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EXPLOSIVES, SELF-REACTIVE SUBSTANCES AND ORGANIC PEROXIDES

A review of the modified vented pipe test

Transmitted by the expert from Australia

A copy of the review is attached.

# **A Review of the Modified Vented Pipe Test**

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## Summary

This report reviews the 87 Modified Vented Pipe Test (MVPT) trials conducted prior to September 2003 in Australia and in Spain on a variety of compositions including pure ammonium nitrate (AN) and AN-based emulsions and suspensions. It analyses the thermocouple traces and accompanying video records for trials of pure AN, of a typical emulsion and of several typical suspensions, providing schematic interpretations at key stages throughout each trial. These interpretations are consistent with the known decomposition reactions of AN and the phase and vapour pressure diagrams of AN/water systems. The analysis highlights that the production of toxic fume from various decomposition pathways can become a definite hazard at lower temperatures and at earlier times in the heating process than does the possible risk of explosion.

Based on this review, it is recommended that a revised criterion and set of procedures for the MVPT be adopted for the Series 8(d) test. In particular, it is proposed that the acceptance criterion be based on whether or not a trial of the candidate ANE concludes within a defined run-time, which while defined explicitly in the procedure from the heating rate of water, has been based implicitly on the time measured to completely decompose AN prill under identical heating conditions. This proposal has several advantages:

- Basing the criterion upon time and not upon the presence or absence of vessel rupture removes any dependence upon experimental factors that would otherwise be difficult to measure and to control. Such factors include the quality of the welds between the vessel walls and endplates, and the yield strength of the steel at elevated temperatures.
- The procedure describes how each MVPT apparatus can be calibrated against a uniform international standard, and how variations in the initial temperature of the ANE candidate can be corrected for.
- The criterion is an inclusive and all embracing one, in that an MVPT trial can finish prematurely not only in explosion (producing blast and shrapnel), but also as a consequence of rapid decomposition (forming toxic products) or of prolonged vessel overflow (intensifying the fire and producing toxic fume).
- Recourse to archival information on the observed behaviour of AN in historical accidental fires during transport should then allow quantitative risk assessments to be made of the hazards involved in the transport of ANE.
- The criterion delineates the time-scale before which any major hazards develop, and hence the time-scale available to the authorities to respond to an accidental fire involving ANE. This time-scale is in excess of one hour under heating conditions that match those of the MVPT.

Application of the revised criterion to the existing set of data generated during past MVPT trialing led to negative outcomes for the majority of the emulsion compositions that lay within the current UN3375 ANE definition, with those compositions thus being deemed suitable for transport in bulk. An emulsion composition that lay outside the current UN3375 definition due to the inclusion of sodium perchlorate gave two positive outcomes in Australian trials, with a similar composition giving one positive and one negative outcome in Spanish trials.

Hence the proposed MVPT appears to discriminate between emulsions that have traditionally been judged suitable for bulk transport and those that have not.

It was observed that all suspension compositions overflowed their vessels at much lower temperatures, at much earlier times, and for much longer periods than did any of the emulsion compositions. It is believed that by reducing the amount of material left in the vessel to be

heated and by intensifying the fire under the vessel, this excessive overflow invariably contributed to greatly decreasing the time taken to empty the vessel. While the majority of the overflow material could drain away harmlessly in the MVPT, such overflow material in a tanker fire would most likely increase the intensity of the fire and accelerate the rate of toxic fume production. All chemically sensitised suspension compositions tested to date gave positive outcomes under the proposed procedure of the MVPT, with some trials finishing in less than half the time allowed under the proposed criterion.

It is recommended that Special Provision 309 should not be amended to include chemically sensitised suspensions.

## Abbreviations

AN	Ammonium nitrate.
ANE	Substance conforming to Special Provision 309 [17], which reads “ <i>This entry applies to non-sensitised emulsions, suspensions and gels consisting primarily of a mixture of ammonium nitrate and a fuel phase, intended to produce a Type E blasting explosive only after further processing prior to use. The mixture typically has the following composition: 60-85% ammonium nitrate; 5-30% water; 2-8% fuel; 0.5-4% emulsifier agent; 0-10% soluble flame suppressants; and trace additives. Other inorganic salts may replace part of the ammonium nitrate.</i> ”
DO	Diesel oil.
EG	Ethylene glycol.
GMB	Glass micro-balloons.
HMN	Hexamine nitrate.
MAN	Methylamine nitrate.
MVPT	Modified Vented Pipe Test. The proposed procedure is given in Appendix A2.
NO <sub>x</sub>	Oxides of nitrogen including N <sub>2</sub> O, NO and NO <sub>2</sub> .
PO	Paraffin oil.
SN	Sodium nitrate.
SP	Sodium perchlorate.

## **1. Introduction.**

Over the past few years, the United Nations Sub-Committee of Experts on the Transport of Dangerous Goods (SCETDG) has been discussing various proposals for a large scale test to determine if an Ammonium Nitrate Emulsion (ANE) meeting the criteria for UN3375 is suitable for transport in bulk. At the 21<sup>st</sup> session in July 2002, the Australian Competent Authority submitted a procedure [1] for a Modified Vented Pipe Test (MVPT), based on the analysis of a series of experiments performed in Australia on behalf of the Australian Explosives Manufacturing Safety Committee. This series of experiments included tests performed on ammonium nitrate (AN) prill, on a number of emulsions whose composition conformed to Special Provision 309 of UN3375 [17], and on several emulsions whose composition lay outside UN3375. The ANE Working Group requested that this MVPT be developed further over the 2003/2004 biennium, with both Australia and Spain agreeing to perform further studies.

Since then, MVPT trials in Spain have been performed on a variety of suspensions and emulsion compositions [2, 3 and 4]. Further testing in Australia has yielded MVPT results for a variety of proprietary emulsion compositions, and for a variety of AN based suspensions [8].

To date, there have been 2 MVPT trials of AN prill, 47 MVPT trials in total of 18 different emulsion compositions, and 34 MVPT trials in total of 14 different suspension compositions. This work reviews the range of behaviours observed during these trials and discusses the nature of the identifiable hazards.

Based on this review, the criterion for the MVPT has been redefined, with the proposed procedure attached as Appendix A2.

## **2. Compositions.**

All compositions tested to date are listed in Table 1. Throughout this document, each composition has been assigned a country code (A for Australia, E for Spain), a type (EM for emulsion, SP for suspension), and a number. Each MVPT trial has been assigned a country code (A for Australia, E for Spain), and a two digit number.

In two cases, similar compositions have been trialed both in Australia and in Spain. The first example includes AEM3, AEM4 and EEM2, all with the same nominal composition, differing possibly in the type of emulsifier used and probably in the molecular weights of the paraffin oils used. The second example includes AEM11 and EEM3, both falling outside the ANE definition due to the presence of sodium perchlorate. Both have the same nominal composition, differing possibly in the type of emulsifier used and probably in the molecular weights of the paraffin oils used.

The Australian suspension compositions were not intended to represent those of current commercial interest, but rather to probe the boundaries of proposed amendments to Special Provision 309 for suspensions [10], and to investigate the effect of various components. Hence, some of the suspensions omitted ethylene glycol and as a consequence were deficient in fuel.

**Table 1. Compositions tested in MVPT trials.**

Composition	AN	SP	Other	Water	Fuel	EG	Em	Th	OB
AAN <sup>6</sup>	100.0								+20.0
EEM1	76.0			17.0	PO 5.6		1.4		-8.7
AEM13	78.2			16.0	DO 4.2		1.4		-3.7
AEM1 <sup>1</sup>	82.1			12.3	DO 4.2		1.4		-2.3
AEM2 <sup>2</sup>	82.1			12.3	DO 4.2		1.4		-2.3
AEM12 <sup>2</sup>	82.1		GMB	12.3	DO 4.2		1.4		-2.3
AEM3 <sup>3</sup>	82.1			12.3	PO 4.2		1.4		-2.7
AEM4 <sup>4</sup>	82.1			12.3	PO 4.2		1.4		-2.7
EEM2	82.1			12.3	PO 4.2		1.4		-2.7
EEM4	67.7		SN 12.2	14.1	PO 4.8		1.2		-1.2
AEM5 <sup>2</sup>	68.3		SN 17.6	6.5	DO 5.7		1.9		-3.4
AEM14	89.5			4.7	DO 5.3		0.5		-1.5
AEM11 <sup>5</sup>	74.9	9.7		9.0	PO 3.7		2.7		-1.6
EEM3	74.9	9.7		9.0	PO 3.7		2.7		-1.6
AEM6	Proprietary emulsion								
AEM7	Proprietary emulsion								
AEM8	Proprietary emulsion								
AEM9	Proprietary emulsion								
AEM10	Proprietary emulsion								
ESP1	62.3	11.0		13.0		13.0		0.7	+0.6
ASP1	82.5	5.0		12.0				0.5	+18.5
ASP2	86.5	5.0		8.0				0.5	+19.3
ESP2	55.0	8.0	SN 8.0	14.0		14.0		1.0	-0.3
ASP3	74.5	5.0	SN 8.0	12.0				0.5	+20.7
ESP5	66.4	8.0	HMN 7.0	12.0		6.0		0.6	+0.5
ASP4	60.5		HMN 17.0	12.0		10.0		0.5	-22.1
ASP5	74.5		HMN 17.0	8.0				0.5	-6.5
ESP4	71.4		HMN 14.0	14.0				0.6	-3.5
ESP6	68.4		MAN 10.0	13.0		8.0		0.6	-0.8
ESP3	67.4		MAN 15.0	12.0		5.0		0.6	+1.2
ASP6	70.5		MAN 17.0	12.0				0.5	+7.7
ASP7	70.2		MAN 16.9	11.9				1.0	+7.1
ASP8	60.5		MAN 17.0	12.0		10.0		0.5	-7.2

Abbreviations: AN ammonium nitrate; SP sodium perchlorate; EG ethylene glycol; Em emulsifier; Th thickener; OB oxygen balance; DO diesel oil; PO paraffin oil; SN sodium nitrate; HMN hexamine nitrate; MAN methylamine nitrate; GMB glass microballoons.

1. Diesel oil distilled for Australian summer conditions.
2. Diesel oil distilled for Australian winter conditions.
3. Paraffin oil had a boiling point range of 235°C to 278°C.
4. Paraffin oil had a boiling point range of 344°C to 683°C.
5. High molecular weight paraffin oil.
6. Non-porous prill.

### 3. Interpretation of thermocouple traces in MVPT trials.

Figure 1 compares representative thermocouple traces from the Australian MVPT trials for water, for pure ammonium nitrate prill, for a representative emulsion (Trial A07 of composition AEM1) and for a representative suspension (Trial A46 of composition ASP7). A detailed interpretation of each of these representative traces is given in Appendix A1 and in the accompanying file [Thermocouple\\_interpretation.pps](#).

The thermocouple traces, the video clips of the final minute or so of each trial, and the photographs of the vessel from each of the Spanish trials published by Quintana et al. [4] showed similar behaviours to those observed during the Australian trials of similar compositions for both emulsions and suspensions. All interpretations of suspension behaviour made throughout this review have been based solely on the data collected and the observations made during the Australian trials.

There were three obvious differences between the emulsion trials (such as in Figure 1(c)) and the suspension trials (such as in Figure 1(d)):

- The suspension trials were of much shorter duration than the emulsion trials in both the Australian and the Spanish investigations. As described in greater detail in Appendix A1, the short duration of each suspension trial was a consequence of the vessel overflowing vigorously once the suspension began to boil. This overflow reduced the amount of material left in the vessel at a relatively early stage of the process, whilst simultaneously increasing the intensity of the fire under the vessel following the ignition and fierce combustion of that material overflowed onto the pad within the shroud. Figure 10 shows a frame from the video of Trial A48, the HMN suspension composition ASP4, where this fire was so intense that roughly a quarter of the brass gas burner jets were melted to some extent. Any similar overflow during a tanker fire could markedly increase both the intensity of the fire and the rate of toxic fume production.
- Suspensions always reacted visibly to the fire at temperatures about 100°C to 140°C lower than emulsions. The suspensions typically started to overflow the vessel once the temperature was around 140°C to 150°C and entered the final stage of rapid decomposition and venting once the temperature was around 160°C to 200°C. In contrast, the emulsions only started to overflow the vessel at temperatures of around 250°C to 260°C and only entered the final stage of rapid decomposition and venting once the temperature was around 280°C to 300°C.
- The suspension trials produced fume in copious amounts at much earlier times than did the emulsion trials, due to some of the overflow material from the vessel decomposing in the fire or in contact with the hot pad under the gas burner. In the MVPT, a significant amount of overflow material was able to flow harmlessly away from the limited area heated by the gas fire and hence not decompose completely. Figure 10 also includes several photographs showing the copious amounts of degraded suspension left on the pad outside the shroud after two of the suspension trials. However in a tanker fire, fume production would be at an accelerated level if the material boiling out of the tanker overflowed into a diesel oil pool fire underneath the tanker.

## 4. Hazards

### 4.1 Background issues

The hazards associated with the MVPT may be discussed in two rather different contexts. Firstly, the results from the MVPT exemplify some of the potential hazards that transport staff, emergency response personnel and the general public might be exposed to in the event of an accidental fire during the transport of ANE. Secondly, the performance of actual MVPT trials exposes R&D staff to a range and a level of hazards that are seldom encountered in traditional research, development, quality assurance and compliance test activities involving the surface firing of industrial explosives. While the impact of the hazards may be greater in the former context, the hazards are encountered far more frequently and with greater certainty in the latter context. The procedure (including whatever acceptance criteria are deemed appropriate) of the MVPT must be written in such a way as to maximise the information generated about potential hazards in the former context, while minimising the actual hazards facing personnel in the second context.

The major hazards associated with the exposure of ANE to prolonged heating arise from the assured generation of toxic fume and from the consequences of possible explosion (which could include injuries to personnel and damage to property from blast overpressures, from direct shrapnel impact, and from fires started by super-heated shrapnel.)

The time scale over which any hazard develops is also of importance. The fuel available during an MVPT trial is effectively infinite, so that every MVPT trial must end in one way or another with the complete emptying of the sample from the vessel. In contrast, the fuel available in the majority of potential fires caused by accidents during road transport would be limited to the fuel, hydraulic oil and tyres on the tanker (with the possible exception of a collision between an ANE tanker and a fuel source such as a petrol tanker). Venart has estimated that the duration of a “typical” road tanker fire would be about 30 minutes [9]. Provided the ANE does not react too quickly to the fire, the fire could burn out before any significant hazard developed, with the ANE remaining in the tanker (albeit in an altered and possibly degraded state). Furthermore, longer times taken before an ANE develops a hazard in an accidental fire would provide the authorities longer to respond and to evacuate the surrounding area.

Hence, the information that is required to assess the potential hazards resulting from exposure of ANE to prolonged heating during transport should include:

- Over what time-scale is potentially toxic fume generated?
- Over what time-scale does explosion become possible?

### 4.2 Toxic fume generation

The decomposition products of ANE will be dominated by those of its major ingredient, ammonium nitrate. The principal decomposition reactions of AN [7] are shown in Table 2.

**Table 2. Decomposition reactions of Ammonium Nitrate [7].**

Number	Reaction	$\Delta H$ (MJ/kg)
1	$\text{NH}_4\text{NO}_3 \rightarrow \text{N}_2\text{O} + 2\text{H}_2\text{O}$	-0.73
2	$\text{NH}_4\text{NO}_3 \leftrightarrow \text{NH}_3 + \text{HNO}_3$	+2.00
3	$2\text{NH}_4\text{NO}_3 \rightarrow \text{N}_2 + 2\text{NO} + 4\text{H}_2\text{O}$	-0.35
4	$4\text{NH}_4\text{NO}_3 \rightarrow 3\text{N}_2 + 2\text{NO}_2 + 8\text{H}_2\text{O}$	-1.16
5	$5\text{NH}_4\text{NO}_3 \rightarrow 4\text{N}_2 + 2\text{HNO}_3 + 9\text{H}_2\text{O}$	-1.54
6	$2\text{NH}_4\text{NO}_3 \rightarrow 2\text{N}_2 + \text{O}_2 + 4\text{H}_2\text{O}$	-1.47
7	$\text{NH}_4\text{NO}_3 + \text{CH}_2 \rightarrow \text{N}_2 + \text{H}_2\text{O} + \text{CO}_2$	-3.80

Reactions 1 to 4 inclusive are the major reactions during the *thermal* decomposition of AN. Reaction 1 is the dominant decomposition pathway below about 250°C, at which temperature Reaction 2 becomes increasingly important. When heating pure AN, the competition between exothermic Reaction 1 and endothermic Reaction 2 can lead to the decomposition self-stabilising at a temperature of 292°C, as observed in the MVPT trial of chemically pure AN prill described in Appendix A1.2. The white fume observed during the MVPT while the temperature is between 250°C and 300°C would probably include superfine AN crystals formed by Reaction 2 operating in the reverse direction in the headspace. Reactions 3 and 4 begin to dominate once the temperature is around 300°C, being replaced by the more strongly exothermic Reactions 5 and 6 once the temperature has risen higher. Indeed, many MVPT trials involving ANE emulsions do show the emission of brown fume ( $\text{NO}_2$  from Reaction 4) during the early stages of rapid venting, followed quickly by the emission of white fume (perhaps  $\text{HNO}_3$  from Reaction 5). Hence heating experiments such as the MVPT will produce some benign gases such as water vapour and nitrogen, but also copious amounts of toxic fume including  $\text{NO}_x$ , ammonia and nitric acid. With the exception of ammonia and  $\text{NO}$ , the toxic fume species formed all have molecular weights higher than that of air (ie. nitrogen and oxygen), with nitric acid being a particularly heavy gaseous molecule. Direct observations from numerous MVPT trials indicate that the clouds of toxic fume do tend to disperse poorly, flowing along the low-lying contours of the ground surface for distances considerably greater than those required for protection from blast and shrapnel effects following any explosion. During MVPT trials, this poor dispersal is exacerbated by the need to conduct the trial under conditions of light winds.

For emulsions, the presence of water and of organics complicates slightly the interpretation of fume production. During the early stages of a MVPT trial, the “fume” being seen to rise gently from the vent is predominantly water being driven from the AN solution. It is believed that this is the case until the temperature in the vessel has risen to about 230°C. Detailed comparison of the video records with the thermocouple traces shows that the rate of fume production increases perceptibly and that its visual appearance begins to change above this temperature. It is believed that this stage represents the onset of AN decomposition via Reaction 1. Hence, the onset time for increased rates of toxic fume production from may be inferred indirectly from the thermocouple traces, though it has not (and in all probability cannot) be measured directly.

The presence of organics appears to prevent the system self-stabilising at 292°C, with Reaction 7 instead promoting the rapid attainment of temperatures above 300°C and the onset of exothermic Reactions 3, 4, 5 and 6 which further accelerate the decomposition rate.

The substitution of some of the AN by inorganic nitrates would not alter the nature of the fume produced to any great extent. The addition of perchlorates would add hydrochloric acid to the list of potential toxic gaseous products.

The situation is slightly different for suspensions. It is likely that the fume emission from the vent accompanying the first overflow event (Stage ⑥ in Figure 8) was predominantly water vapour being lost from the boiling solution. However, material overflowing the vessel onto the hot pad was observed to produce copious amounts of fume, and this was most likely as a consequence of accelerated decomposition there. The discolouration of the subsequent overflow material (Stage ⑧ in Figure 8) indicates that some decomposition had commenced inside the vessel despite the temperature being below 150°C. Certainly, the rate at which fume was emitted from the vent at this stage was too high to be caused only by driving off water. The brown fume generated towards the end, especially for the SP suspensions, was undoubtedly NO<sub>x</sub>.

In contrast to AN decomposition under prolonged heating, the main decomposition reaction of AN under *detonation* conditions is believed to be Reaction 5, generating no toxic products. In general, industrial explosives are usually deliberately formulated close to oxygen balance to minimise the generation of toxic products to minimise the risks to mine personnel. Personal experience from over twenty years of surface test firing of industrial explosives indicates that their detonation products (even in cases where the detonation has failed) disperse far more quickly than do the clouds of fume from the MVPT trials. Hence, test sites that adequately protect the on-site personnel from detonation fumes may not in fact be suitable for conducting MVPT trials. Furthermore, issues of environmental compliance need to be considered carefully while choosing a site for MVPT trials, as the deliberate release of large volumes of NO<sub>x</sub>, ammonia and nitric acid may violate local air pollution laws.

Hence, it is the case that the production of toxic fume should be recognised as a major hazard both during accidental fires involving ANE transport (and of straight AN for that matter), and during the deliberate performance of MVPT trials. Even if the risk of explosion could be discounted, the possible generation of toxic fume would require the immediate evacuation of a large area around an accidental transport fire. Indeed, Adams [13] has investigated the generation of toxic fume from fires involving AN, concluding that the toxic effects from such fires can dominate risk assessments of off-site risks at AN sites. The generation of toxic fume mandates that an extensive exclusion zone be implemented and maintained around an MVPT site for an extended duration for each trial.

### **4.3 Thermal Explosion.**

Prolonged heating of pure ammonium nitrate does not often lead to a thermal explosion, with the competition between the exothermic Reaction 1 and endothermic Reaction 2 (listed in Table 2) usually able to stabilise the decomposition at a temperature of about 292°C at atmospheric pressure [7]. In the MVPT, once pure AN has melted and reached a temperature of about 290°C or so, the vessel contents are observed to fume off fairly gently over a period of about 11 minutes (as seen in Figure 2 for Trial A26), a period consistent with published decomposition rates at this temperature [7].

In contrast, many trials to date involving emulsions and suspensions have ended more dramatically with what appears to be a deflagration starting usually at the top of the vessel, and quickly consuming the contents of the vessel. Sometimes, the pressures generated within the vessel did not exceed its strength, with the result that the reaction products vented to form

a visible and audible high velocity plume. Other times after a short period of such venting, the base plate failed and the vessel was launched vertically to a height of up to 200 m. On some occasions, the deflagration appeared to transition to a detonation, so that after a short period of venting, the vessel disintegrated into numerous fragments.

#### *4.3.1 Hazards during trialing.*

The steel fragments from an MVPT explosion can be much hotter than those normally generated by surface firing of steel-confined explosive charges. It is to be expected that the plastic work performed on the steel during its initial explosive expansion and rupture would heat the fragments. However, the steel in most conventional tests starts at ambient temperature of 25°C or so, whereas in the MVPT, the steel in the side walls starts at about 300°C, while the steelwork at the base of the vessel could be at about 900°C prior to the explosion. The projection of such hot steel fragments markedly increases the risk of starting fires around the test pad compared to conventional surface firing.

#### *4.3.2 Hazards during transport.*

Unfortunately, the occurrence or non-occurrence of an explosion terminating an MVPT trial does not necessarily imply that an accidental fire engulfing a tanker of the ANE would or would not terminate with an explosion respectively.

For example, the majority of the Australian and Spanish suspension trials ended with the vessel intact. However, this was a consequence of the contents of the vessels having largely emptied onto the pad prior to the attainment of high temperatures, with little material remaining to participate in any final deflagration once they had been heated to high temperature. A vessel design which inhibited the overflow of its contents may well have led to more frequent explosions during suspension trials. In a tanker fire, any overflow is more likely to intensify the fire and increase the heat flux into the remaining inventory than to drain away harmlessly as in the MVPT. Such increased heat flux would accelerate subsequent decomposition.

Furthermore, as discussed previously by Kennedy [5], rough engineering calculations of the relative strength of the MVPT vessel compared with typical transport tankers indicates that the former is about an order of magnitude stronger than the latter. This has two consequences.

Firstly, on the one hand, any deflagration would be more likely to lead to rupture of a weaker vessel than a stronger vessel. Hence, it is probable that some of the compositions whose MVPT trial ends with a vented plume of reaction products could develop sufficient internal pressurisation during a transport fire to rupture the transport tanker.

Secondly, on the other hand, rupture of a weaker vessel would lead to a less violent explosion in three different ways.

- It is a common feature of deflagrations that their propagation velocities are linearly proportional to the pressure. Hence, the deflagration velocity at the pressure at which a transport tanker ruptures should be an order of magnitude slower than the deflagration velocity at the pressure at which an MVPT vessel ruptures. Furthermore, inspection of the 500 fps digital videos taken during the Australian MVPT trials showed that invariably any deflagration was quenched by adiabatic cooling within a few milliseconds of vessel rupture. Consequently, an explosion following a deflagration in a transport tanker should consume a smaller fraction of the total inventory than would an explosion following a deflagration in an MVPT vessel.
- Following on from the first point, a slower deflagration velocity with its slower pressurisation rate should be less likely to lead on to a transition to detonation.

Consequently, the likelihood of a detonation during an accidental fire during transport should be lower than in the MVPT trials.

- If the peak internal pressure is an order of magnitude lower, then the acceleration of the walls upon rupture should be an order of magnitude less, leading to much lower final fragment velocities.

Furthermore, there have been several occasions where substances that have not led to explosions during MVPT trialing have led to explosions during accidental fires during storage or transport. For example, there have been a number of accidental fires during which straight AN and its mixtures with combustible materials have exploded [14, 15 and 16]. However as shown in Figure 3 and discussed in Appendix A1.2, pure AN decomposed without venting or explosion in the MVPT. The Scandinavian consortium found that a mechanical (ie unemulsified) mixture of AN solution and fuel did not explode in their wood-fired USA Vented Pipe Test [17]. Similarly, a mechanical mixture of ANFO and emulsion (viz Trials A19 and A21 of low-water composition AEM14) decomposed without venting or explosion in the Australian trials [5].

Hence in summary, it is to be expected that explosions should in general be more frequent but less violent during accidental fires of infinite duration involving transport tankers compared to the case during MVPT trials. However, there are sufficient exceptions to indicate that explosion by itself does not prove a reliable criterion on which to base the outcome of MVPT trials.

## **5. Proposed procedure and criteria for the MVPT.**

The recommended revised procedures and criteria for the Modified Vented Pipe Test are given in Appendix A2. The considerations underlying these recommendations are discussed below.

### **5.1 Proposed run-time.**

The outcome of the traditional wood-fired USA Vented Pipe Test is determined solely by whether or not the vessel explodes before the fire burns out. However, as discussed previously, the definite hazard from toxic fume production develops at a lower temperature and at an earlier time before there is even a possible risk of explosion. Hence basing the outcome solely on explosion ignores a potential major hazard that must be included in risk assessments. Consequently, it is the recommendation of this work that the outcome of the MVPT should be judged on how long it takes the trial to conclude, regardless of whether or not the trial concludes with an explosion. The suitable choice of the allowable period of heating, which will be referred to here as the “run-time”, would exclude the premature development of hazards from both toxic fume production and possible explosion during this defined period.

Direct observations made during each of the 50 MVPT trials conducted in Australia have established that it is without exception obvious when a trial has concluded, and that a conclusion time can be measured unambiguously from the thermocouple traces. Visual and aural observation would usually note either an explosion or a brief period of vigorous venting, accompanied by a rapid rise in thermocouple traces to a sharp peak followed by a gradual decline. In those few instances where visual and aural observation were inconclusive, notably for those trials of suspensions containing sodium perchlorate, the thermocouple traces provided a clear indication when the period of rapid decomposition had concluded and the temperatures had peaked inside the vessel.

As described in Appendix A1.2 and shown in Figure 3, Trial A26 of pure ammonium nitrate prill showed that the 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.

Following the discussion in Section 4, it is uncertain exactly when the visible emissions from an emulsion change from predominantly water being driven from the solution to include toxic fume from chemical decomposition. Nonetheless, the period of elapsed time between the vessel overflow and the final venting shown in Figure 4 for Trial A07 was comparatively very short, being only about 3 minutes in duration. Since it is believed that vessel overflow for emulsion is an ultimate consequence of a rapid increase in the decomposition rate, it may be inferred that the period of intense toxic fume production for this emulsion is considerably shorter than the period for pure AN.

The experimental evidence indicates that this is a general feature of emulsion behaviour in the MVPT. Figure 12 collates data from all Australian and Spanish emulsion trials, with the blue bar for each trial extending from the commencement of vessel overflow to the completion of the trial. In every emulsion trial, the period of time when copious amounts of fume were being produced, between vessel overflow (signifying the onset of rapid decomposition) and trial conclusion, was much shorter than the equivalent period for the pure AN.

**This suggests that a logical and convenient criterion for ANE in the Modified Vented Pipe Test could be based on the adoption of the conclusion time of Trial A26 of pure ammonium nitrate prill as the run-time,  $t_{run}$ .** For the Australian MVPT apparatus, this run-time is determined from the data shown in Figure 3 to be:

$$t_{run} = \mathbf{64 \text{ minutes } 37 \text{ seconds.}}$$

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 30 minutes.

Furthermore, the adoption of a run-time based on the behaviour of AN would assist in the quantification of risks during ANE transport. Historical archives of information relating to accidents during the transport of AN could be used to estimate the frequency with which fires have been of sufficient duration to lead to the total decomposition and loss of the whole AN inventory. This would provide an upper bound on the frequency for which the generation of toxic fume and the possibility of explosion might be encountered during the transport of ANE.

## **5.2 Correction to the run-time for the influence of heating rate and initial temperature.**

Any world-wide test based on the time taken to heat a substance to a given end-point must make allowances for any slight differences in heating rate of different apparatus and in the initial temperature of the test sample.

### *5.2.1 Effect of heating rate: the water calibration time.*

The MVPT can be calibrated by determining how long it takes to heat water, with the vessel filled to the 75% level, to the boiling point from a standard initial temperature of 25°C.

In a typical calibration of the Australian apparatus, it took 21 minutes 30 seconds to heat water to 100°C from an initial temperature of 32°C. The mean calibration heating rate  $\dot{T}_{cal}$  between 40°C and 80°C (where the heating rate was observed to be constant) was measured to be  $\dot{T}_{cal} = 3.50^\circ\text{C}/\text{minute}$ . The calibration time  $t_{cal}$  for the apparatus was then given by:

$$t_{cal} = 21 \text{ minutes } 30 \text{ seconds} + (32^\circ\text{C} - 25^\circ\text{C})/\dot{T}_{cal} = 23 \text{ minutes } 30 \text{ seconds.}$$

Such a calibration would be performed at the start of each round of MVPT testing. In the proposed procedure of Appendix A2, it is recommended that the water calibration time should lie between 21 minutes 30 seconds and 26 minutes 30 seconds. If outside this range, suitable adjustments would be required to the gas flow, or if that proved insufficient, to the height of the stand supporting the vessel above the gas burner.

### 5.2.2 Effect of initial temperature.

Obviously, it would be preferable if all ANE candidates were tested over the temperature range normally encountered during shipping. However, when dealing with relatively small quantities of ANE at remote sites, often during winter to reduce the risk of fire, it may be unavoidable that the ANE has cooled appreciably prior to testing. In such a case, the extra time required to reheat a cool sample back to its normal shipping temperature would need to be taken into account.

The derivation of a suitable correction factor has been based on the observation that the earliest clearly identifiable common state in each trial is when all thermocouple traces first converged, denoting the onset of large scale convection currents. This convergence point is identified for an emulsion in Figure 13(a) and for a suspension in Figure 13(b).

Figure 13(c) collates the average heating rate to this convergence point for every MVPT trial conducted in Australia. Despite including a wide range of emulsion and suspension compositions and despite covering a range of initial temperatures spanning 50°C, it is observed that the water calibration heating rate  $\dot{T}_{cal}$  serves as a convenient lower bound for the complete data set within the observed scatter. Its usage is described in the next section.

The adoption of this lower bound as the correction factor is conservative, in that it leads to longer run-times (and hence greater chance of a positive outcome) in those cases where the initial sample temperature is below the normal shipping temperature.

It is recommended that an ANE candidate should not be tested at an initial temperature above the range of its normal shipping temperature, as there is no convenient upper bound on the observed convergence heating rate data in Figure 13(c) that could serve as a conservative correction factor.

### 5.2.3 Calculation of the corrected run-time $t_{run}$ .

There is now sufficient information to relate and standardise all run-times and correction factors to well defined and convenient values measured during the water calibration. Converting the run-time discussed in Section 5.1 to a multiple of the water calibration time  $t_{cal}$ , and using the water calibration heating rate  $\dot{T}_{cal}$  to correct for the effect of initial temperature leads to the following proposed definition for the run-time for a composition tested at an initial temperature  $T_0$  whose normal shipping temperature is  $T_s$ :

**Run-time:** 
$$t_{run} = 2.75 \times t_{cal} + (T_s - T_0)/\dot{T}_{cal}$$

While explicitly based on the heating rate of water, this run-time definition implicitly accounts for the observed heating rate and decomposition behaviour of pure ammonium nitrate. However, basing the run-time on the heating rate of water rather than of AN permits

the adoption of an international standard, free of the variability that would be introduced by slight differences in packing density of different AN prill types.

### 5.3 Other considerations.

The procedure proposed in Appendix A2 leaves it to the discretion of the personnel performing the trial as to what action to take once the run-time has been reached without observed positive outcome.

There are some advantages in being able to switch off the gas supply at that time and to let the vessel and its contents begin to cool. In particular, for the majority of the emulsion compositions examined to date, it would have avoided heating the emulsion firstly to those temperatures at which intense decomposition generated copious toxic fume and secondly to higher temperatures again where explosion and projection of hot metal fragments became possible. This would have greatly reduced the adverse environmental impacts of fume emission and the risk of starting fires.

However, after an hour of intense heating in the MVPT, all emulsion tested to date would have had its emulsion structure destroyed and the majority of its initial water content driven off. The trial personnel would then be faced with a vessel containing over 30 kg of essentially molten AN contaminated with some hydrocarbon, all at a temperature in excess of 170°C or so. The vessel could not be moved without the risk of personnel being splashed with hot liquid. However, to leave the vessel in place would mean that the test pad would be unavailable for further trials for many hours, as all of the AN remaining in the vessel would have to crystallise before the temperature of the vessel could begin to cool below 160°C or so. Once cooled, the disposal of the vessel and its solidified contents would present a variety of environmental concerns, since the contents could not be recycled but yet its burial could contaminate ground water with AN residues.

Such issues are best dealt with locally on a case by case basis.

### 5.4 Application to all MVPT results.

Figure 12 collates the results for all valid MVPT trials of emulsions and suspensions performed in Australia and in Spain, grouped according to the type of composition. (The results from those few trials where problems were identified either with the gas flow or with the emulsion manufacture have been omitted.) All results relate to vessels filled to the 75% level, with the sole exception of Trial A18 which was filled to the 37.5% level to examine the effect of fill factor. All times have been corrected to a common water calibration heating rate  $\dot{T}_{cal} = 3.50^\circ\text{C}/\text{minute}$ .

For each trial, the blue bar indicates the time period over which toxic fume was most probably being produced at an intense rate, with the lower edge representing the time at which the vessel overflowed, and the upper edge denoting the conclusion time of the trial. Each Australian result is shown with a solid blue bar, signifying that these data were derived by a detailed and joint inspection of the video records and the thermocouple traces. Each Spanish result is shown with a stripped bar, indicating that only the thermocouple traces from reference 4 were available for inspection during the preparation of this report, resulting in some uncertainty particularly in the time of first overflow which had to be inferred by analogy from the behaviours observed in the Australian trials.

The severity of the concluding event for each trial is labelled with ❶ indicating fuming (as in Figure 2), ❷ indicating venting (as in Figure 9), ❸ indicating explosion with failure of an end plate, and ❹ indicating explosion with vessel fragmentation. Each trial is annotated with the vent diameter and with the initial temperature of the sample.

Figure 12 also includes the proposed run-time for each trial, corrected for initial temperature according to Section 5.2.3 and shown by the green line. It has been assumed that the normal shipping temperature for an emulsion is 60°C, while that for a suspension is 40°C. The minimum duration of the USA Vented Pipe Test is denoted by the brown line while the time at which AN begins to decompose vigorously is denoted by the red line – both of these lines have been corrected for the effects of initial sample temperature in a similar fashion as the run-time.

#### *5.4.1 Emulsions conforming to Special Provision 309.*

It can be seen that all emulsion compositions conforming to the current UN3375 ANE [17] definition returned a negative outcome, with two exceptions whose trials concluded before their respective run-times.

The first exception was Trial A33 of composition AEM8. The sample emulsion used in this trial was particularly viscous at its initial temperature of 11°C, which was well below the range of normal shipping temperatures for this composition. It is inferred that the abnormally high viscosity of the composition at this low temperature had inhibited the breakdown of the emulsion, inhibiting the flow of hot liquid up the sides of the vessel (Stage 2 of Figure 6). This allowed localised high temperatures to develop at the base of the vessel, leading to premature exothermic decomposition and an accelerated overall heating rate. When re-tested at normal viscosity at an initial temperature of 55°C (within its range of normal shipping temperatures), this composition returned a negative outcome with 15 minutes to spare.

The second exception was Spanish Trial E29 of composition EEM2. This trial appears to have behaved anomalously, with its trial terminating about 20 minutes earlier than expected from the trends established by the other five trials of similar compositions. No reason for this can be inferred from the information published by Quintana et al. [4].

#### *5.4.2 Emulsions not conforming to Special Provision 309.*

Both Australian trials of emulsion composition AEM11 returned positive outcomes. This composition contained sodium perchlorate, and hence lay outside the current UN3375 ANE [17] definition. While one Spanish trial of the similar composition EEM3 returned a positive outcome, the second trial returned a negative outcome, though the trial did conclude only 80 seconds past its run-time.

Composition AEM12 was tested in the MVPT solely for heuristic reasons. Its sensitisation by the addition of glass micro-balloons would lead to a positive outcome in the Series 8(b) Gap Test, so that it would not normally be considered as a candidate for the Series 8(d) MVPT. It returned a negative outcome in the MVPT. It was inferred that the micro-balloons acted to scavenge all of the hydrocarbon from the solution, and raised it to the top of the vessel where it burnt off harmlessly. The remaining solution fumed off in a similar manner and over a similar time-scale to that observed for pure AN.

#### *5.4.3 Suspensions not conforming to Special Provision 309.*

Every suspension composition tested to date in the MVPT has included one or more chemical sensitisers, and thus lies outside the current Special Provision 309 [17], though within the proposed amendment to Special Provision 309 definition [10] on the agenda for discussion at the December 2003 SCETDG meeting.

It can be seen from Figure 12 that every MVPT trial of all suspension compositions tested to date has concluded well within the run-time proposed for ANE, thus returning positive outcomes according to the proposed MVPT procedure. As discussed previously, the suspensions tested to date have reacted to the fire by boiling and copiously overflowing the vessel at relatively low temperatures and at relatively early times. While this has in general

left too little suspension in the vessel to cause an explosion during the final stages of the trial, the suspension lost from the vessel does have to be accounted for somewhere.

In the MVPT trials, the gas burner is directly underneath the vessel, and is shielded by it from any suspension overflowing from the vent and cascading down the sides of the vessel. As a consequence, the majority of the overflow suspension was observed to drain away harmlessly from the immediate vicinity of the gas burner, though some suspension left lying on the pad inside the protective shroud often ignited, intensifying the fire under and around the vessel, and increasing the overall rate of fume production.

In an accidental fire during transport, the majority of any overflow material from the tanker would follow the ground contours draining into, not away from, any pool of burning diesel and hydraulic oil. The resulting fire intensification and increased levels of heat flux back into the tanker would act to decrease the time available to the emergency services to deal with the rapidly increasing hazard from toxic fume production. Furthermore, since the majority of the overflow material would be expected to contribute to fire intensification during a tanker fire, the intensification would increase at an even faster rate than was the case during the MVPT, where the contribution from the small portion of overflow suspension that ignited was sufficient to melt some of the gas burners.

All suspension compositions tested in the MVPT to date have included either sodium perchlorate, methylamine nitrate or hexamine nitrate as chemical sensitiser. All such compositions have given positive outcomes according to the proposed procedure, with their trials concluding sometimes in less than half the proposed run-time based on the decomposition time of ammonium nitrate.

This should provide sufficient grounds to reject the proposed addition of chemically sensitised suspensions to Special Provision 309 [10].

#### *5.4.4 Suspensions conforming to Special Provision 309.*

No suspension composition tested to date in the MVPT has conformed to the current ANE definition given by Special Provision 309 [17]. Hence, it is not currently known if all suspensions would give positive outcomes in the MVPT or just those containing chemical sensitisers. It is possible that there are thickening agents that would not support the various mechanisms that can lead to premature vessel overflow at the boiling point of the aqueous phase. With the appropriate choice of fuel and in the absence of chemical sensitisers, it is likely that the onset of rapid decomposition could be shifted to temperatures significantly higher than those observed to date for the chemically sensitised suspensions. Both of these compositional choices could contribute to prolonging the duration of suspension trials sufficiently to return negative outcomes under the proposed MVPT procedure.

This is an area that would benefit from further investigation, though there are no plans to perform such work in Australia at the time of writing.

### **5.5. Concluding remarks**

The proposed MVPT would appear to fulfil many of the requirements for a large scale test intended to delineate the response of candidate ANE to prolonged heating in accidental fires during transport.

The procedure is robust. The test apparatus has been assembled in two different countries, and has given reproducible results as exemplified by similar heating conditions, similar thermocouple traces and similar observed behaviours over a range of compositions. Corrections can be made for small differences in heating rate and sample initial temperature. The thermocouple traces and video records can be analysed jointly to give considerable

insight into the physical processes occurring during the breakdown, boiling, concentration and finally decomposition of ANE.

The test heat source and geometry appears to provide a realistic yet conservative simulation of the conditions during a “typical” road tanker fire. The prolonged and constant heat flux into the base of the vessel [5] exceeds by about 25% the *peak* heat flux measured during experimental tests of pool fire engulfment of LPG tanks [11]. The duration of the MVPT (ie the run-time) is roughly twice the duration of a “typical” road tanker fire where the diesel was assumed to pool under the vehicle [9]. The ratio of heated surface area to ANE volume in the MVPT [5] closely matched that of the Kuosanen full-scale burning test [12].

However, this still leaves two issues to be discussed.

- The MVPT cannot delineate the potential risk from explosion during a transport fire involving ANE. On the one hand for example, a deflagration that vented a high velocity plume but left the comparatively strong MVPT vessel intact, could develop sufficient internal pressure to rupture a comparatively weak tanker. As another example, the open MVPT vent allowed suspensions in particular to boil over and overflow the vessel so readily that the vessel was almost empty before reaching the ignition temperature for a deflagration, generating little gas and leaving the vessel intact; the closed hatch on a typical tanker could impede overflow to the extent that a considerably larger fraction of the initial inventory could still be present at the ignition temperature for deflagration, with the greater volume of gas produced more likely to lead to explosion of the tanker. On the other hand, the comparatively strong MVPT vessel can withstand the build up of relatively high internal pressures, increasing the likelihood that an internal deflagration could transition to detonation when compared to the lower pressure regime that could be reached prior to the rupture of comparatively weak tankers. Furthermore, there have been several occasions where substances that have not led to explosions during MVPT trialing have led to explosions during accidental fires during storage or transport.
- While estimates may be made of the conditions during a “typical” tanker fire, there may be a variety of “non-typical” fires where conditions are considerably different.

Both of these issues are addressed by the proposed criterion based on whether the trial of the ANE candidate finishes earlier or later than pure ammonium nitrate being heated under the same conditions (remembering that a trial finishes only once all the decomposable material has emptied by whatever mechanism from the vessel). The proposed criterion offers several advantages.

- Basing the criterion upon time and not upon the presence or absence of vessel rupture removes any dependence upon experimental factors that would otherwise be difficult to measure and to control. Such factors include the quality of the welds between the vessel walls and endplates, and the yield strength of the steel at elevated temperatures.
- The criterion is an inclusive and all embracing one, in that a trial can finish prematurely not only in explosion (producing blast and shrapnel), but also as a consequence of rapid decomposition (forming toxic products) or of prolonged vessel overflow (intensifying the fire and producing toxic fume).
- The criterion allows quantitative risk assessments to be based on the experiences gained historically from a much wider base of transport accidents. Ammonium nitrate has been transported in much greater quantities for a longer period of time, and has as a consequence been involved in many more, and of a wider variety of, transport fires, than has ANE. It is presumed that inspection of historical data could be used to estimate what fraction of AN transport loads have been involved in accidental fires, and of those fires,

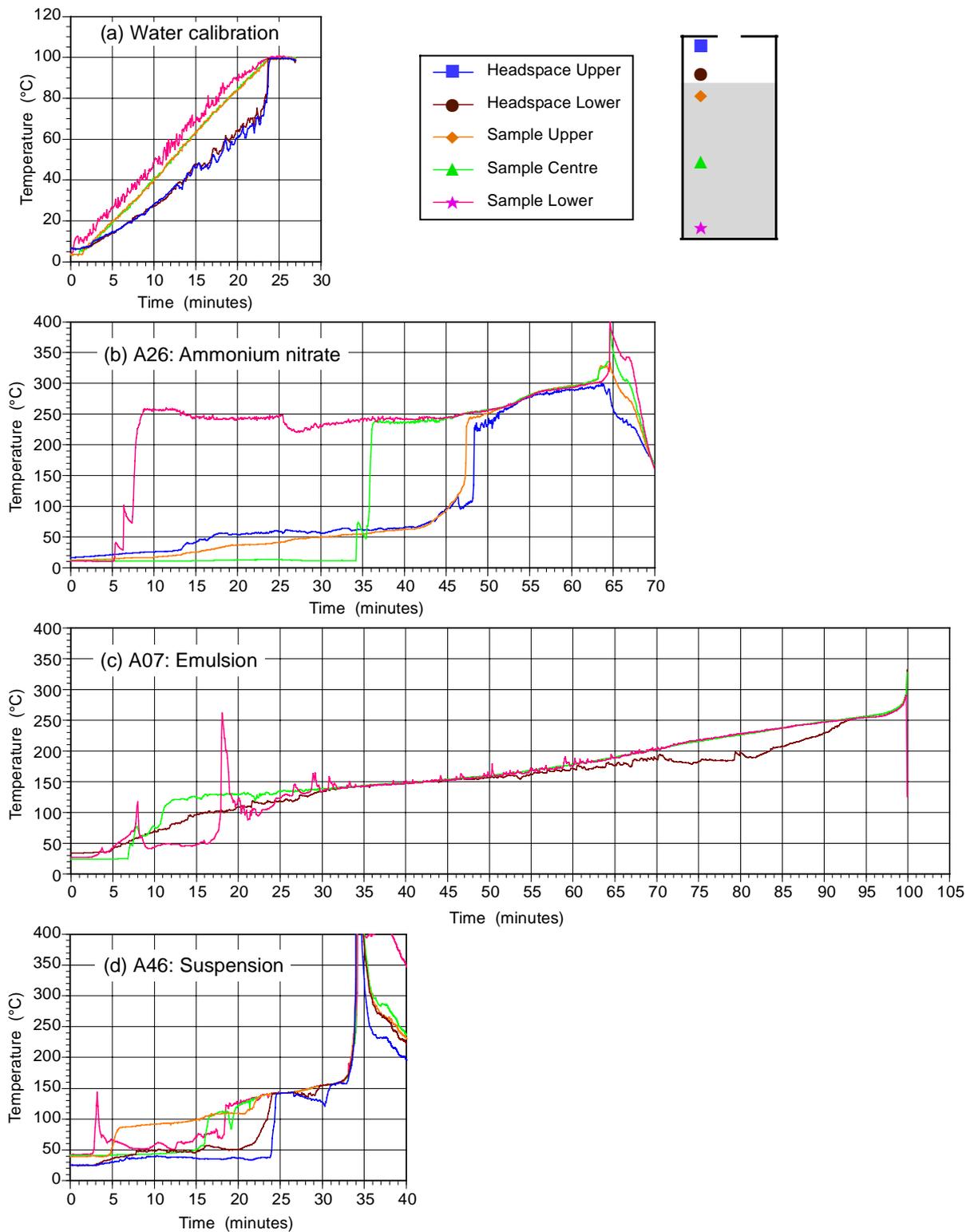
what fraction have been of sufficient intensity and duration to completely empty the tanker of AN (either by explosion or by decomposition). It is the latter case that represents the minimum fire conditions necessary to bring an ANE approved for bulk transport by the MVPT to the stage where major decomposition and fume production may commence and where, at a still later time, explosion becomes possible.

- The criterion delineates the time-scale before which any major hazards develop, and hence the time-scale available to the authorities to respond to an accidental fire involving ANE. This time-scale is in excess of one hour under heating conditions that match those of the MVPT.

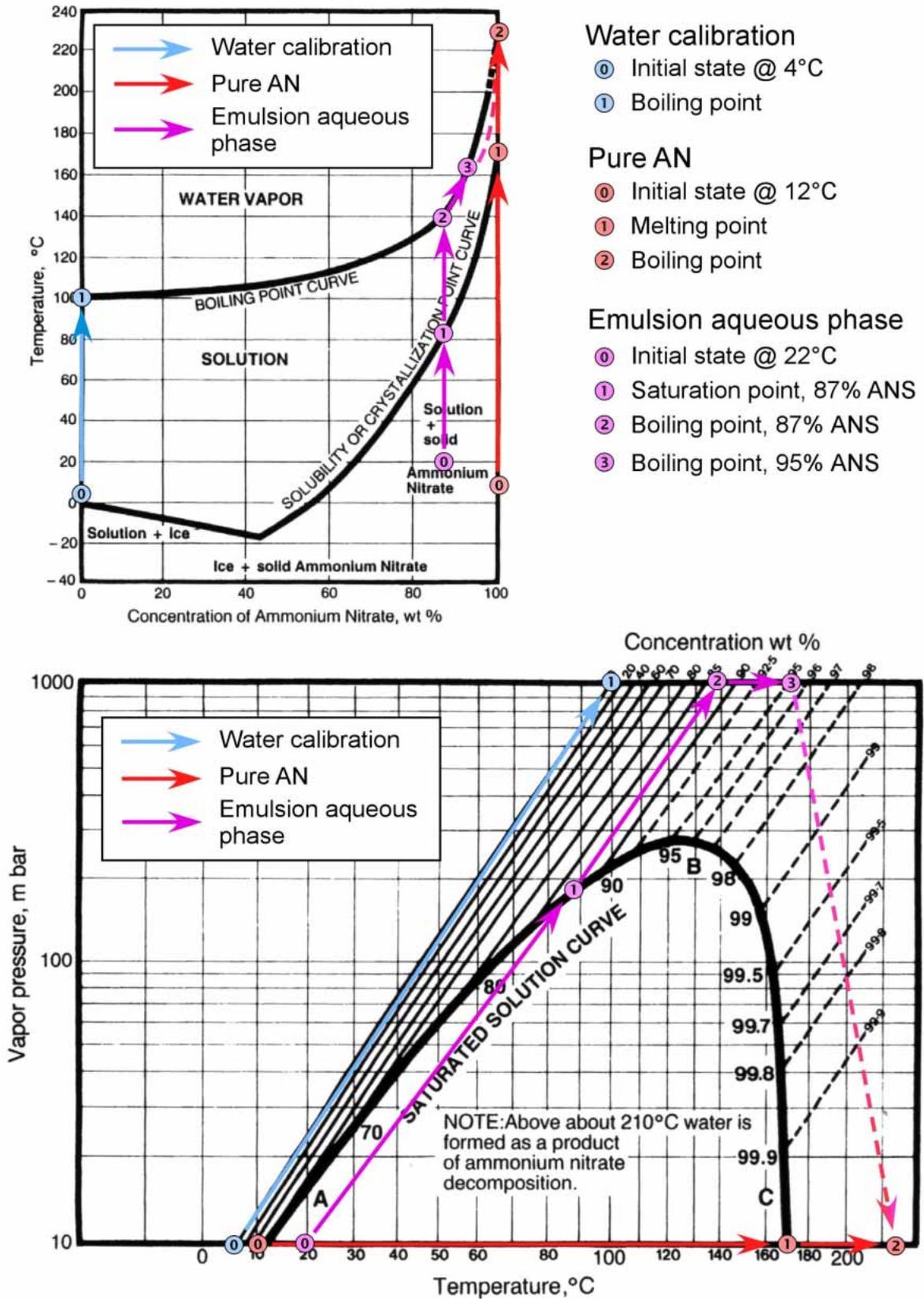
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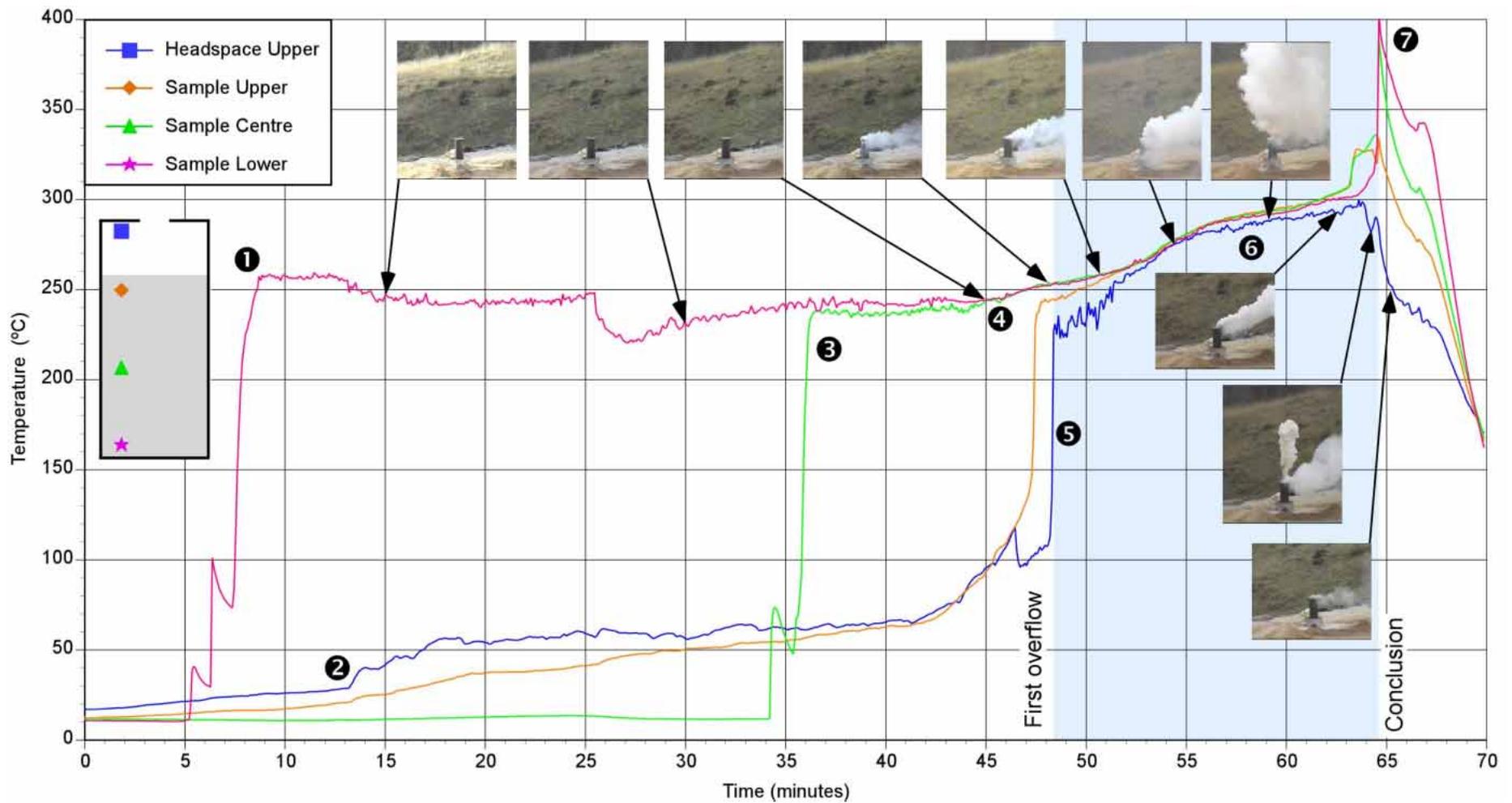


**Figure 1. Thermocouple traces from the Australian MVPT trials for (a) water, (b) pure ammonium nitrate, (c) a representative emulsion and (d) a representative chemically sensitised suspension.**



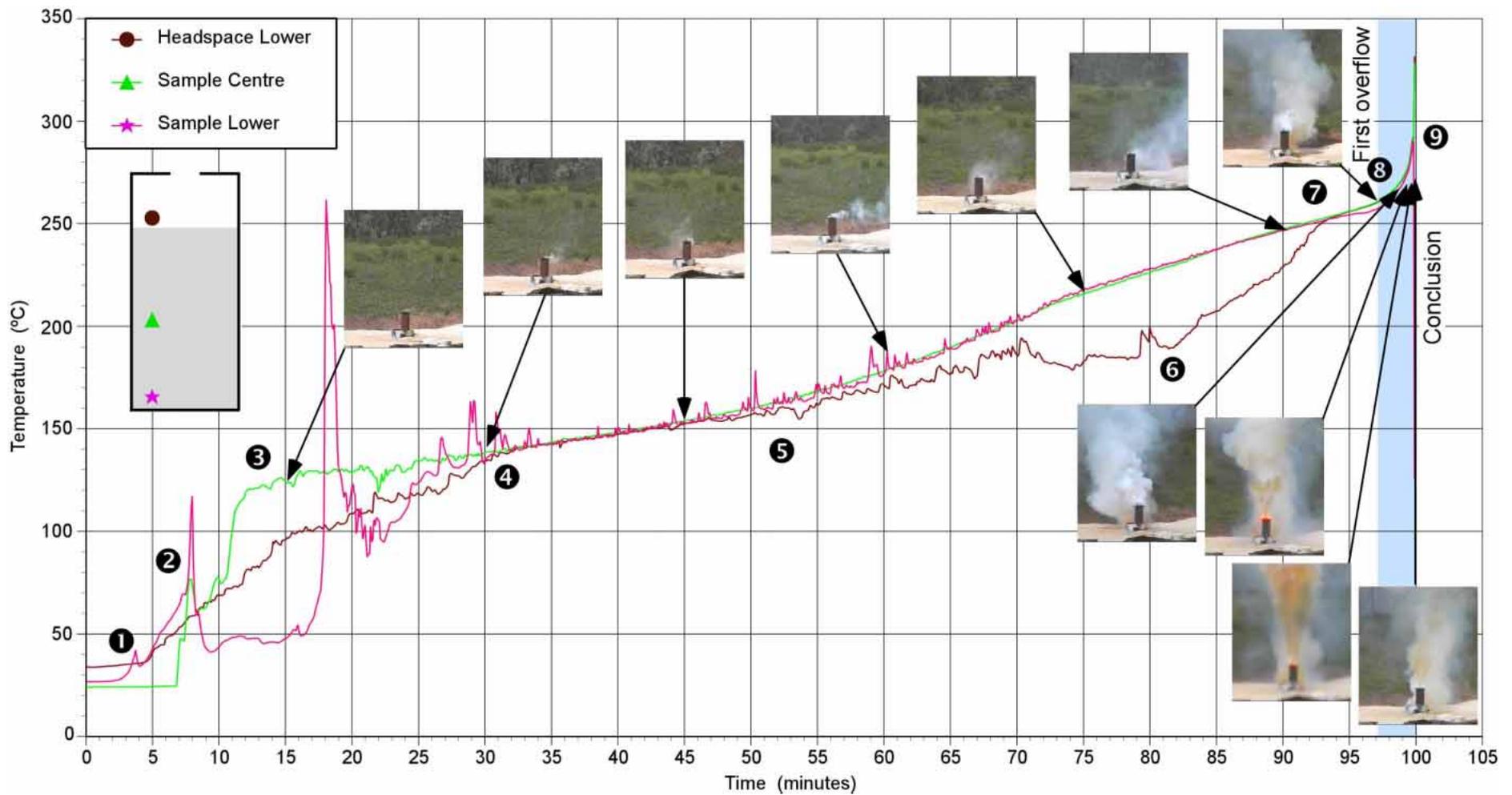
**Figure 2. Phase diagram (upper) and vapour pressure diagram (lower) for ammonium nitrate solutions (ANS).**

Reproduced with additions from Shah and Roberts [7]. The data set referred to here as “Emulsion aqueous phase” relates to Trial A07 of emulsion composition AEM01, whose thermocouple traces are shown in Figure 1(c) and Figure 4.



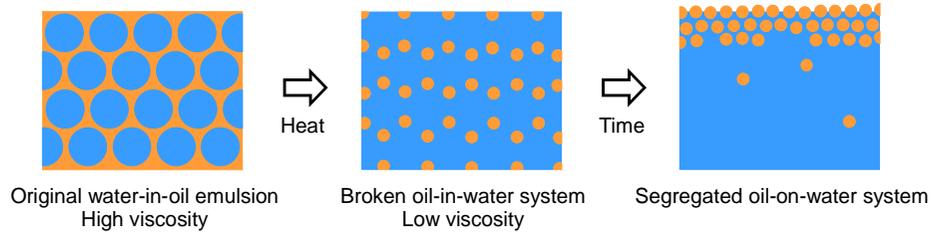
**Figure 3. Thermocouple traces and photographs of Trial A26: Pure Ammonium Nitrate.**

*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 ❷) 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.*

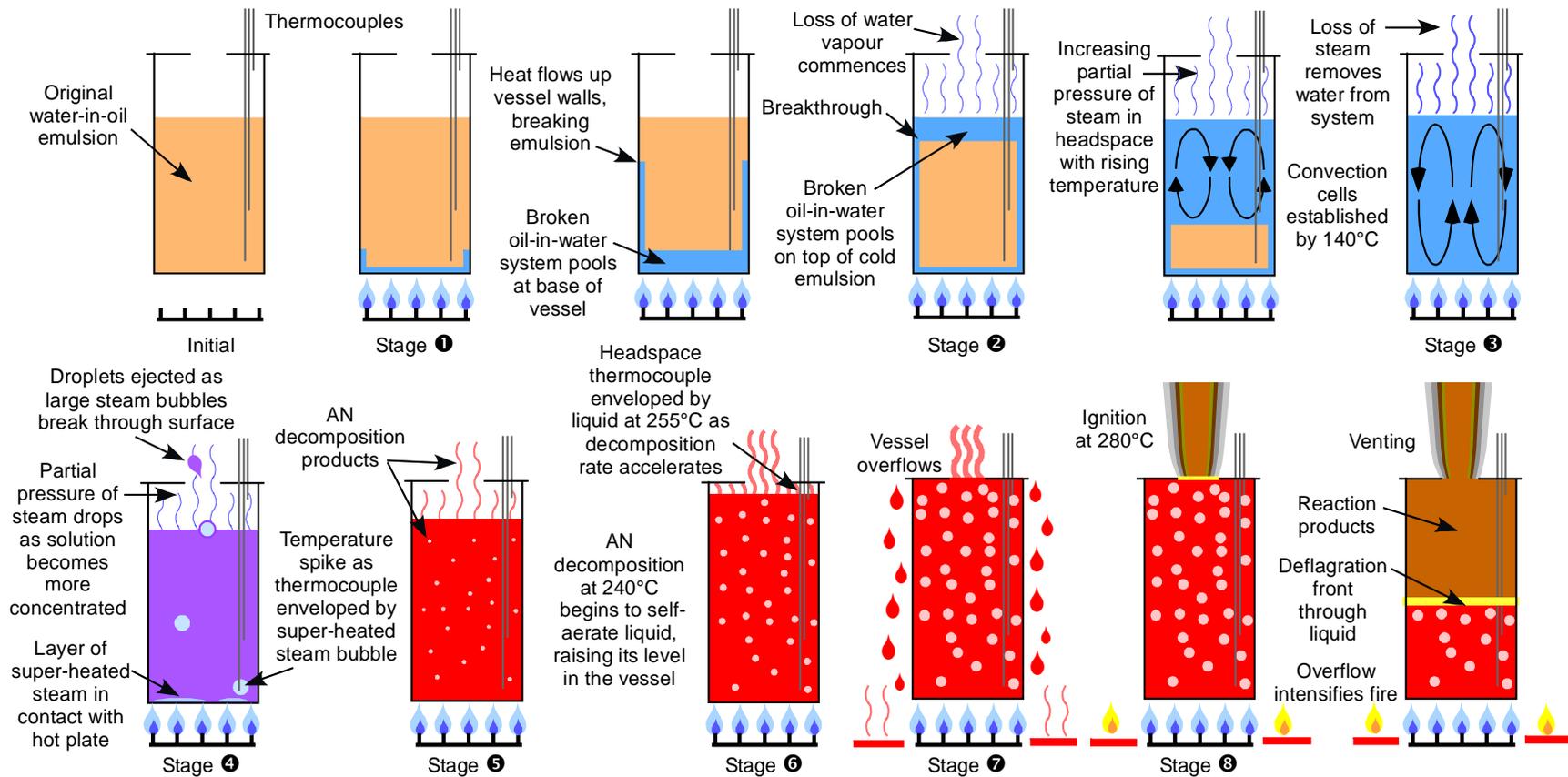


**Figure 4. Thermocouple traces and photographs of Trial A07: Emulsion.**

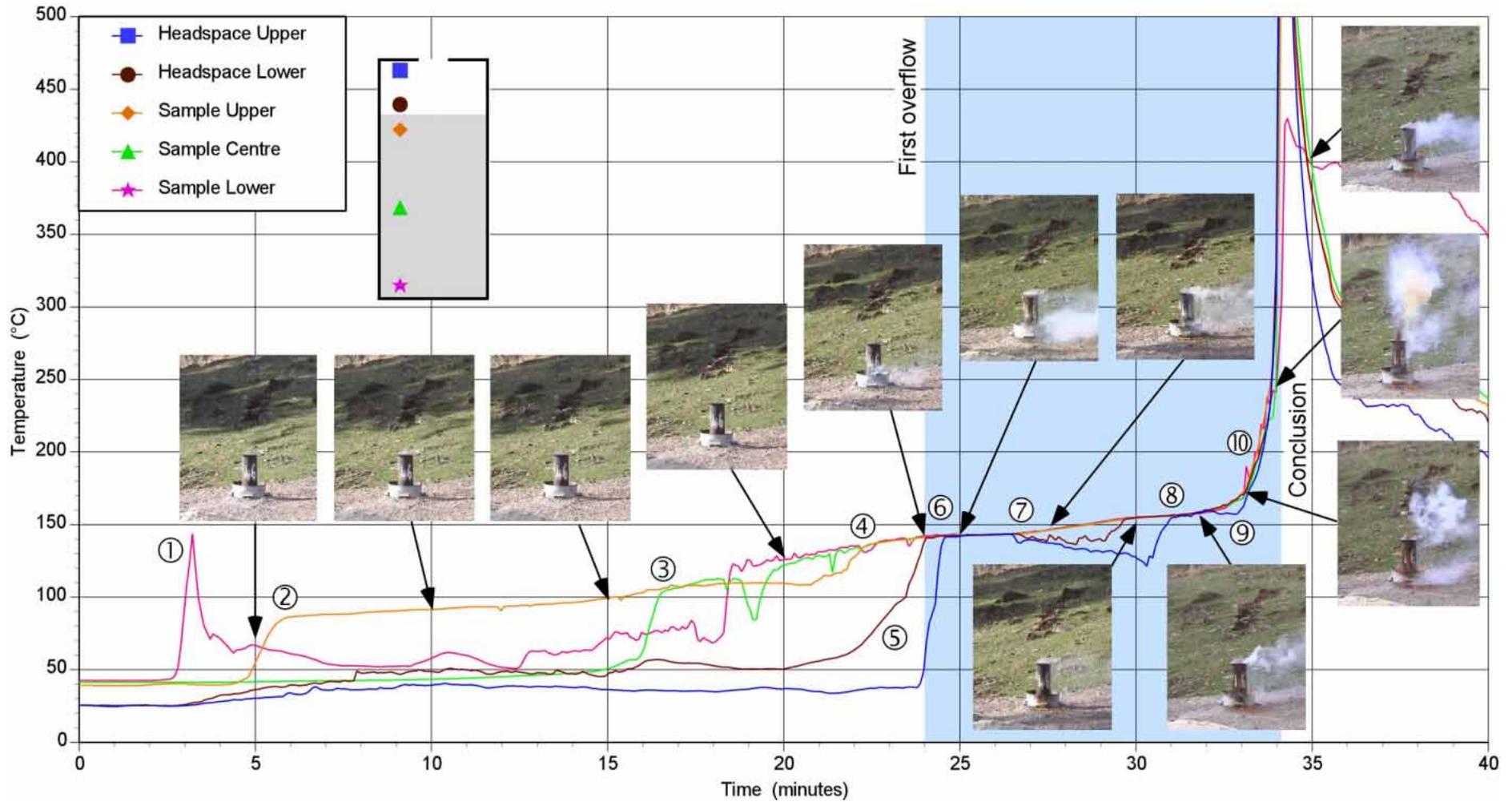
*This trial used a vessel filled to the 75% point with emulsion composition AEM2. The numbered features (1 to 3) are referred to in Appendix A1.3 and illustrated schematically in Figure 6, while the partial blue background denotes the period between the start of vessel overflow and the trial conclusion.*



**Figure 5. Schematic illustration of emulsion breakdown during heating.**



**Figure 6. Schematic illustration of the behaviour of an emulsion in the MVPT.**



**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.*

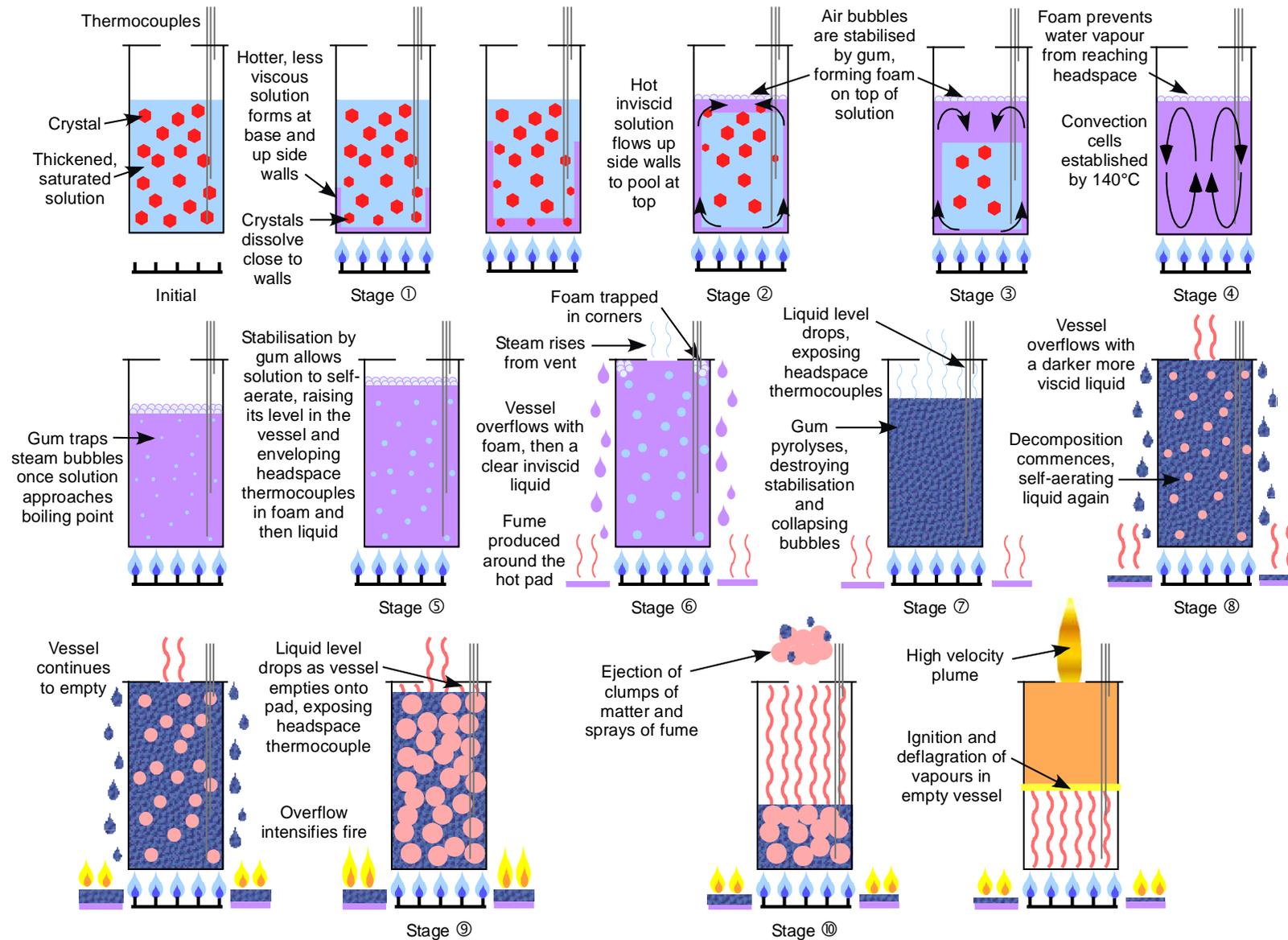
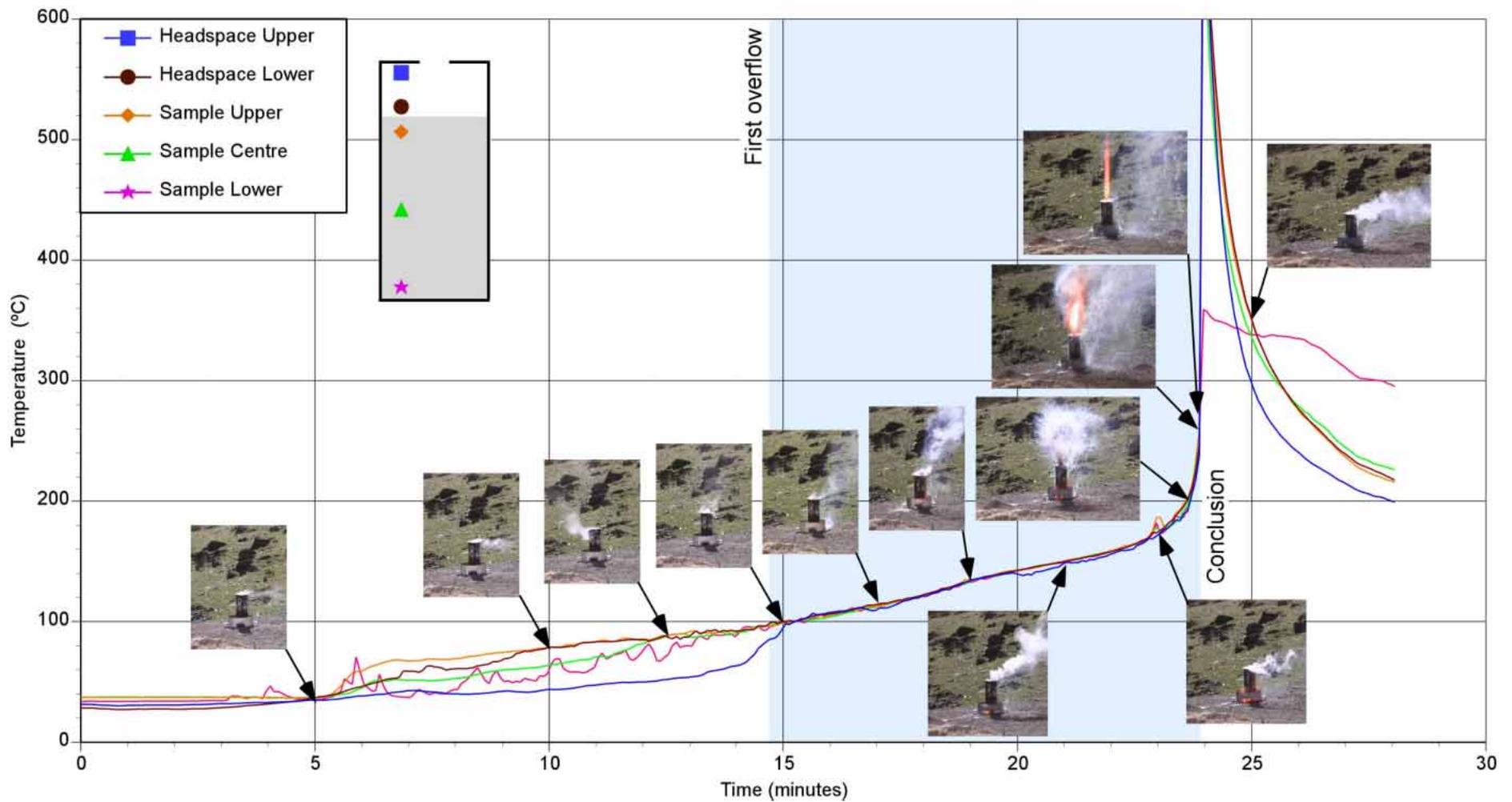


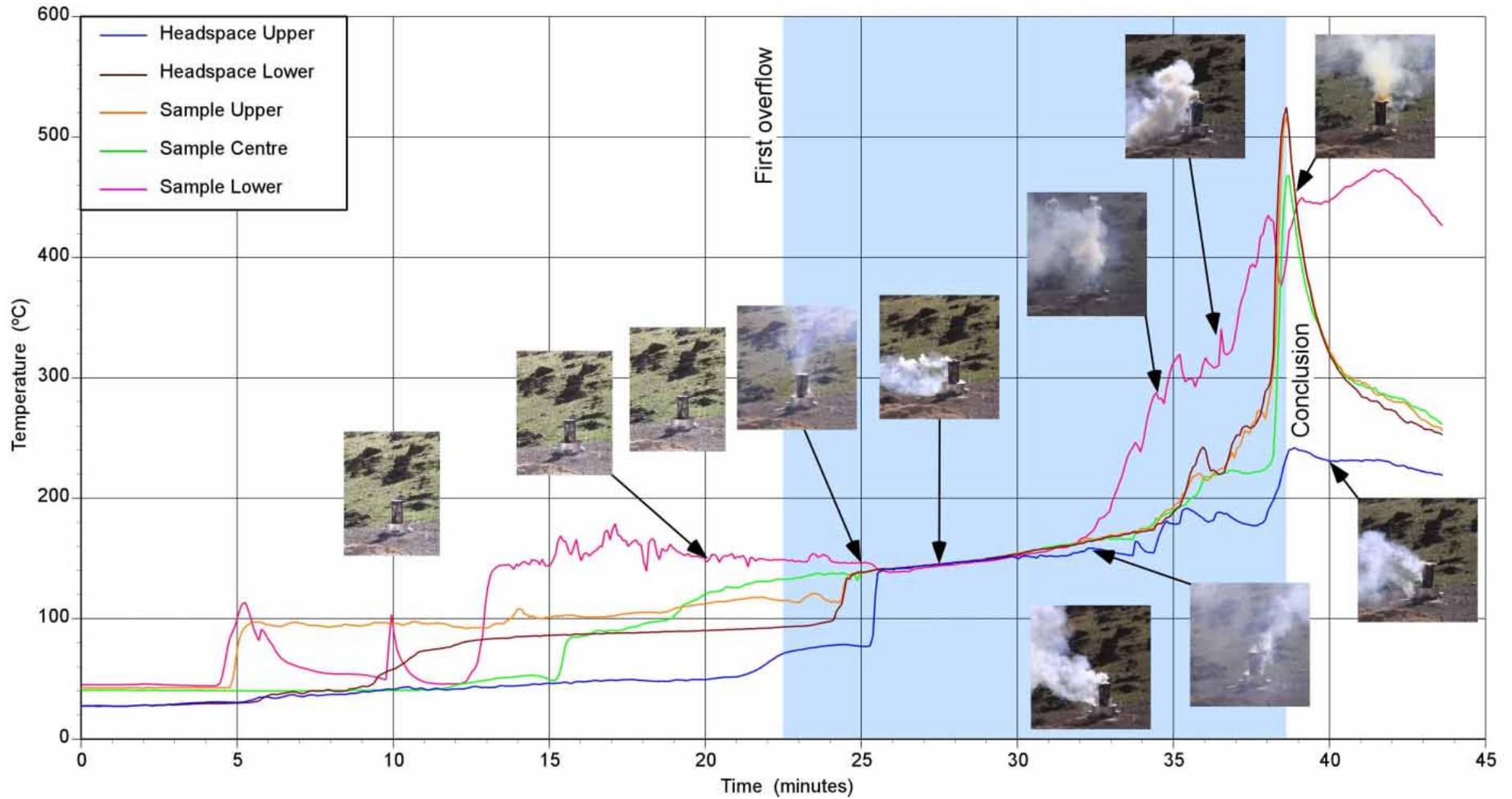
Figure 8. Schematic illustration of the behaviour of an MAN suspension in the MVPT.



**Figure 9. Thermocouple traces and photographs of Trial A48: Hexamine nitrate Suspension.**  
 This trial used a vessel filled to the 75% point with suspension composition ASP4. The partial blue background denotes the period between the start of vessel overflow and the trial conclusion.

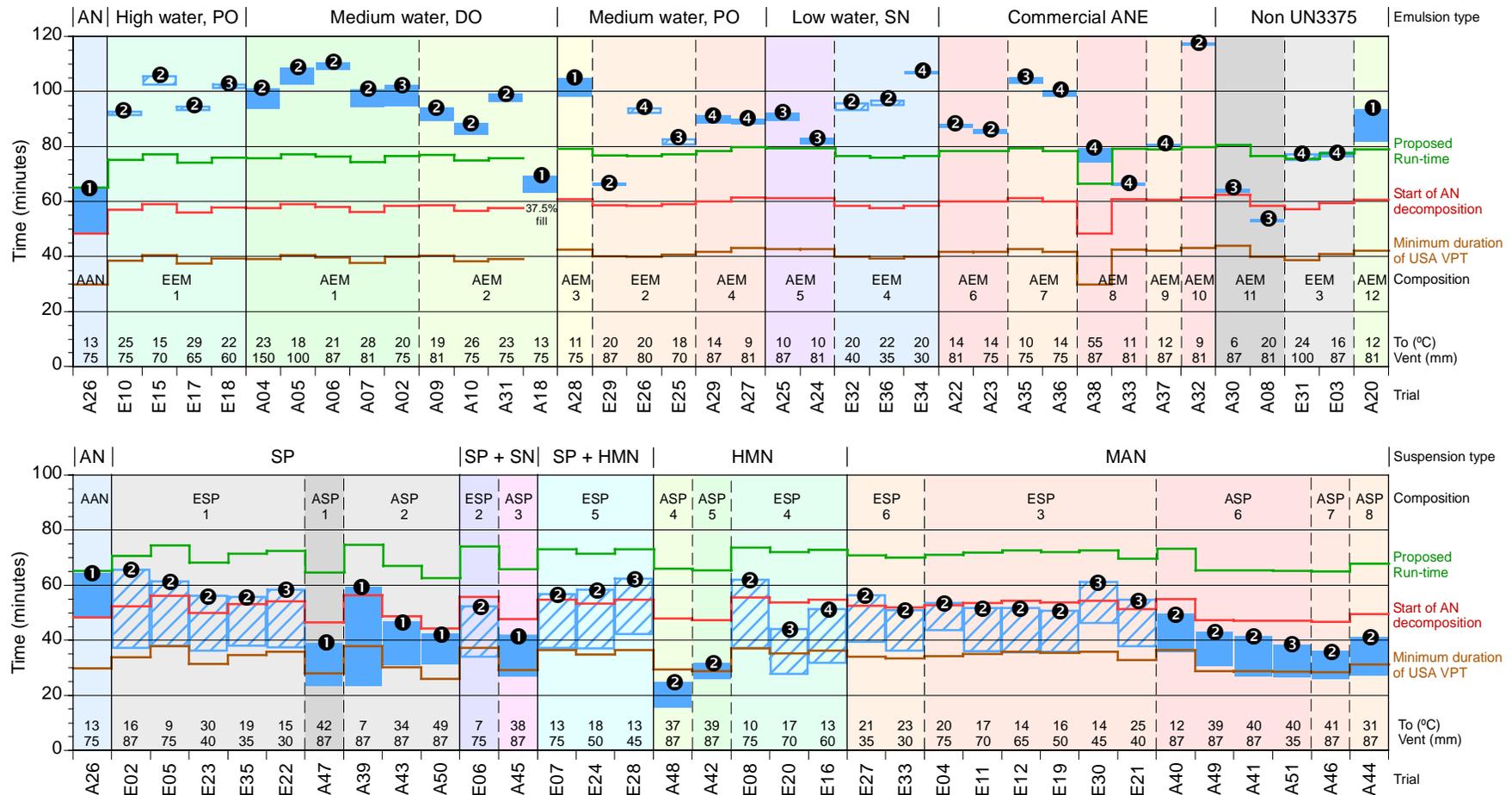


***Figure 10. Vessel overflow by chemically sensitised suspensions.***  
*The photographs on the left show the fire on the pad (upper) and the damage to the gas burner jets (lower) during Trial A48 of ASP4.*  
*The photographs on the right show the state of the pad after Trial A42 of ASP5 (upper) and Trial A50 of ASP2 (lower).*



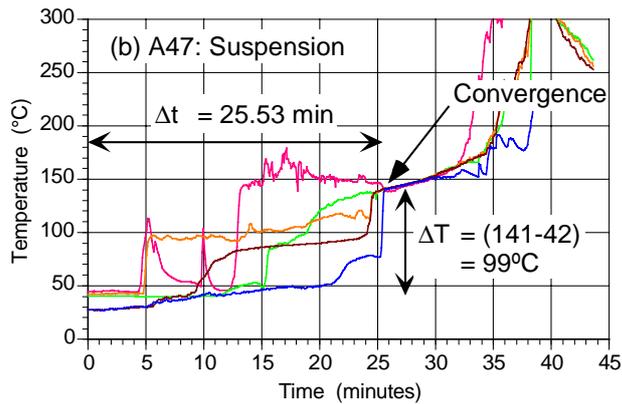
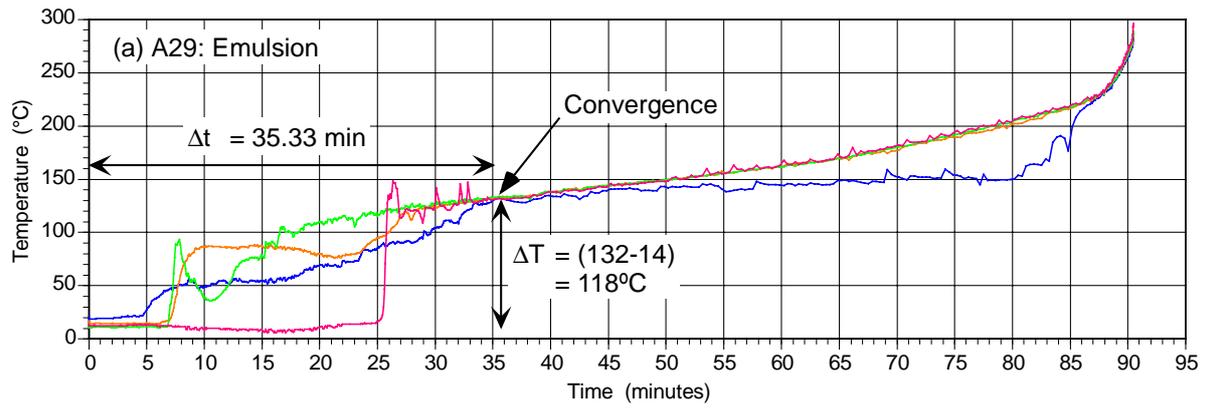
**Figure 11. Thermocouple traces and photographs of Trial A47: Sodium perchlorate Suspension.**

*This trial used a vessel filled to the 75% point with suspension composition ASP1. The partial blue background denotes the period between the start of vessel overflow and the trial conclusion.*

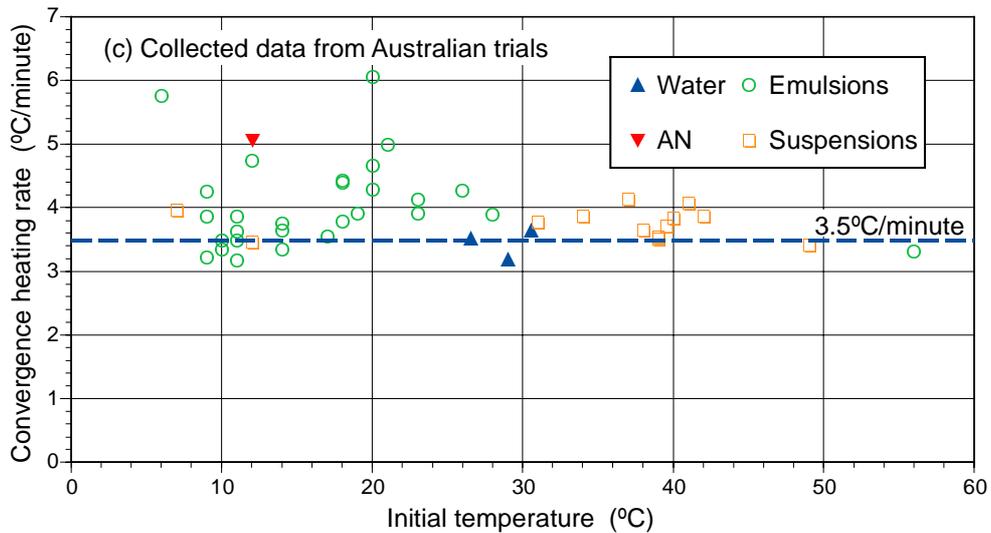


**Figure 12. Collated results for the MVPT.**

The upper diagram summarizes the data for emulsions, and the lower for suspensions. For each trial, the blue bars indicate the period when the vessel was overflowing. The severity of the outcome is labelled with ❶ indicating fuming, ❷ indicating venting, ❸ indicating failure of the end plates, and ❹ indicating explosion with vessel fragmentation. The green line indicates the proposed run time for each trial, and has been corrected for the difference between the initial temperature during the trial and the intended shipping temperature. The red and brown line indicate possible alternative run-times based on the start of decomposition in Trial A26 of pure ammonium nitrate and on the minimum burn time in the USA Vented Pipe Test respectively, corrected for the difference between the initial temperature and the intended shipping temperature.



$$\text{Convergence heating rate} = \frac{\Delta T}{\Delta t}$$



**Figure 13. Convergence heating rate.**

The convergence heating rate is defined as the average heating rate up to the point where all thermocouple traces converge. Typical results are shown here for (a) an emulsion and (b) a suspension. The data from all the Australian trials are plotted in (c) against the initial sample temperature.



## Appendix A1. Detailed interpretation of thermocouple traces.

Figure 1 compares representative thermocouple traces from the Australian MVPT trials for water, for pure ammonium nitrate prill, for a representative emulsion (namely Trial A07 of composition AEM1) and for a representative suspension (namely Trial A46 of composition ASP7). In all cases, the vessel was filled to 75% of its internal height and was heated under similar conditions. The graphic included in Figure 1 shows schematically the named locations of five thermocouples – some of the early trials had some thermocouples in other locations inside or outside the vessel, but experience gained during 50 trials showed that these five locations provided the maximum amount of interpretable information.

Interpretation of these thermocouple traces and of the video records from these trials will be assisted here by reference to information published by Shah and Roberts [7] concerning the decomposition reactions of ammonium nitrate (given in Table 2), and concerning the phase diagram and the vapour pressure diagram for ammonium nitrate solutions (ANS), reproduced here as Figure 2.

The interpretation given in subsequent sections will require the reader to flip frequently between the text and several figures. The reader may be assisted by viewing the presentation [Thermocouple interpretation.pps](#) that collates the required visual information while stepping through the thermocouple traces discussed in Sections A1.2, A1.3 and A1.4.1.

### A1.1 Features of the water calibration thermocouple traces.

Figure 1(a) shows that once the gas flame had been ignited, the thermocouple trace at the base of the vessel (namely Sample Lower) rose first, showed the greatest amount of noise (indicating a region of high turbulence at the base of the vessel), and was consistently higher than all other traces prior to all traces merging at the boiling point of water. The Sample Centre thermocouple trace started to rise after a minute, followed soon afterwards by the Sample Upper trace. These two traces then tracked each other closely throughout, indicating that large scale convection currents were operating in the upper layers of the water, keeping it well mixed thermally.

Both headspace thermocouples started to rise after a minute, and again tracked each other closely during the first 15 minutes, though with the lower headspace thermocouple trace registering temperatures up to 6°C higher than the upper headspace thermocouple trace for several minutes prior to their remerging as boiling commenced. During the mid stage, the temperature of the water vapour in the headspace was up to 20°C cooler than the temperature of the water itself. However, as the water approached boiling and the partial pressure of steam in the headspace increased, the temperature of the emitted water vapour (steam) in the headspace rose rapidly until all thermocouple traces merged at 100°C after 23 minutes, 54 seconds. This behaviour is consistent with the vapour pressure diagram shown in Figure 2. The partial pressure of water vapour in the headspace is described by the blue line superimposed over this diagram – at the initial state at 4°C (denoted by point ①), water vapour would comprise less than 1% of the atmosphere; the water vapour concentration would be about 14% above water at 50°C, about 50% at 80°C, and 100% at 100°C (denoted by point ② in Figure 2). It is the sharp increase of water vapour partial pressure as the boiling point is approached that is responsible for the sharp rise in the temperature measured by the headspace thermocouples.

## A1.2 Features of the ammonium nitrate thermocouple traces.

Figure 1(b), showing the thermocouple traces from Trial A26<sup>†</sup> of loose poured pure ammonium nitrate prill, is shown enlarged and annotated in Figure 3. Its interpretation is assisted by reference to the principal decomposition reactions of AN [7], which are given in Table 2. Key features in the thermocouple traces and accompanying images from the video record are identified by the numbers ❶ to ❷ in Figure 3. These features are:

- ❶ The temperature was seen to rise first at the base of the vessel up to about 260°C. Since the melting point of AN is 170°C, and its boiling point is estimated to be about 230°C [7], it is inferred that there was a pool of super heated molten AN at the base of the vessel, with solid prill higher up the vessel. No fume emission was observed at this stage.
- ❷ After about 13 minutes, the Headspace Upper trace started to rise more rapidly, in conjunction with a drop in the Sample Lower trace. The first faint wisps of white fume were observed rising from the vent. (These wisps are not discernible in the photographs included in Figure 3, but were evident from the videotape record of the trial.) It is inferred that some settling and stirring of the contents occurred, releasing a pocket of (most likely) N<sub>2</sub>O and H<sub>2</sub>O product gases from decomposition Reaction 1 from deep in the vessel. Reaction 1 is reported to be the dominant decomposition pathway at temperatures below about 250°C [7].

Since the density of liquid AN is about 1.4 mg/mm<sup>3</sup>, and the initial bulk density of the AN prill was about 1.17 mg/mm<sup>3</sup>, the top surface of the column of AN prill must have dropped as the AN melted. Hence, the Sample Upper thermocouple must have become exposed at some stage.

- ❸ After about 35 minutes, the Sample Centre trace rose to about 230°C, slightly below the Sample Lower trace. It is inferred that the level of molten AN had risen to envelop the Sample Centre thermocouple. The presence of prill would have hindered the establishment of convection cells in the melt, allowing a temperature difference to be maintained between the Sample Lower and Centre thermocouples at this stage.
- ❹ After about 45 minutes, the Sample Lower and Sample Centre thermocouple traces converged, and began to rise at a higher rate. Simultaneously, both the Sample Upper and Headspace Upper thermocouple traces began to rise. This coincided with a visible increase in the rate of fume emission. It is inferred that this stage corresponded to the completion of melting all solid prill (removing the latent heat of fusion as a heat sink) and the establishment of large scale convection cells throughout the molten AN. Being exothermic, decomposition Reaction 1 would have contributed to the faster overall heating rate.
- ❺ Soon afterwards, both Sample Upper and Headspace Upper thermocouple traces rose sharply. After 48 minutes and 22 seconds of heating, a clear inviscid liquid was observed to overflow from the vent, forming a stream of droplets cascading down the side of the vessel. At this point, the average density of the molten AN in the vessel must have been about 0.88 mg/mm<sup>3</sup>.

King et al. [6] measured the density of molten ammonium nitrate at elevated temperatures. Between the melting point at 170°C and the boiling point at 230°C, the density decreased gradually as expected from normal linear thermal expansion. At 230°C, the density of molten AN was about 1.38 g/cm<sup>3</sup>. At higher temperatures, the

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<sup>†</sup> Figure 36 of reference 5 incorrectly listed the fill factor for Trial A11 of AN prill as being 75%; this should have read 92%. The fill factor for Trial A26 was 75%, requiring 28 kg non-porous AN prill.

density began to show marked departures from normal thermal expansion due to the onset and increasing rapidity of decomposition reactions that self-aerated the molten AN. At a temperature of 260°C, the self-aeration was so vigorous that the density of the gassy liquid had decreased to about 0.80 g/cm<sup>3</sup>.

It is concluded that the sharp rise in headspace thermocouple trace (as it is enveloped from below by hot foamy liquid) and the attendant vessel overflow denotes the onset of rapid decomposition and the attainment of low density in the vessel contents.

- ⑥ After about 54 minutes, all thermocouple traces converged at a temperature of about 275°C. Subsequently, the rate of temperature increase slowed. It is inferred that this signifies the onset of the endothermic decomposition Reaction 2, which would have contributed NH<sub>3</sub> and HNO<sub>3</sub> gas to the emitted fume. It is also possible that the fume could include superfine crystals of AN formed from the reverse Reaction 2 in the gases above the vessel. When heating pure AN, it is known [7] that the competition between exothermic Reaction 1 and endothermic Reaction 2 can lead to the temperature self-stabilising at a temperature of 292°C at atmospheric pressure.

Meanwhile, the Headspace Upper trace began to fall below all other traces. It is believed that the level of liquid in the vessel was gradually dropping as decomposition progressed, to the point where the Headspace Upper thermocouple was once more exposed.

- ⑦ Finally after 64 minutes and 37 seconds, the Headspace Upper trace began to drop sharply as the lower thermocouple traces began to rise sharply, shortly after the ejection of a brief plume from the vent. All thermocouple traces then began to fall steadily, as did the level of fume emission. This signified that the vessel was now empty and that the trial had concluded.

Pure ammonium nitrate follows a particularly simple pathway across the phase diagram, shown by the red lines in Figure 2 connecting the initial solid state at point ① through the melting point ① to the boiling point ②.

### A1.3 Features of the emulsion thermocouple traces.

The thermocouple traces, together with images captured from the video record, for Trial A07 of emulsion composition AEM1 are shown in Figure 4. Schematic interpretations are given in Figures 5 and 6. Key stages are identified by the numbers ① to ③ in Figures 4 and 6, and are discussed below. The pathway followed by the aqueous phase of this composition through the phase diagram and the vapour phase diagram is shown by the purple lines and points in Figure 2.

- ① The initial temperature of the emulsion was 22°C. Once heating commenced, the first thermocouple trace to register an increase in temperature was invariably Sample Lower at the base of the vessel.
- ② However, within a few minutes, the temperature usually dropped at the base of the vessel, and increased sharply at the top of the sample. (This interpretation is based on those trials that had a Sample Upper thermocouple in place.) The headspace temperature also started to rise at this stage.

It is believed that this signified physical break-down of the emulsion, shown schematically in Figure 5. The breakdown of the emulsion structure would have caused a collapse in its viscosity. This hot broken liquid would initially have been trapped to pool at the base of the vessel. During these initial stages, the main heat transfer mechanism towards the top of the vessel would have been by conduction through the steel walls. This would have broken down an annulus of emulsion in contact with the

walls, eventually forming a complete passageway whereby low-viscosity broken emulsion could flow up the inside of the walls to pool on top of the cold emulsion. The plug of cold emulsion (being of higher density than the hot liquid) would then sink to the base of the vessel. The arrival of some of the hotter liquid at the top of the vessel would have released some warmer water vapour into the headspace. This process is shown schematically in Figure 6.

This is consistent with the information in Figure 2. Referring to the phase diagram and water vapour pressure diagram, the aqueous phase of this emulsion started at the state identified by point ① in Figure 2. Normally, an 87/13 AN / water system would include solid AN at the initial temperature of 22°C. However, the emulsification process allowed the solution to remain supersaturated. Heating has moved the system along the purple line from ① onto the saturated solution curve at point ②, where it could support a partial pressure of almost 0.2 bar water vapour in the headspace.

Further heating would have moved the state away from point ② towards the boiling point ③ of Figure 2.

- ③ After a period of typically 20 to 30 minutes, all liquid thermocouples converged to a common temperature reading (though sometimes with occasional temporary spikes in temperature). It is believed that this signified the onset of large scale convection cells in the now low-viscosity broken emulsion (which might still have contained some pockets of colder, unbroken emulsion), shown schematically in Figure 6.

The headspace temperature was usually slightly below the liquid temperature at this stage, though rising steadily. Faint wisps of white fume (water vapour) were being emitted by the vent. The partial pressure of the water vapour in the headspace would have been gradually increasing as the temperature of the aqueous solution approached its boiling point ③ of Figure 2.

Shortly afterwards, the headspace temperature converged with the liquid temperature at the boiling point of the original AN / water system (about 140°C for the 87/13 AN/water system used here). The system had reached the boiling point ③ of the aqueous solution in Figure 2. At this point, the 87/13 AN/water system could support a water vapour partial pressure of a full one atmosphere in the headspace.

Over the next 15 to 20 minutes, the headspace thermocouple trace rose slowly in concert with the sample traces. The aqueous solution would have been following the (purple) boiling point curve connecting points ③ and ④ in Figure 2, supporting a full atmosphere of steam in the headspace as a consequence. However, the steam emission from the vent represented a continual loss of water from the system.

The thermocouple traces often showed an occasional sharp spike in temperature, though just for a single temperature reading. It is believed that there was a layer of super-heated steam in contact with the hot base plate, with a few large steam bubbles occasionally break away from it. The thermocouple trace would jump when its tip happened to be enveloped by one of these bubbles. The temperature spikes were always greatest at the base of the vessel, and smaller higher up the liquid column (where heat conduction from the steam bubble to the surrounding liquid would have cooled the bubble). During this stage, visual observation noted the ejection of small droplets out the vent; it is presumed that such droplets were ejected as the large bubbles broke through the surface. (A useful analogue would be to consider the behaviour of low-water foods such as pumpkin soup or tomato paste being boiled.)

- ④ Once the temperature had reached about 170°C, the sample thermocouple traces continued to climb, whereas the headspace thermocouple trace began to level out.

According to the water vapour pressure diagram in Figure 2, the aqueous system would have been at point ③, having lost over half its initial water content to be about 95/5 AN/water. There would then have been too little water left in the system for it to support a full one atmosphere partial pressure of steam in the headspace. Instead, the system would have started along the dashed purple line towards the boiling point ② of pure AN. The size and the frequency of the occasional temperature spikes fell away towards the end of this stage, as did the visual observation of droplet ejection from the vent.

- ⑤ After a further 30 minutes or so, the headspace temperature began to climb again. This invariably coincided with the liquid temperature reaching about 230°C, the melting point of pure AN. It is believed that this signifies that all the water had been driven from the system, which had now reached point ② of Figure 2. Visual observation would note a small but perceptible increase in the rate of fume production at this point, signifying the onset of decomposition Reaction 1 of the AN to N<sub>2</sub>O and H<sub>2</sub>O. The temperature spikes ceased, as did droplet ejection.
- ⑥ Over the next 10 minutes or so, the headspace temperature rose at an increasing rate, until it converged with the liquid temperature at about 255°C. This is a consequence of the increasing decomposition rate forming in-situ gas bubbles that self-aerated the liquid, raising its level until it enveloped the headspace thermocouple. This is shown schematically in Figure 6. (A useful analogue would be to consider the behaviour of milk boiling over.)
- ⑦ Within minutes with the liquid temperature at about 265°C, visual observation noted a clear inviscid liquid overflowing the vessel, shown schematically in Figure 6. To overflow the vessel in this manner, the average density of the liquid must have decreased from its initial value of about 1.35 g/cm<sup>3</sup> to about 1.0 g/cm<sup>3</sup>. The liquid spilt onto the pad occasionally ignited and intensified the gas fire.

Within a few minutes once the temperature had reached about 275°C, there were increasing amounts of dense white fume being produced. It is believed that this signifies the onset of decomposition pathway 2 of the AN to NH<sub>3</sub> and HNO<sub>3</sub>.

- ⑧ Soon afterwards at about 285°C, there was usually an abrupt transition to high velocity venting of brown fume signifying the onset of various exothermic decomposition pathways to species including NO<sub>x</sub>. This is shown schematically in Figure 6. A fire at the top of the vessel is visible in the third last photograph in the series included in Figure 4, with the venting shown in the second last photograph.

It is believed that a deflagration then proceeded downwards through the liquid contents of the vessel with the products being emitted as a high velocity plume of gas, shown schematically in Figure 6. In this particular trial, the pressure developed inside the vessel was sufficient to bulge the endplates. In some trials, the base plate was torn from the vessel; in other trials, there was evidently a transition from deflagration to detonation, with the vessel being fragmented into numerous pieces.

## **A1.4 Features of the suspension thermocouple traces.**

### *A1.4.1 MAN suspension.*

The thermocouple traces, together with images captured from the video record, for Trial A46 of suspension composition ASP7 containing methylamine nitrate (MAN) are shown in Figure 7, with typical key stages identified by the numbers ① to ⑩. A schematic interpretation of these stages is given in Figure 8. No phase diagram or water vapour pressure diagram for a mixed AN/MAN/water system were known to the author.

The thermocouple traces and the video records during trials of suspensions containing either hexamine nitrate (HMN) or sodium perchlorate (SP) did differ in various ways from those described below for this MAN system. These differences will be discussed briefly in following sections.

The behaviours observed during the suspension trials showed some similarities, but many differences, compared to trials involving emulsions.

- ① The initial temperature of the suspension was 41°C. As with the emulsion, the first thermocouple trace to register an increase in temperature for the MAN suspension was Sample Lower at the base of the vessel.
- ② Again, within a few minutes, the temperature usually dropped at the base of the vessel, and increased sharply at the top of the sample. It is believed that as the suspension was heated, the solid oxidiser salt crystals gradually dissolved, increasing the percentage of solution phase and hence decreasing the overall viscosity of the suspension. During the initial stages of heating, this would occur primarily at the vessel walls, opening up a passage way for the hotter, lower viscosity solution to flow to the top of the suspension. The plug of cooler suspension would then have sunk to the base of the vessel. The temperature at the Sample Upper thermocouple of about 85°C was most likely above the saturation temperature of this AN/MAN/water system, with all components being in the solution phase.

The headspace traces for the MAN suspension behaved differently from those of emulsions. Here, after an initial gentle rise, the temperatures in the headspace levelled off at around 40°C to 50°C for an extended period, instead of climbing to meet the sample temperature. It is believed that this was due to a layer of foam forming on top of the solution, with the air bubbles stabilised by the guar gum used to thicken the suspension. This foam layer would have prevented any significant amount of water vapour from escaping the hot solution, isolating the headspace from the sample. As seen from the photographs included in Figure 7, no vapours could be seen escaping from the vent at this stage.

- ③ After about 16 minutes, the pool of hot solution at the top had deepened to the point where the Sample Centre thermocouple was enveloped.
- ④ After about 22 minutes, all three thermocouples in the sample converged at about 135°C. This would have been close to the boiling point of this AN/MAN/water system.
- ⑤ Meanwhile, the temperature at the Headspace Lower thermocouple was climbing, whereas the temperature at the Headspace Upper thermocouple was steady. It is believed that bubbles of water vapour were being trapped throughout the solution, causing its level to gradually rise in the vessel, and enveloping the Headspace Lower thermocouple in increasingly deeper and hotter layers of foam. At this stage, there was still no fume visible at the vent.
- ⑥ Finally after 24 minutes, the vessel was observed to overflow, firstly with foam for a few seconds, and then with a clear inviscid liquid which fumed off when it dropped onto the hot pad surrounding the gas burner. This coincided with the four lower thermocouple traces all converging at 142°C. The Headspace Upper thermocouple trace required an extra 30 seconds to reach convergence – it is believed that a pocket of foam could have become trapped in the corner where this thermocouple was placed, taking some time to be flushed out.

To overflow the vessel in this manner, the average density of the liquid must have decreased from its initial value of about 1.4 g/cm<sup>3</sup> to about 1.0 g/cm<sup>3</sup>. Since all

thermocouple traces were reading the same temperature, it is inferred that the aeration was relatively uniform throughout the vessel, rather than the reduction in average density being due to a single large gas pocket forming somewhere at depth in the vessel.

From this point onwards, fume was continually emitted from the vent.

- ⑦ The overflow continued for several minutes before ceasing with a concomitant slight decrease in the level of fume emission from the vent when the liquid temperature was about 144°C. Firstly the Headspace Upper and then the Headspace Lower thermocouple traces began to fall below the three sample thermocouple traces, with the Headspace Upper trace eventually dropping to be about 35°C below the sample traces.

It is believed (on the basis of what was observed subsequently) that this was a consequence of the guar gum being partially or perhaps completely decomposed, with a concomitant loss of bubble entrapment, causing an increase in average density and lowering of the top surface of the liquid.

- ⑧ After about 30 minutes, the Headspace Upper thermocouple trace began to climb, reconverging with the other four traces at a temperature of 156°C. The vessel was then observed to overflow with copious amounts of a more viscous, brown liquid. This liquid soon ignited and burnt fiercely on the pad, obviously intensifying the heat generation at the foot and half way up the sides of the vessel. It is believed that some unidentified decomposition was occurring at a sufficient rate to once again self-aerate the liquid with its gaseous decomposition products.
- ⑨ The Headspace Upper thermocouple trace then dropped away from the others for a minute or so. The impression gained from visual observation was that so much of the liquid had overflowed from the vessel that it was now close to empty.
- ⑩ The concluding stage of this trial occurred after 33 minutes with the temperature in the vessel at about 170°C. There were a series of eruptions where spouts of a dark grey liquid and clouds of mixed white and brown fume were ejected several metres into the air. Each eruption commenced with an abrupt temperature rise at the base of the vessel. All thermocouple traces rose sharply by hundreds of degrees, presumably signalling the decomposition of whatever gaseous vapours still remained inside the vessel. This particular trial did not exhibit the final high velocity plume shown schematically in Figure 8, though other trials of compositions containing MAN did conclude in brief periods of venting, none of which produced any significant amount of fume.

#### *A1.4.2 HMN suspension.*

The thermocouple traces, together with images captured from the video record, for Trial A48 of suspension composition ASP4 containing hexamine nitrate (HMN) are shown in Figure 9. The major difference in behaviour between this HMN suspension and the MAN suspension discussed in Appendix A1.4.1 is that the presence of HMN appeared to cause the degradation of the guar gum at a much earlier stage of the heating. Figure 9 shows fume emission from the vent together with a steady rise in the Headspace Upper thermocouple trace from very early times, indicating that no isolating layer of foam had been formed, unlike the MAN case shown schematically at Stages ③ to ⑤ of Figure 8. The Headspace Lower trace converged with the Sample Upper trace after about 9 minutes, suggesting the top surface of the sample was gradually rising due to bubble entrapment even at this early stage.

The first liquid to overflow the vessel for the HMN suspension was brown and slightly viscous, unlike the clear inviscid liquid in the MAN case. Hence the HMN suspension seemed to jump from Stage ④ of Figure 8 straight to Stage ⑦.

The overflow of this liquid during the two HMN suspension trials led to the most intense fires on the pad inside the shroud ever seen during MVPT trialing, with a frame from the video of Trial A48 included in Figure 10. Each fire was sufficiently hot to melt many of the brass jets off the gas burner; Figure 10 includes a photograph of the burner after Trial A48, with over a quarter of the brass jets having melted away. Large pools of dark brown sludge were left on the pad outside the shroud after each trial; Figure 10 includes a photograph of the pad following HMN Trial A42.

Each HMN suspension trial terminated with an intense and spectacular standing jet of banded yellow and orange fire erupting from the vent. However, since neither jet produced any significant volume of fume, and since neither the top plate nor the base plate was bulged in either trial, it is concluded that very little material still remained in the vessel at the point of ignition at a temperature of about 220°C.

#### *A1.4.3 SP suspension.*

The thermocouple traces, together with images captured from the video, for Trial A47 of suspension composition ASP2 containing sodium perchlorate (SP) are shown in Figure 11.

This suspension appeared to form a very viscous, cool cap of greyish sludge that was observed to rise out of the vent after 22 minutes and 30 seconds, forming a crown several centimetres high and taking about a minute to spread over the top plate before falling in clumps to the ground to ignite and intensify the fire. It was difficult to determine exactly when this sludge made way for the clearer, less viscid liquid that first poured and finally trickled from the vent over the next five minutes or so. It is believed that most of the oxidiser salt solution had escaped from the vessel by about 32 minutes.

Over the next few minutes, the rate of fume emission gradually picked up as the temperature began climbing at the base of the vessel. At 33 minutes and 30 seconds, there began the remarkable sight of smoke rings being puffed out of the vent at regular intervals – three such rings are visible in the photograph shown at 34 minutes 30 seconds in Figure 11. The white fume was increasingly mixed with brown fume (presumably NO<sub>x</sub>) as time went on.

After about 36 minutes with the temperature at the base of the vessel being around 300°C, a thick dark sludge was first spat out of the vent, and then started oozing out and piling up to form a miniature volcano on the top plate, with a mixture of white and brown fume forcing its way through multiple small vents. The temperatures inside the vessel peaked at over 500°C and then fell away, denoting the completion of the trial.

A photograph of the sludge left on top of the vessel after SP Trial A50 is included in Figure 10.

# APPENDIX A2: Recommended procedure for the MVPT

## EXPLOSIVES, SELF-REACTIVE SUBSTANCES AND ORGANIC PEROXIDES.

### Classification of Ammonium Nitrate Emulsions, Suspensions and Gels.

#### Manual of Tests and Criteria. Test 8(d) – Modified Vented Pipe Test

##### 1 Introduction

The vented pipe test is used to assess the effect of exposure of a candidate for “ammonium nitrate emulsion or suspension or gel, intermediate for blasting explosives” to a large fire under confined, vented conditions. It will determine whether or not an ANE can be transported in tanks as a dangerous good of Class 5.1.

The ANE is subjected to this test **only** after it has passed Test 8(a), Test 8(b) and Test 8(c) and deemed to be a dangerous good of Class 5.1.

##### 2 Apparatus and materials

The following items are needed:

- (a) A vented vessel consisting of mild drawn steel pipe with an inner diameter of  $265 \pm 10$  mm, a length of  $580 \pm 10$  mm and a wall thickness of  $5.0 \pm 0.5$  mm. Both the top and the base plates are made from 300 mm square,  $6.0 \pm 0.5$  mm thick mild steel plates. The top and base plates are fixed to the pipe with a single 5 mm fillet weld. The top plate has a central vent diameter of  $87 \pm 1$  mm. A minimum of three, and preferably up to five, small holes are drilled in the top plate to accommodate neatly thermocouple probes, these holes being equally spaced around a circle of radius  $90 \pm 5$  mm concentric with the vent;
- (b) A concrete block about 400 mm square and 50 to 75 mm thick;
- (c) A metal stand for supporting the vessel at a height of 150 mm above the concrete block;
- (d) A gas burner capable of accommodating an LPG flow rate of up to  $35 \pm 2$  litres per minute. This rests on the concrete block under the stand. A typical example of a suitable burner is a 32-jet Mongolian wok burner;
- (e) A sheet metal shield to protect the LPG flame from side winds. This can be fabricated from approximately 0.5 mm thick galvanised sheet metal. The diameter of the wind shield is 600 mm and the height is 250 mm. Four adjustable vents 150 mm wide and 100 mm high are spaced equally around the shield to ensure adequate air reaches the gas flame;
- (f) LPG bottle(s) connected via a manifold and fed into a pressure regulator. The pressure regulator should reduce the LPG bottle pressure from 650 kPa down to about 250 kPa. The gas then flows through a gas rotameter capable of measuring up to 40 litres per minute of LPG gas. An electrical solenoid valve is used to switch the LPG flow on and off remotely. Typically four 9kg LPG bottles will achieve the desired gas flow rate for the duration of up to five tests.
- (g) One thermocouple with 600 mm long stainless steel probe and a minimum of three, though preferably five, thermocouples with 500 mm long stainless steel probes and fibre-glass coated lead wires;
- (h) A data-logger capable of recording the output from the thermocouples;
- (i) Cine or video cameras, preferably high speed and normal speed, to record events in colour.
- (j) Pure water for calibration.
- (k) The ANE to be tested.

Blast gauges, radiometers and associated recording equipment may also be used.

##### 3 Calibration

- 3.1 The vessel is filled to the 75% level (ie to a depth of  $435 \pm 10$  mm) with the pure water, and heated using the procedure specified in Section 4. The time taken to reach the boiling point of the water is recorded, and is used to define the “calibration-time” for the given combination of vessel and heat source. The boiling point has been reached when all thermocouple traces converge at approximately 100°C (or lower if at altitude).
- 3.2 If the initial temperature of the water was not 25°C, corrections to the calibration-time must be made based on the measured mean heating rate,  $\dot{T}_{cal}$ , over the temperature interval between 40°C and 80°C as recorded by the thermocouple T3 in the water.

- 3.3 The calibration-time,  $t_{cal}$ , is defined as the corrected time taken to heat water from 25°C to boiling point within the test equipment, and must be 24 minutes  $\pm$  2 minutes 30 seconds. If  $t_{cal}$  lies outside this time window, the calibration must be repeated from step 3.1 with a fresh sample of water making appropriate adjustments to the gas flow. If sufficient adjustment is not available from the gas flow, it may be necessary to alter the height of the metal stand supporting the vessel above the gas burner.
- 3.4 This calibration must be performed prior to the testing of any ANE substance, though the same calibration-time,  $t_{cal}$ , and mean heating rate,  $\dot{T}_{cal}$ , can be applied to any test conducted within a week of the calibration provided no change is made to the vessel construction, LPG burner type or gas supply.

#### 4 Test Procedure

- 4.1 The concrete block is placed on a sandy base and levelled using a spirit level. The LPG burner is positioned in the centre of the concrete block and connected to the gas supply line. The metal stand is placed over the burner.
- 4.2 The vessel is placed vertically on the stand and secured from tipping over. The vessel is filled to 75 % of its volume (to a height of  $435 \pm 10$  mm) with the ANE under test. The substance is carefully packed to prevent adding voids. The wind shield is positioned around the base of the assembly to protect the LPG flame from heat dissipation due to side winds. The test should not be performed under conditions where the wind speed exceeds 6 m/s.
- 4.3 The thermocouple positions are:
- the first 500 mm long probe (T1) in the LPG flame;
  - the second 500 mm long probe (T2) in the headspace  $20 \pm 5$  mm into the vessel;
  - the third 500 mm long probe (T3) in the sample  $175 \pm 5$  mm into the vessel;
  - the 600 mm long probe (T4) in the sample  $570 \pm 5$  mm into the vessel;

If used, the extra two thermocouples are placed

- the fourth 500 mm long probe (T5) in the sample  $360 \pm 5$  mm into the vessel;
- the fifth 500 mm long probe (T6) in the headspace  $100 \pm 5$  mm into the vessel.

The thermocouples are connected to the data-logger and the thermocouple leads and data-logger are adequately protected from the test apparatus in case of explosion.

- 4.4 LPG pressure and flow rate are checked and adjusted to the values used during the water calibration described in Section 3. Appropriate values for the pressure and the flow rate at which to conduct the first water calibration procedure are 250 kPa and 35 litres per minute respectively. Thermocouple functioning is checked and data logging is started, with a time step between thermocouple readings not exceeding 20 seconds, and preferably shorter. The initial temperature of the ANE must be recorded. Video cameras and any other recording equipment are checked and started.
- 4.5 The LPG burner may be started locally or remotely and all workers immediately retreat to a safe location. Progress of the test is followed by monitoring thermocouple readings and closed circuit television images. The start time of the trial is defined by the time at which the flame thermocouple trace T1 first begins to rise.
- 4.6 The “run-time”  $t_{run}$  for the ANE is calculated as 2.75 times the calibration-time  $t_{cal}$  for water, adjusted by a suitable correction based on the measured heating rate  $\dot{T}_{cal}$  for water if the initial temperature of the ANE is below the normal shipping temperature. The ANE should not be tested at an initial temperature above the normal range of shipping temperatures.
- 4.7 The ANE is heated for this run-time or longer. At the end of this run-time, or earlier if the test is deemed to have reached its conclusion according to section 4.9, the LPG supply may at the discretion of the workers be switched off remotely using the solenoid valve. Alternatively, the ANE may continue to be heated until the test is deemed to have reached its conclusion according to section 4.9. The choice as to how long to prolong heating past the run-time should be based on a detailed risk assessment of the relative hazards and environmental impacts of handling and disposing of hot degraded ANE versus the generation of toxic fume and the possible projection of hot metal shrapnel.
- 4.8 Once the vessel and any remaining ANE have cooled to a safe handling temperature, the vessel and any remaining ANE should be disposed of in an environmentally responsible manner and according to local statutory requirements.
- 4.9 The test outcome is determined by whether or not the test reaches a conclusion prior to the run-time. Evidence of test conclusion is based on:

- The visual and aural observation of vessel rupture accompanied by possible loss of thermocouple traces, or
- The visual and aural observation of vigorous venting accompanied by peaking of two or more vessel thermocouple traces, or
- The visual observation of decreased levels of fuming following the peaking of two or more vessel thermocouple traces at temperatures in excess of 300°C.

In all cases, the conclusion time is taken as the time at which the maximum temperature was recorded inside the vessel.

## 5 Test criteria and method of assessing results

The ANE is heated under the set test conditions for its run-time or longer.

If the test concludes within the run-time, the outcome of the test would be recorded as being positive (+) and the ANE is not suitable for transportation in tanks as a dangerous good of Class 5.1.

If the test does not conclude within the run-time, the outcome of the test would be recorded as being negative (-) and the ANE is suitable for transportation in tanks as a dangerous good of Class 5.1.

## 6 Examples of results

### Example of calibration calculation:

#### Calibration for water:

Initial temperature of water = 32°C.

Time to heat water from 32°C to 100°C = 21 minutes 30 seconds.

Mean heating rate between 40°C and 80°C  $\dot{T}_{cal} = 3.50^\circ\text{C}/\text{minute}$ .

Calibration-time  $t_{cal} = 21 \text{ minutes } 30 \text{ seconds} + (32 - 25)/3.50 \text{ minutes} = 23 \text{ minutes } 30 \text{ seconds}$ .

### Example of run-time correction:

#### Example run-time correction for Test Substance 2:

Initial temperature of substance = 21°C.

Normal shipping temperature = 60°C.

Run-time =  $2.75 \times (23 \text{ minutes } 30 \text{ seconds}) + (60 - 21)/3.50 \text{ minutes} = 75 \text{ minutes } 46 \text{ seconds}$ .

Observed conclusion time = 109 minutes 48 seconds.

Test outcome: Negative

#### Example run-time correction for Test Substance 5:

Initial temperature of substance = 6°C.

Normal shipping temperature = 60°C.

Run-time =  $2.75 \times (23 \text{ minutes } 30 \text{ seconds}) + (60 - 6)/3.50 \text{ minutes} = 80 \text{ minutes } 3 \text{ seconds}$ .

Observed conclusion time = 58 minutes 35 seconds.

Test outcome: Positive

#### Example run-time correction for Test Substance 6:

Initial temperature of substance = 37°C.

Normal shipping temperature = 40°C.

Run-time =  $2.75 \times (23 \text{ minutes } 30 \text{ seconds}) + (40 - 37)/3.50 \text{ minutes} = 65 \text{ minutes } 29 \text{ seconds}$ .

Observed conclusion time = 23 minutes 59 seconds.

Test outcome: Positive

### Example of typical results:

Substance	Result
1. 76.0 AN / 17.0 Water / 5.6 paraffin oil / 1.4 emulsifier	-
2. 82.1 AN / 12.3 Water / 4.2 diesel oil / 1.4 emulsifier	-
3. 82.1 AN / 12.3 Water / 4.2 paraffin oil / 1.4 emulsifier	-
4. 68.3 AN / 17.6 SN / 6.5 Water / 5.7 diesel oil / 1.9 emulsifier	-
5. 74.9 AN / 9.7 SP / 9.0 Water / 3.7 paraffin oil / 2.7 emulsifier <sup>(1)</sup>	+
6. 60.5 AN / 17.0 HMN / 12.0 Water / 10.0 EG / 0.5 guar gum <sup>(1)</sup>	+
7. 60.5 AN / 17.0 MAN / 12.0 Water / 10.0 EG / 0.5 guar gum <sup>(1)</sup>	+
8. Dense AN prill <sup>(1)</sup>	-

<sup>(1)</sup> Composition lies outside definition of UN3375 ANE.