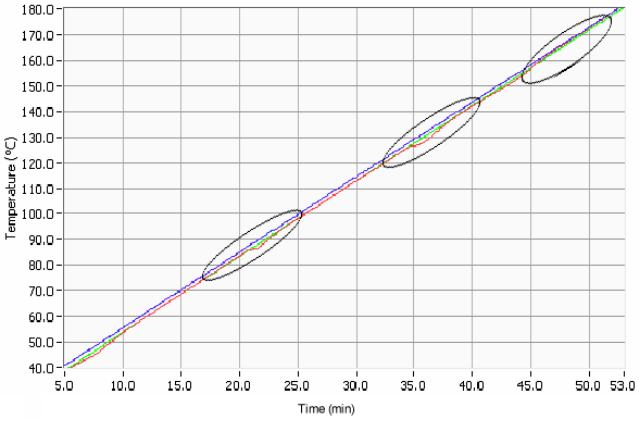
Ammonium Nitrate Prill

The experiments were conducted using a small glass insert placed inside a standard tube-bomb. These inserts were used to ensure that there was no metal-sample contact other than with the thermocouple (for highly sensitive samples the thermocouple can be encased in glass). A sample of alumina powder was placed in an identical holder to ensure that a representative reference was utilised.

The RSD was run using a 4°C/minute ramp rate and was run from 40°C - 350°C to allow study of both phase transitions and decomposition however only the phase transitions will be discussed here. Sample sizes of 100mg were used.

Results

A general figure showing the progress of the reaction can be seen below. Because of the magnitude of the transitions compared to the scale of the figure the transitions have been highlighted. The ability of the RSD to apply a subtraction of a representative baseline allows users to view these small transitions without the influence of the heating ramp.



Temperature:Time for AN

These data are shown overleaf.

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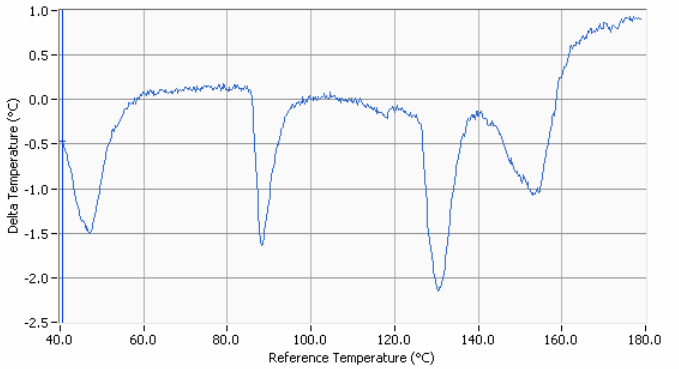
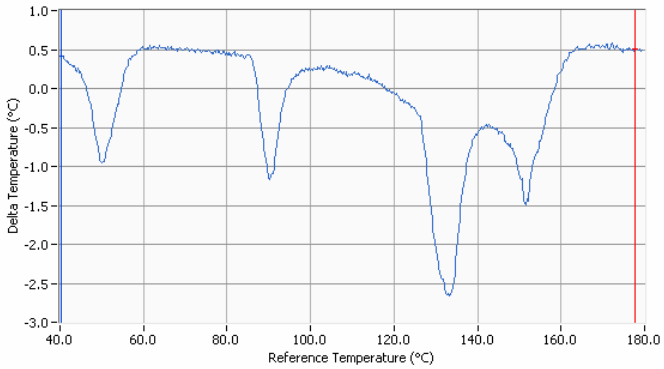


Subtracted data : Full Prills



Subtracted data : Ground Prills

The data above show the comparison between the two AN samples, one as supplied and one ground. There is a clear similarity between the two samples with a series of 4 endotherms. The details of these peaks are shown in the table below.

Peak Number	Onset Temperature	Peak Maxima
1	40.5	49.7
2	85.6	87.2
3	125.9	133.1
4	146.3	151.3

Peak Data for Ground Prill Test

These data appear to correlate well with the literature data measured elsewhere* although the initial peak is a little high (probably a function of the proximity to the start of the experiment).

Data from this reference indicate that polymorphic phase transitions should occur at 32°C, 83°C, 125°C with a melting at 168°C. The low melting point of this material may suggest that it is impure in some away.

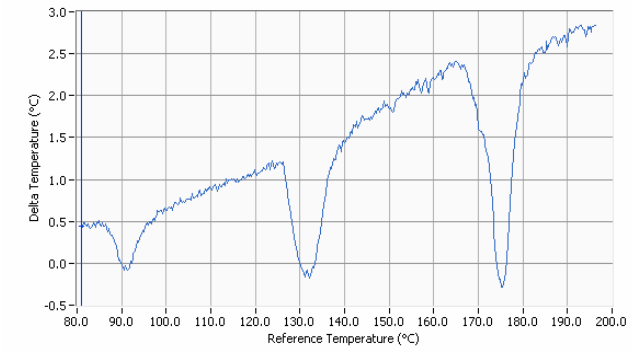
A further test looking at a high purity laboratory standard material is also shown. Here the material transitions are at 84°C, 125°C and melting at 167°C which agrees better with the literature which supports the theory that the prill sample is impure. (This sample was only run from 60°C)

Discussion and Conclusions

As can be seen in these data the peak maxima and general peak shapes are consistent between the two samples. This shows that the technique for the analysis of the sample is reproducible.

The main difference between the two results is the peak width. It is clear that in the ground sample there is a generally narrower peak width which may indicate that there is either a density or particle size effect in the phase transitions within ammonium nitrate.

These data clearly show that the RSD can provide useful information on phase transitions within crystalline materials. Further studies will be performed to show the ability of the RSD to study material impurities.



Subtracted data : Pure sample

* Differential Thermal Analysis volume 1, *Mackenzie.R.C*, Academic Press, **1970**.