Committee of Experts on the Transport of Dangerous Goods and on the Globally Harmonized System of Classification and Labelling of Chemicals

Sub-Committee of Experts on the Transport of Dangerous Goods **19 June 2024**

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Item 2 (b) of the provisional agenda
Explosives and related matters:
Improvement of test series 8

Proposal to review requirement of Test Series 8 for assessing the suitability of ANEs for transport in portable tanks

Submitted by the Australasian Explosives Industry Safety Group Inc. (AEISG) and Institute of Makers of Explosives (IME)

I. Introduction

1. Ammonium nitrate emulsions or suspensions or gels (ANEs) have been transported in tanks on road since the 1980s. There have been several fires reported during transport of bulk ANEs that have not resulted in an explosion.

2. In 2022 there was a fire on a road tanker that was carrying an ANE. The fire began in the tires, involved 26 tires and burned for more than two hours, ultimately leading to an explosion. This was the first recorded explosion involving ANE transport.

3. The ANE involved in the explosion had passed the 8(d) test, which according to the *Manual of Tests and Criteria* (MTC), made it suitable for containment in portable tanks as an oxidising substance and hence suitable for transport in portable tanks as an oxidizing substance.

4. This paper presents context on the 8(d) test and proposes that its requirement be reviewed in the light of recent transport events.

5. Much of the limitations of the 8(d) test have been presented over the years to the UN TDG Sub-Committee. These are included for comprehensiveness and totality to enable a detailed review of this test by the Explosives Working Group.

6. All tables and figures referred to in this document may be found in the Annex hereto.

II. Background

7. ANEs are a relatively new dangerous good – in 1999 a working group was established to determine the classification and testing regime for these substances since there was not a single UN classification for this substance; member states were transporting ANEs as Class 1, Class 5, Class 9 and some were transporting it as unclassified (not dangerous goods).

8. The timeline imposed on the working group precluded comprehensive testing of all ANE formulations made by all manufacturers, however, in 2003/2004 the substance was defined with a UN number – 3375, a special provision – SP309, and a testing regime – Test Series 8.

9. The testing regime includes three classification tests and one additional test, 8(d), which is not for classification but to determine if the substance can be contained in portable tanks as an oxidising substance.

10. In subsequent years it was shown that certain ANEs respond differently to the classification test 8(c) – the Koenen Test, since these ANEs have a formulation that consists

of high boiling point oils and a high water content. The Koenen Test was developed in the 1950s (ANEs were not developed at that time) and was established for rapidly reacting substances – those that reacted in the order of 1 to 10 seconds. This short duration was insufficient to alter the tensile strength of the steel tube that contained the substance. These certain ANEs required over 120 seconds to show a response during which time the steel tube had a significant reduction in its tensile strength. With such a long duration for reaction, the Koenen Test was no longer a test of the substance alone but also that of the containing vessel (tube).

11. Test 8(e), or the Minimum Burning Pressure (MBP) test, was introduced in the MTC Revision 7 (2019) to enable such ANEs to continue to be classified as a Division 5.1 oxidizer, provided that the reaction time in the 8(c) Koenen Test exceeded 60 seconds and that the ANE had a water content greater than 14 per cent.

12. The criterion for ANEs that go through the 8(e) test is that the MBP must be equal to, or greater than, 5.6MPa for it to be considered a UN 3375 substance.

13. Tests evolve or get modified as new information becomes available, for example, when the nature of the substance being tested has additional properties not considered when the Test Series was established, or the test has limitations due to application differences, or the substance exhibits a behaviour that was not considered at the time of the development of the test. In the case of an ANE all three conditions applied when a deeper analysis was carried out on the behaviour of the ANE in the 8(c) Koenen Test.

14. The introduction of the 8(e) MBP test to accommodate the differences cited above is an illustration of the test series evolution.

15. Some ANE manufacturers have determined, and still do determine, the MBP of ANEs to satisfy the basis of safe pumping: the MBP must be higher than the maximum pumping pressure used to move the ANE. This requirement is part of the basis of safety for the ANEs for surface and underground applications. Specifying an intrinsic value of MBP within the ANE that is higher than the maximum pump discharge pressure ensures that if there is an accidental initiation in the hose there will be no propagation back to the pump and the tank containing the ANE.

III. Discussion

16. The composition of an ANE (UN 3375) is defined in SP309, and given the ranges of the many components that make up an ANE its resulting properties could vary accordingly. Indeed, UN 3375 is not a specific substance but rather a generic entry.

17. ANEs for underground applications, for example, could be subjected to higher pumping pressures due to operational requirements and may have higher boiling point organic fuels and also a high water content. These and similarly formulated ANEs have high MBPs by design to ensure safe pumping in that environment. Such ANEs were shown to take longer in reacting in the 8(c) Koenen Test, as previously discussed.

18. The behaviour of these ANEs is completely different in the 8(c) and 8(d) test since these ANEs stay in the vessel over a longer time compared to AN emulsions formulated with lower boiling point oils, and water gels, which get expelled from the vessel during the initial heating period. The latter ANE formulations typically pass the 8(c) and 8(d) test due principally to their early ejection from the heated vessel.

19. A detailed analysis of the behaviour of emulsions, water gels, and the active ingredient in an ANE, namely, ammonium nitrate, was presented at the 24th session of the TDG Sub-Committee (informal document INF.45). The thermocouple traces and photographs of the tests carried out according to test 8(d)(ii) are given in Figures 1 to 3.

20. The emulsions do not begin to overflow the vessel until over 95 minutes of heating (Figure 1) in comparison to a water gel which begins to overflow around 24 minutes into heating. The longer residence time in the vessel of an emulsion versus a water gel leads to more failures of this type of ANE, especially those with higher boiling point oils and high water content.

21. The 8(d) test was added to Test Series 8 to determine whether there is an effect of scale in transporting the substance in bulk, specifically in portable tanks.

22. The 8(d) test is effectively a larger scale 8(c) Koenen Test, since it determines the effect of intense heating under confinement. ANEs that fail (i.e. produce a positive result) in the 8(c) test typically fail (i.e. produce a positive result) in the 8(d) test since the behaviour of these ANEs under these conditions is the same irrespective of scale.

23. Although the 8(d) (i) test specified the vessel configuration, neither the wood pile nor the ambient conditions are prescribed to the same detail. This means that the outcome of the test can be dependent on the type of wood used, e.g. dry vs less-dry wood (specific calorific value), ambient conditions such as temperature, and how much wood is used. These parameters have a direct impact on the heat flux imparted to the ANE-filled vessel and on the duration of the wood burn, thus potentially affecting the outcome of the test, which is based entirely on the effect on the vessel.

24. In the period 2004 to 2006, the Australasian Explosives Industry Safety Group (AEISG) developed a variation of the 8(d) test using gas (e.g. propane) as the fuel to control the heat flux at a calibrated amount. A duration of one hour was proposed to limit the heat input to that seen during a tire fire – double the allowed time for the wood fire test in Test 8(d) (i). Unlike a wood fire that consumes itself with time and its heat flux diminishing accordingly, the gas flame provides a constant heat flux, which is conservative. The rate of heat input was also specified with it being estimated by using the rate of temperature increase of water heated in the vessel. This test was introduced into the MTC as 8(d) (ii) in 2007.

25. There was not unanimous agreement on the duration of 8(d) (ii) and when the test was introduced into the MTC the proposed duration of one hour was not included.

26. With the introduction of the 8(d) (ii) test into Test Series 8, the 8(d) test for bulk transport of ANEs in portable tanks had two variations that were not equivalent with respect to the extent of heat input, including the test duration, sample quantity, ullage and test vessel design. These variations are listed in Table 1.

27. A parametric analysis of the Koenen Test and the 8(d) (i) and 8(d) (ii) tests was presented at the 49th session (Figure 4). The analysis shows that the 8(d) (ii) test is well within the parameters of a transport tank, in comparison to the Koenen and 8(d) (i) tests.

28. The parametric analysis also showed the significant differences between the burst pressures of the test vessels compared to the portable tanks used for transportation (Figure 5). The portable tank burst pressure is at least one order of magnitude lower than the vessels used in the 8(d) tests, and two orders of magnitude lower than that of the Koenen test vessel.

29. In 2015 the time specification was added to the 8(d) (ii) test, being prescribed as a minimum duration.

30. A summary of the changes made to 8(d) (i) and 8(d) (ii) is given in Table 2 and a timeline of the key events is shown in Figure 6.

31. The fire during an ANE transportation in Western Australia in October 2022 involved 26 tires and persisted for just over two hours before there was an explosion. The Department of Energy, Mines, Industry, Regulation and Safety (DEMIRS) of Western Australia released a detailed investigation report[1], in which they concluded that the ANE over that prolonged heating period lost most of its water resulting in a substance close to a decomposing ammonium nitrate (AN) melt. The resulting explosion was attributed to this AN melt on the ground, with the melt being the result of ANE, released from the melted aluminium tank, being exposed to prolonged and extreme heating.

32. That the explosion was from a decomposing AN melt is consistent with experimental observations. A thermogravimetric analysis of an ANE is shown in Figure 7, where on heating the ANE loses its water and potentially any organic material that has a boiling point

[1] chrome-extension://efaidnbmnnnibpcajpcglclefindmkaj/https://www.dmp.wa.gov.au/Documents/Dangerous-Goods/ANETankerExplosion_Report.pdf.

below 240ºC as the curve shows a slight decline in weight. Once the temperature of the sample reaches 240ºC there is a greater loss in weight with a corresponding exothermic reaction as is typical for a decomposing melt of AN. A differential scanning calorimetric (DSC) trace of AN prill is shown in Figure 8. The initial endotherms are from the phase transitions of solid AN at 85ºC and 125ºC, and the final endotherm around 168ºC is that of the AN solid melting. Continued heating results in the exotherm that begins around 250ºC. In the case of the ANE, the presence of organics as fuel lowers the temperature of decomposition by about 10ºC. This lowering of AN's decomposition temperature by organics is a well-known effect.

33. Based on Figures 7 and 8 the exothermicity is from the decomposition of AN. It follows that an ANE on heating loses water and any low-boiling organic fuels leaving a substance that is no longer the ANE loaded into a portable tank.

34. For ANEs, and for AN, the principal hazard during transportation is a fire. Known transportation fires over the years involving ANEs are described in the DEMIRS[1] report, where none of them resulted in an explosion. In sharp contrast, there has been a number of transport events of AN involved in a fire where a mass explosion has followed.

35. Unlike ANEs, AN prill does not have a UN test to determine its suitability for transport in bulk. AN is however the principal energetic ingredient of an ANE.

36. The tests for suitability for containment in tanks as an oxidising substance are designed to elucidate the nature of the substance in an abnormal condition, such as a fire. The tests provide information on what type of emergency response will be required in the event of such an abnormal condition. Transportation incidents where an ANE is involved in a tire fire and has remained in the tank have shown that the ANE is barely heat damaged after the fire has died down or is extinguished. The key contributing factor to this outcome is the high water content of the ANE, which provides a heat sink and also an inerting medium. The thermal diffusivity of the ANE is also very low resulting in little heat being transferred to the bulk.

37. In the only case to date of the fire with an ANE[2] leading to an explosion, the estimated time to the explosion was just over two hours. Such a long duration provides sufficient time to carry out an evacuation of the area. In contrast, transportation fires involving AN, which have progressed to an explosion, have done so in less than half the time taken in the WA incident.

38. For both substances, Emergency Response Guides specify evacuation when the fire involves the substance.

39. ANEs have been safely transported for over 40 years, and there has been one known mass explosion with this substance over this period. The ANE involved did pass the 8(d) test. The precursor event to the explosion was a prolonged and extreme fire involving 26 tires over more than two hours.

40. Test Series should evolve with new information from incident data, empirical studies, and formulation changes. A review of the 8(d) tests is advocated on the following basis:

(a) There are two tests 8(d) (i) and 8(d) (ii), which are not equivalent;

(b) The 2022 explosion involved an ANE that passed the 8(d) (ii) test;

(c) The explosion took place after two hours of exposure to extreme heat radiation and flames from a fire involving 26 tires, indicating that the event was one of an explosion of AN, as reported in the DEMIRS report, and likely any molten aluminium, remaining fuel or oil residue;

[2] There was a tire fire in a truck carrying an AN emulsion in Novosibirsk, Russia on June 14, 2004. There is no information on whether this product was an ANE as defined by UN 3375. (SAFEX Incident database).

(d) AN, the principal reactive ingredient of an ANE, requires no bulk test, and yet has resulted in mass explosions during transportation. These events have been preceded by a fire;

(e) AN, used as an example substance in the MTC for Test Series 8, passes both the 8(c) Koenen test (MTC; 18.6.1.5) and the 8(d) (ii) test (informal document INF.45);

(f) The emergency response for both AN and ANEs in a fire situation is the same. ANEs because of the high presence of water provide a significantly longer time for evacuation or response than AN prill;

(g) The significant risks associated with performance of the 8(d) tests should be offset by some realistic, meaningful and beneficial information obtained; and

(h) The parameters of the test vessels are far removed from a portable tank in terms of absorbed heat flux with respect to the heated surface area to volume ratio.

IV. Proposal

41. That the working group review the value and perceived benefits of, and the ongoing requirement for, the 8(d) tests for ANEs in the light of the information presented.

Annex

Table 1. Comparison between the 8(d)(i) – Vented Pipe Test and 8(d)(ii) – Modified Vented Pipe Test

	8d(i)	**8d(ii)**
Pipe Dimensions		
Internal Diameter of pipe, mm	310±10	265±10
Length, mm	610±10	580±10
Wall thickness, mm	10.0	5.0±0.5
Base plate top, mm sq	380	300
Base plate bottom, mm sq	380	300
Thickness of top plate, mm	10±0.5	6.0±0.5
Diameter of hole in top plate, mm	78	85±1.0
Nipple length, mm	152	None
Product fill	Full	75% level
Heat rate calibration	None	3.3±0.3K/min

Figure 1. Thermocouple traces and photographs of an emulsion in the modified vented pipe test 8(d) (ii).

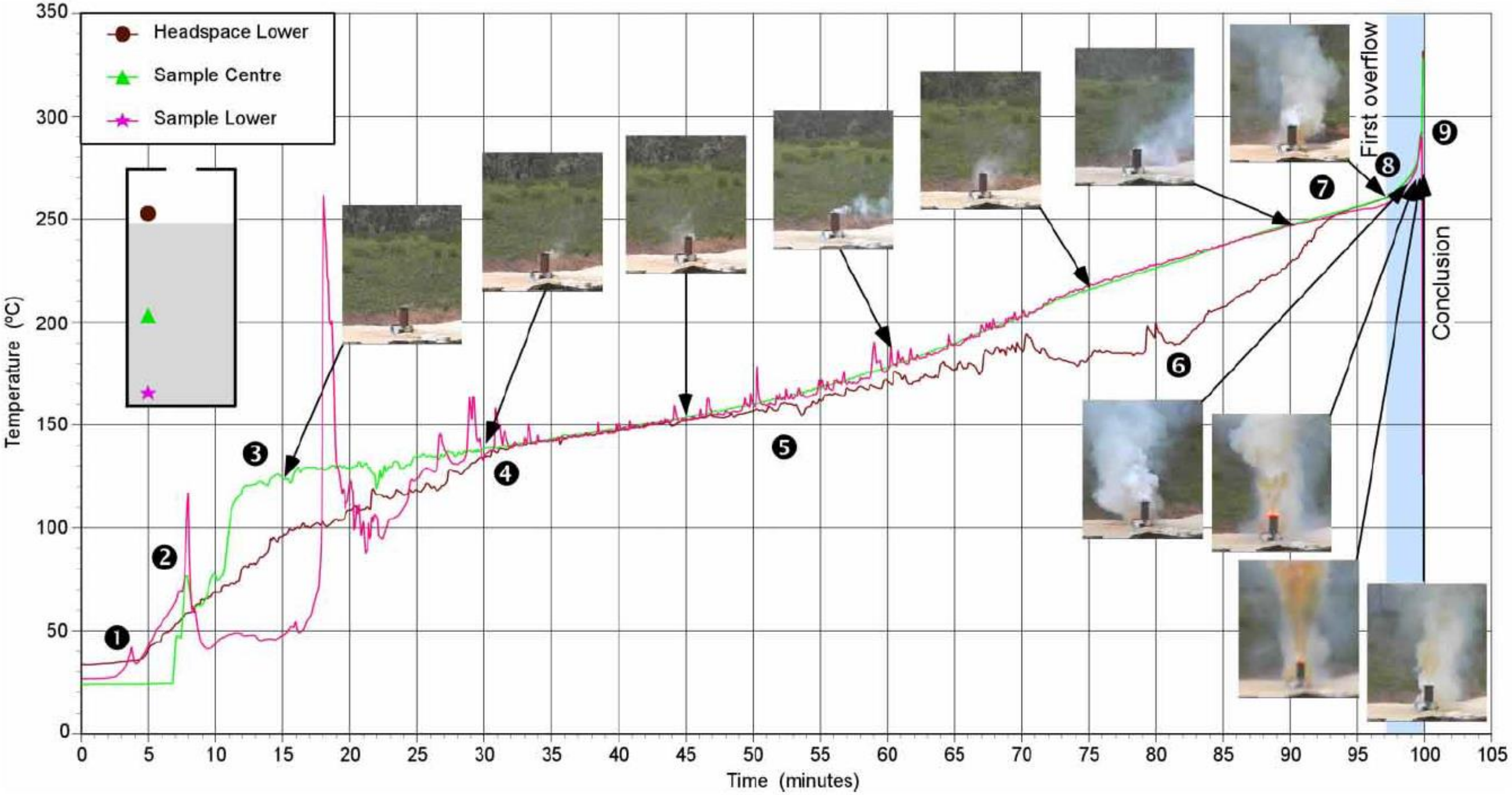

Figure 4. Thermocouple traces and photographs of Trial A07: Emulsion.

This trial used a vessel filled to the 75% point with emulsion composition AEM2. The numbered features (❶ to ❽) are referred to in Appendix A1.3 and illustrated schematically in Figure 6, while the partial blue background denotes the period between the start of vessel overflow and the trial conclusion.

Figure 2. Thermocouple traces and photographs of a water gel in the modified vented pipe test 8(d) (ii).

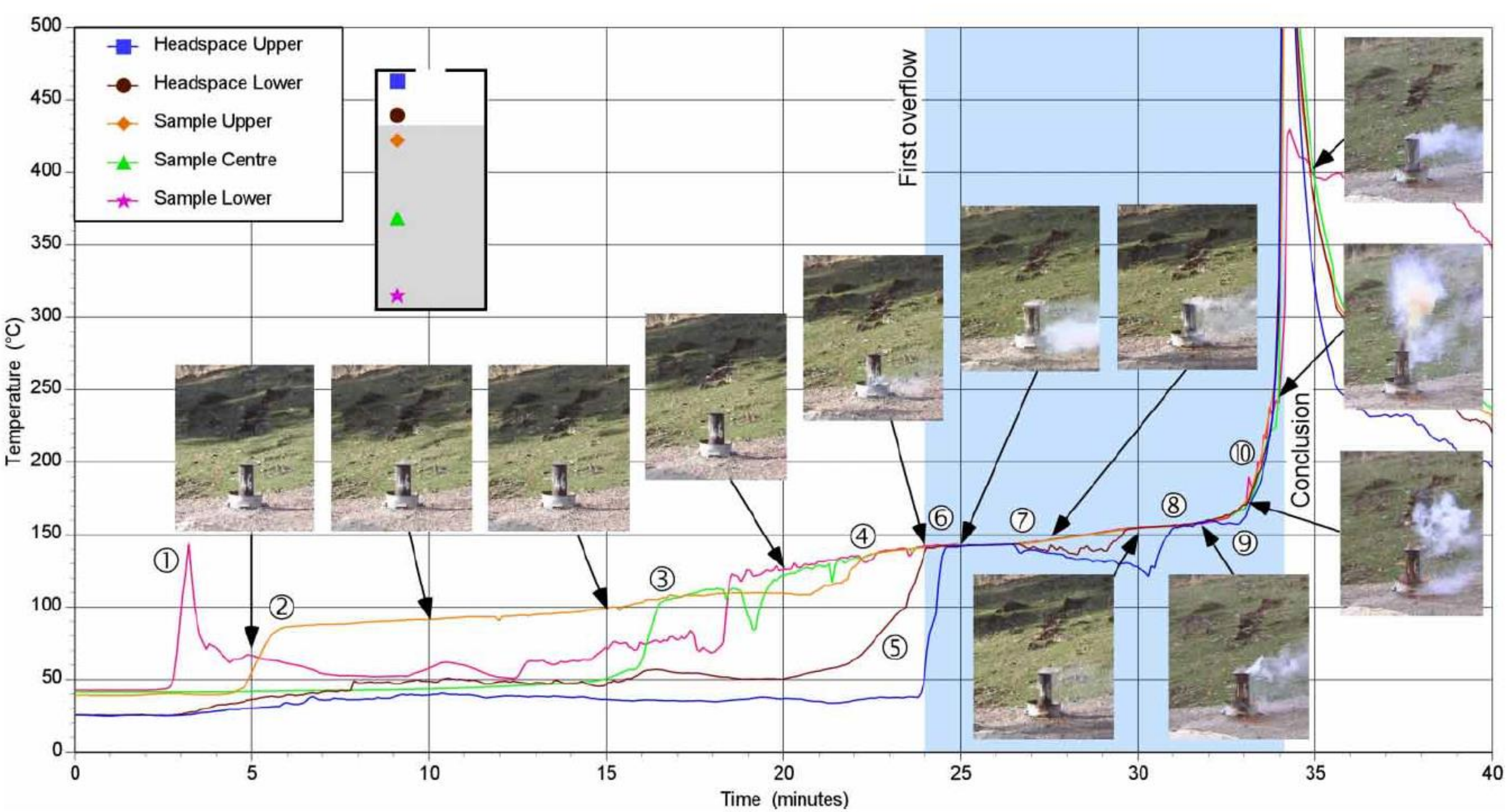

Figure 7. Thermocouple traces and photographs of Trial A46: Methylamine nitrate Suspension.

This trial used a vessel filled to the 75% point with suspension composition ASP7. The numbered features (① to ⑩) are referred to in Appendix A1.4 and illustrated schematically in Figure 8, while the partial blue background denotes the period between the start of vessel overflow and the trial conclusion.

Figure 3. Thermocouple traces and photographs of ammonium nitrate in the modified vented pipe test 8(d) (ii).

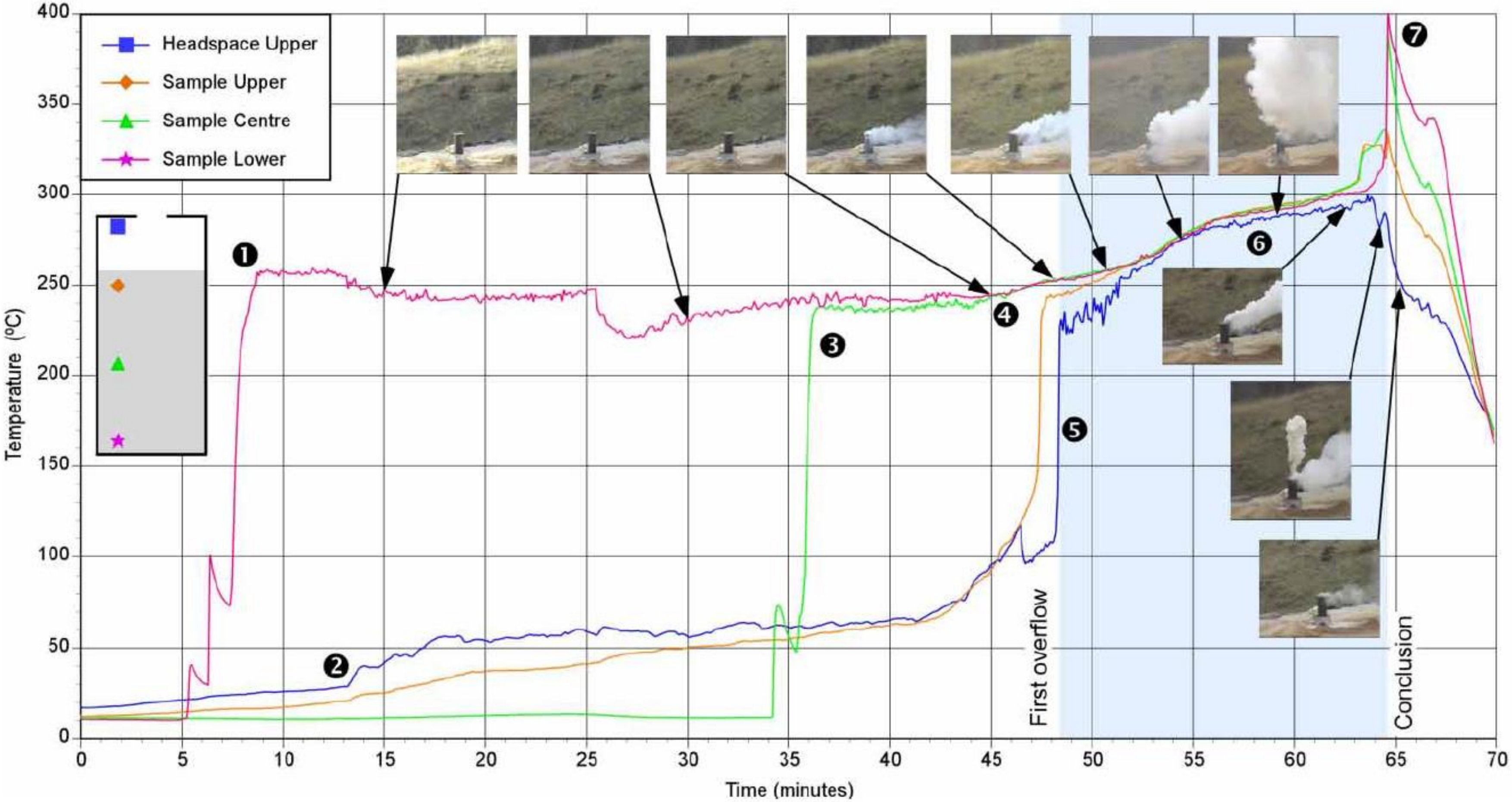

Figure 3. Thermocouple traces and photographs of Trial A26: Pure Ammonium Nitrate.

This trial used a vessel filled to the 75% point with 28 kg loose poured non-porous prills of pure ammonium nitrate. The numbered features (❶ to ❼) are referred to in Appendix A1.2, while the partial blue background denotes the period between the start of vessel overflow and the trial conclusion.

Figure 4. Parametric Analysis for the Koenen, 8(d) (i) (VPT), and 8(d) (ii) (MVPT) tests (UN/SCETDG/49/INF.60).

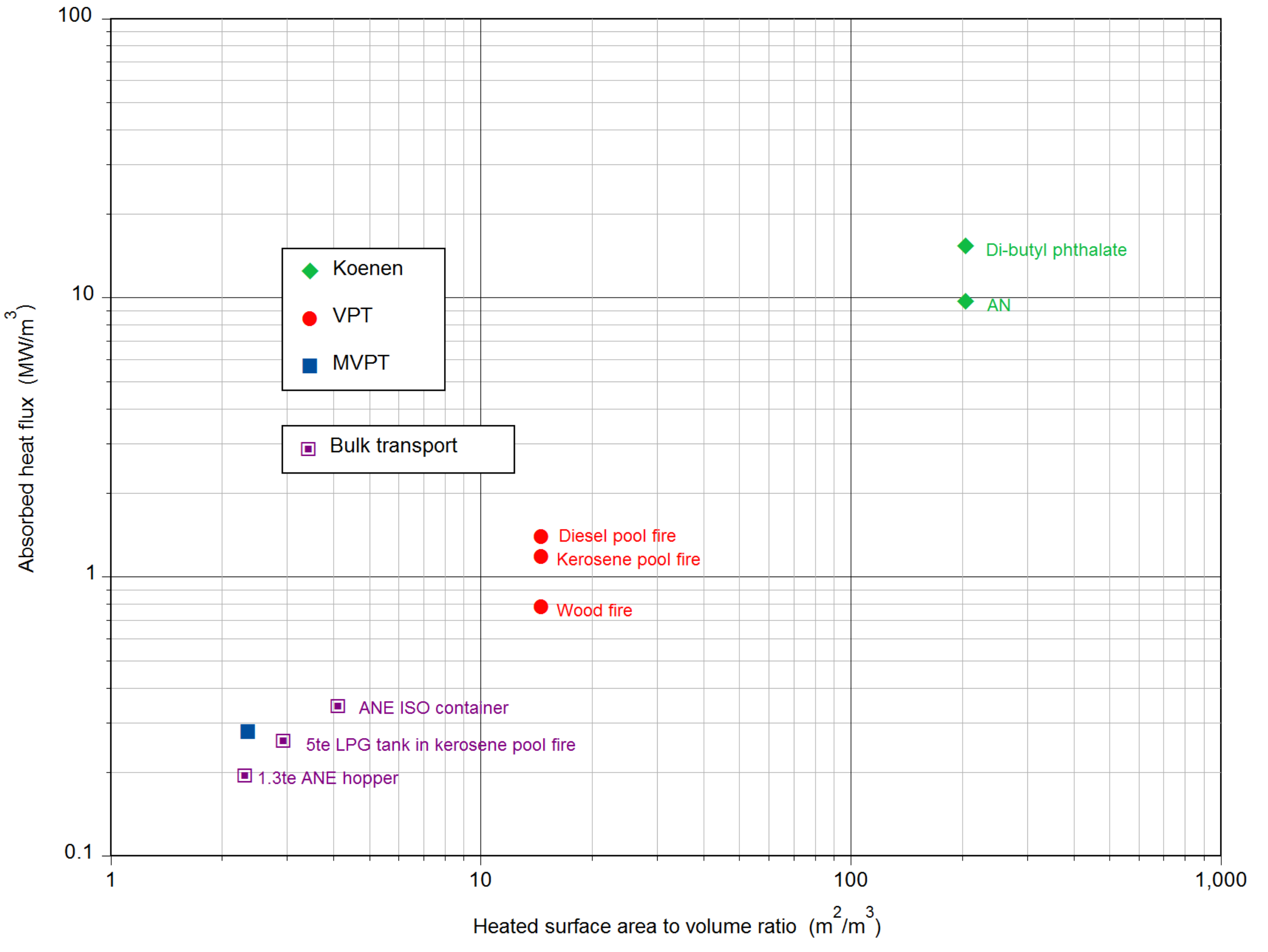

Figure 5. Parametric Analysis of Burst Pressure versus Temperature (UN/SCETDG/49/INF.60); VPT = 8(d)(i) and MVPT = 8(d)(ii).

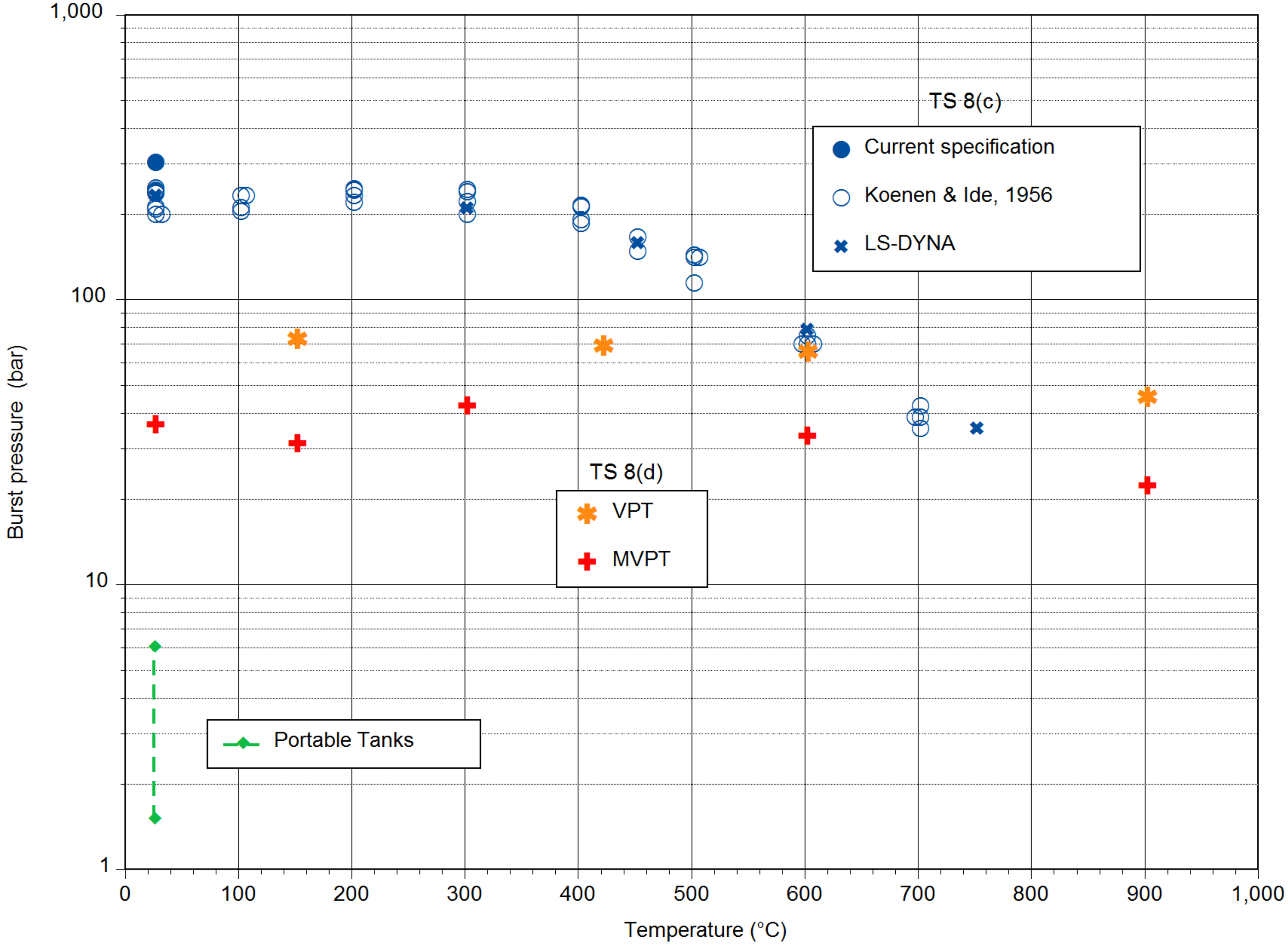

Table 2. Summary of Developments in the 8(d)(ii) Test.

Sub-Committee of Experts on the Transport of DG, 2003 SCETDG, 2003	A Review of the Modified Vented Pipe Test Dr David Kennedy Proposed Procedure and Criterion for the Modified Vented Pipe Test Meeting minutes	AN was tested in MVPT - Major emission of toxic fume started after about 45 minutes of heating, shortly before overflow of the vessel. Fume production then continued for about 20 minutes until the vessel had been drained completely of its contents, predominantly by decomposition but also by some limited overflow. Runtime proposed. “For the Australian MVPT apparatus, this runtime is determined from the data to be: t_{run} **= 64 minutes 37 seconds.** Any test ANE whose MVPT trial concluded after this run-time would begin to produce significant amounts of toxic fume and could explode no earlier than would pure ammonium nitrate under the same heating conditions. This would be judged a negative outcome, with the test ANE suitable for transport in bulk. Conversely, any MVPT trial that concluded earlier than this run-time would be judged to have a positive outcome with the test ANE not suitable for transport in bulk, regardless of whether or not the trial terminated with an explosion. This run-time is roughly twice the duration of a “typical” road tanker fire as estimated by Venart [9] and is roughly twice the minimum duration of the traditional USA Vented Pipe Test which required sufficient fuel to keep the fire burning for at least 30 minutes.
SCETDG, 2004	Proposal for the adoption of a “Modified” Vented Pipe Test as the optional Test Series 8(d) - Sweden	Sweden proposed the adoption of the Modified Vented Pipe Test with a run time calculated as 2x the calibration time for water
SCETDG, 2004 SCETDG, 2005	Procedure and criterion for the modified vented pipe test – Spain 2004 Procedure and criterion for the modified vented pipe test – Spain 2005	Spain proposed the adoption of the Modified Vented Pipe Test without a run time – vessels must be empty at the conclusion of the test, and conducted in duplicate
UNECE, 2007	Modified Vented Pipe Test included in *UN Manual of Tests and Criteria*	The Modified Vented Pipe Test was adopted as UN Test 8(d)(ii) without a run time – vessels must be empty at the conclusion of the test, and conducted in duplicate.
SCETDG, 2015 UNECE, 2015	Amendments to Test 8(d)(ii) Modified Vented Pipe Test approved by the Subcommittee and the Committee of Experts on the Transport of Dangerous Goods. Amendments to Test 8(d)(ii) Modified Vented Pipe Test included in the UN *Manual of Tests and Criteria* Rev 6	8(d)(ii) Modified Vented Test was modified to introduce a 60 minute run time. A test is considered valid if observation criteria outlined in Section 18.7.2.4.4 (a) to (d) have been met. a) Wind speed < 6m/s b) Fire duration of at least **<u>60 minutes</u>** or until the substance has clearly had enough time to react to the fire, with 800°C reached at the external base of the pipe. c) Temperature at the external base of the pipe >800°C d) Substance reacting to the fire as evidenced by: ejection of material, smoke, fumes, flames, etc., from the top of the pipe. The test result is considered “-“ if no explosion and/or fragmentation of the pipe is observed. Splitting of the pipe or its separation from the end plates, as specified in Section 18.7.1.3.3 is evidence of a “-“ result.

Figure 6. Timeline of Key Events in the Development of Test Series 8.

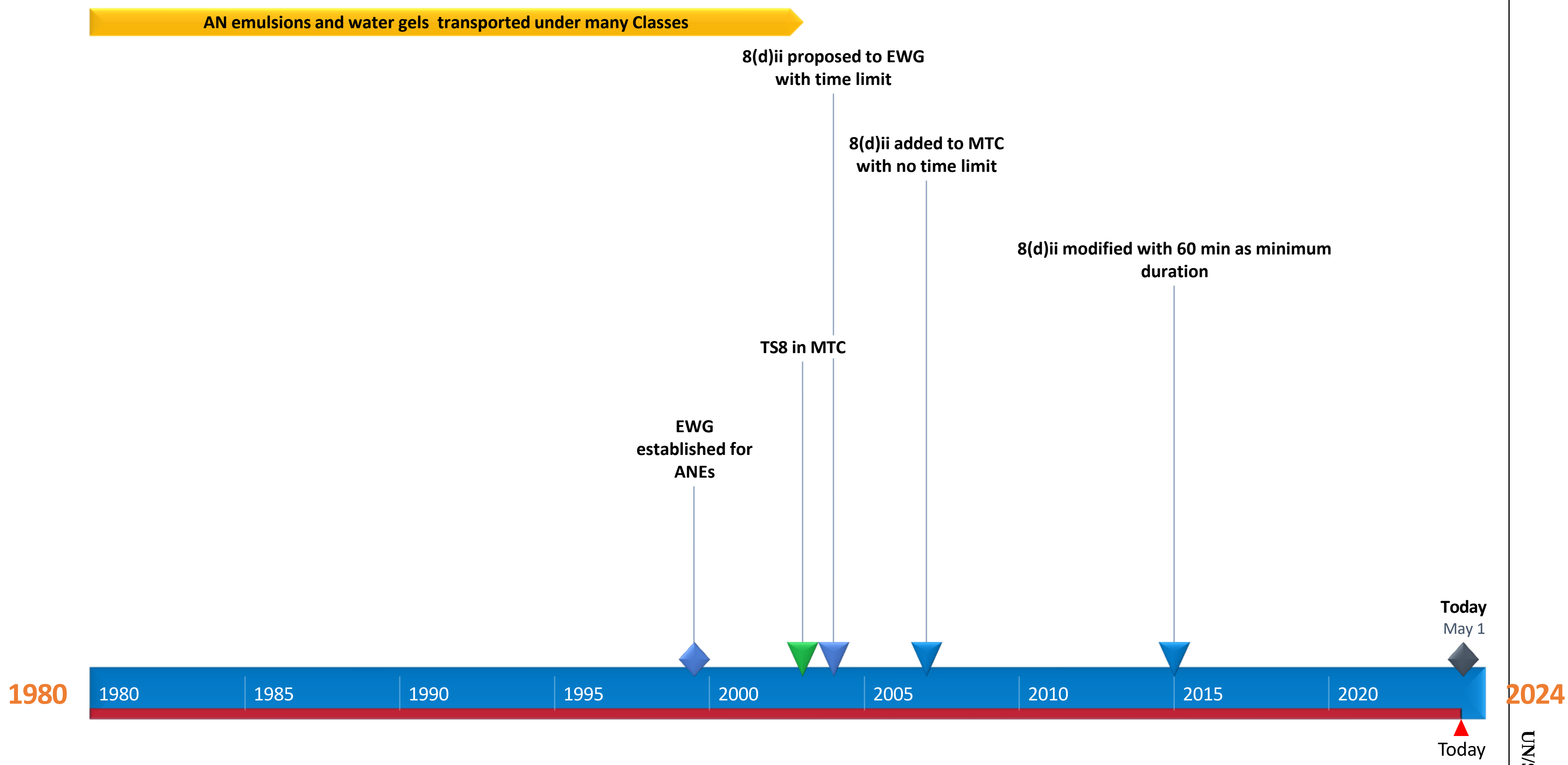

Figure 7. Thermogravimetric Analysis of an ANE.

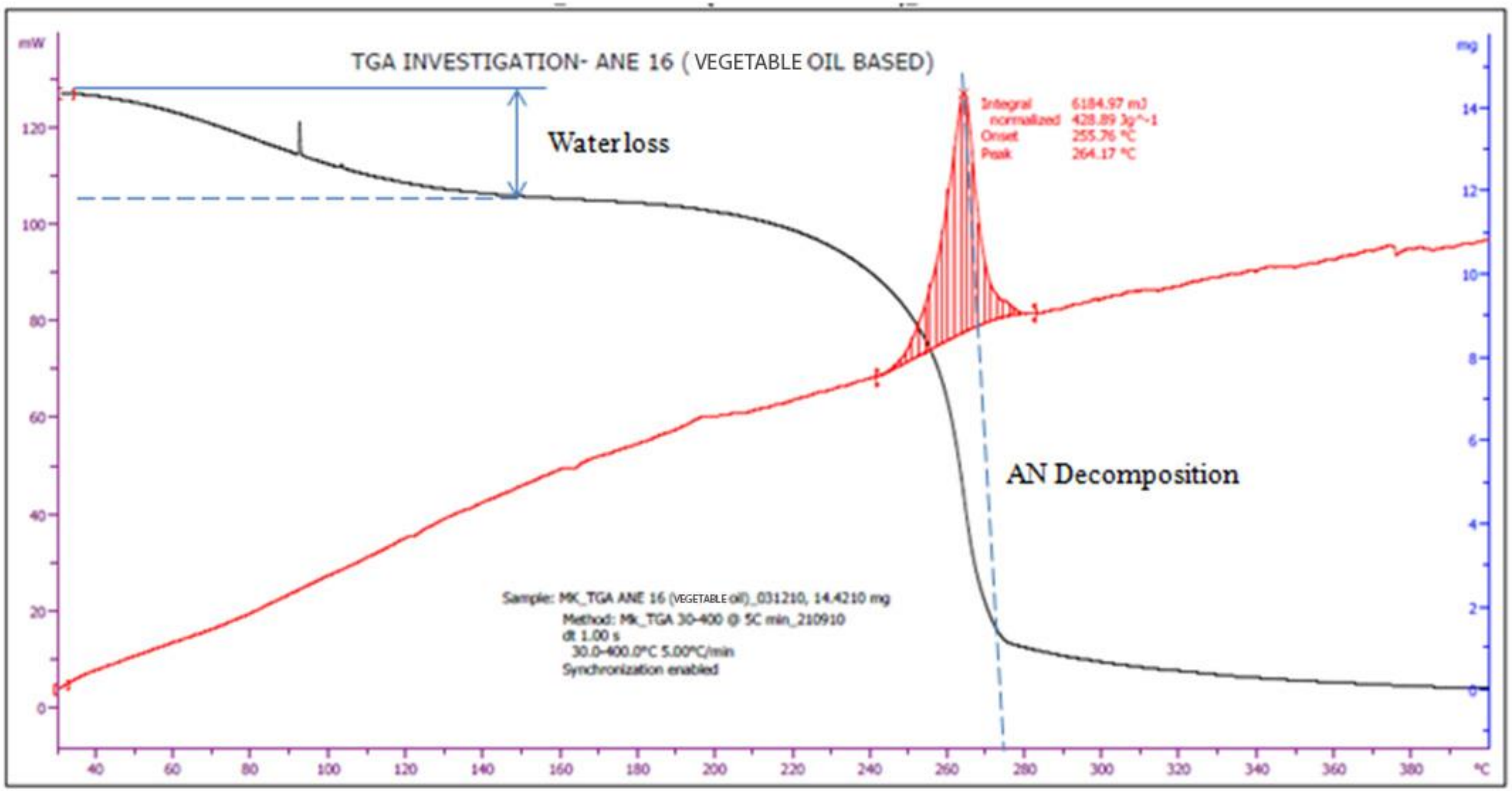

Figure 8. DSC Scan of AN Prill Showing its Thermal Behaviour.