

CRANFIELD UNIVERSITY

Daniel M^cAteer

The Development of Novel, Low Sensitivity, Gas-generating Formulations
for Hotwire Ignited Devices

Department of Engineering and Applied Science

PhD

Academic Year: 2012 - 2013

Supervisors: Professor J Akhavan & Dr A Contini

April 2013

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Abstract

A novel, low sensitivity, gas-generating composition was developed to replace an existing primary explosive, potassium picrate, for use in a generic squib device. The novel composition was based on energetic materials researched from the open literature. The chosen materials were synthesised or purchased and combined in order to produce formulations which would reproducibly ignite when contacted with a hotwire. The formulations were assessed for their chemical compatibility and homogeneity by small-scale hazard testing, differential scanning calorimetry (DSC) and nuclear magnetic resonance (NMR) spectroscopy. The compositions were test fired within squibs coupled to a pressure bomb and the pressure generation and rise time was measured using a piezoelectric gauge.

Keywords:

Squib, Bridgewire, Electroexplosive Device, Igniter

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Glossary

<i>Acicular</i>	-	<i>Needle-like crystal shape</i>
<i>Activation Energy</i>	-	<i>The energy required allowing a reaction to occur.</i>
<i>All-Fire</i>	-	<i>The level of current, power, voltage or energy that required for reliable firing of a device.</i>
<i>Anaerobic Combustion</i>	-	<i>Thermal oxidation reaction that does not involve atmospheric oxygen.</i>
<i>Booster</i>	-	<i>An intermediate explosive compound or composition that is used to amplify energetic output in an explosive train by responding reproducibly to the ignition or primer charge.</i>
<i>Bridgewire</i>	-	<i>The section of a firing circuit which is designed to heat upon application of the all-fire current and ignite the explosive in contact with it.</i>
<i>Burn Rate Modifier</i>	-	<i>A compound added to a formulation, which is designed to modify the mixture's burn rate, usually by affecting the burn rate's relationship with reaction pressure as outlined by Vieille's law.</i>
<i>Chemical Compatibility</i>	-	<i>The ability for 2 or more compounds to exist in intimate contact with each other without reacting under standard operating or storage conditions.</i>
<i>Critical Diameter</i>	-	<i>The minimum diameter of an explosive charge at a given density which can sustain detonation.</i>
<i>Cutter</i>	-	<i>see Pyromechanisms</i>
<i>Deflagration</i>	-	<i>Thermal decomposition occurring at a sub-sonic velocity and propagated by thermal conduction and convection.</i>

- Detonation* - *Super-sonic thermal decomposition propagated by shock compression.*
- Dextrinated Lead Azide* - *Lead azide crystallised with dextrin to enhance the material's physical characteristics, namely impact and friction insensitivity.*
- Down selection* - *A screening method used to reduce the number of candidate materials in a project.*
- Electric Match* - *A device consisting of a small quantity of primary explosive usually bound directly to a bridgewire and used to translate an electric input into an explosive output.*
- Electro-Explosive Device* - *Any device which uses an electrical input to achieve an explosive output (see Pyromechanism also).*
- Electrothermal Response Test* - *A diagnostic test used to measure the thermal contact of a bridgewire with an explosive composition utilising the change in resistance or heat flux when a small current is applied.*
- Endothermic* - *A reaction or compound whose completion or formation results in a net reduction in energy.*
- Energetic Binder* - *A compound, usually a polymer, which is designed to enhance a material's physical properties but also incorporates energetic functional groups or explosophores and therefore may contribute to the decomposition reaction.*
- Enthalpy* - *The net energy released or absorbed by a reaction at constant pressure.*
- Exothermic* - *A reaction or compound whose completion or formation results in net increase in energy.*

- Exploding Bridgewire* - An ignition device which uses a large current to explosively vaporise a bridgewire into plasma which in turn may ignite an energetic compound by shock.
- Exploding Foil Initiator* - An ignition device which uses the explosive generation of plasma from a thin foil bridgewire to propel a plastic projectile into an explosive and induce ignition by the resulting shockwave.
- Explosive Train* - A device in which progressively less sensitive explosives are arranged. Ignition of the most sensitive can then lead to eventual initiation of the least sensitive explosive by progressive chain reaction.
- Explosophore* - A functional group which imbues a molecule with an explosive performance (such as the nitro group).
- Gas-Generator* - A device or compound that evolves a large volume of gas upon decomposition.
- Heat of Explosion* - The energy released upon the anaerobic combustion of one mole of an explosive.
- Heat of Formation* - The energy released or absorbed upon the formation of one mole of a compound.
- High Nitrogen Compounds* - Compounds that incorporate a large proportion of nitrogen and have recently become popular as possible green explosives as they decompose to release mostly nitrogen gas as opposed to CO₂ and CO.
- Hotwire* - A bridgewire which is involved in ignition solely through resistive heating and conduction of that heat to the explosive in contact with it.
- Igniter* - A device whose ignition and decomposition is used to ignite a less sensitive compound.

- Ignition* - *The provision of sufficient energy to a compound to induce self-sustained thermal decomposition.*
- Insensitiveness* - *The antonym of Sensitiveness.*
- Insensitivity* - *The antonym of Sensitivity.*
- Laser Driven Flyer* - *A device similar to the slapper or EFI, which uses the destruction of a metal foil, in this case by laser ablation, to propel a plastic projectile and initiate an explosive by shock.*
- Main Charge Explosive (MCE)* - *A low sensitivity explosive used as the major ingredient in all of the formulations tested in this thesis. The MCE chosen here was N-guanylurea dinitramide.*
- Nichrome* - *An alloy of nickel and chromium commonly used to manufacture bridgewires.*
- Nitrogen Content Modifier* - *A compound that consists of a high proportion of nitrogen and can be used to increase the proportion of nitrogen in a formulation.*
- No-Fire* - *The antonym of the All-Fire level that defines the current, power, voltage or energy that a device is guaranteed to be impervious to.*
- Oxygen Balance* - *The proportion of oxygen present in a compound represented as a percentage of the quantity required to achieve complete combustion.*
- Oxygen Balance Modifier* - *A compound that possesses a high or low oxygen balance and may be incorporated into a formulation to increase or reduce the overall oxygen content.*
- Performance Modifier* - *In this thesis, the compounds that are added to the main charge explosive to alter its response to the hotwire stimulus.*

- Polymer Bonded Explosive* - *An explosive formulation that incorporates a polymeric material to modify the physical properties of the explosive and enhance its practicality in a given application.*
- Primary Explosive* - *An explosive compound that is readily initiated to detonation using a low to moderate quantity of energy (activation energy < 170kJmol⁻¹).*
- Propagation* - *Sustained decomposition of an explosive after ignition from the ignited end of the charge to the other.*
- Propellant* - *In general terms non-detonating gas-generating explosives.*
- Protractor* - *see Pyromechanism*
- Pyromechanism* - *A selection of electrically and mechanically actuated explosive devices that are used to carry out a number of well-defined tasks such as the cutting of cables (cutter), releasing bolts (exploding bolts), generating gas (gas-generators), mixing or isolating fluids (protractor or retractor).*
- Pyrotechnic* - *A commonly metal-based explosive that is typically ignited to release large quantities of heat and light but minimal quantities of gas.*
- Radio Frequency Interference* - *The induction of currents in unshielded circuitry by electromagnetic radiation (also known as RADHAZ).*
- Retractor* - *see Pyromechanism*
- Safe and Arm Units* - *A mechanically isolated igniter which is moved into the explosive train prior to actuation.*
- Secondary Explosive* - *An explosive that requires a substantial stimulus to initiate detonation (typically the activation energy > 170kJmol⁻¹).*

Sensitiveness - *An expression of the energy required to illicit an undesirable explosive response (see Sensitivity).*

Sensitivity - *An expression of the energy required to illicit an explosive decomposition of an energetic material. Usually quantified by measurement of response to varying levels of impact, friction and electrostatic discharge (Appendix 8.8).*

Slapper - *see Exploding Foil Initiator*

Squib - *A generic term for a small, electrically actuated explosive device.*

Strand Burner - *A closed vessel in which strands of explosive or propellant are burned at controlled pressure regimes and the burn rates measured.*

List of Abbreviations

<i>5AT.H₂O</i>	-	<i>5-Aminotetrazole monohydrate</i>
<i>5ATzT</i>	-	<i>5-Aminotetrazolium 5,5'-azotetrazolate</i>
<i>ADN</i>	-	<i>Ammonium dinitramide</i>
<i>ADNQ</i>	-	<i>Ammonium dinitroguanidine</i>
<i>ADNT</i>	-	<i>Ammonium 3,5-dinitro-1,2,4-triazolate</i>
<i>AN</i>	-	<i>Ammonium Nitrate</i>
<i>ANTA</i>	-	<i>3-Amino-5-nitro-1,2,4-triazole</i>
<i>ANTX</i>	-	<i>Ammonium 5-nitrotetrazolate-2N-oxide</i>
<i>BAM</i>	-	<i>The German Federal Institute for Materials Research and Testing</i>
<i>BPT</i>	-	<i>3,6-Bis(3,5-dimethyl-pyrazol-1-yl)-1,2,4,5-tetrazine</i>
<i>BTAT</i>	-	<i>3,6-(Bisnitroethylamino)-1,2,4,5-tetrazine</i>
<i>BTATz</i>	-	<i>3,6-Bis(1,2,3,4-tetrazol-5-ylamino)-1,2,4,5-tetrazine</i>
<i>C4</i>	-	<i>Composition 4, a name given to a formulation consisting of RDX and polyisobutylene.</i>
<i>CHN</i>	-	<i>Elemental analysis for Carbon, Hydrogen and Nitrogen</i>
<i>C_p</i>	-	<i>Specific Heat Capacity</i>
<i>C_v</i>	-	<i>Volumetric Heat Capacity</i>
<i>DAAF</i>	-	<i>3,3'-Diamino-4,4'-azoxyfurazan</i>
<i>DAAT</i>	-	<i>3,3'-Azobis(6-amino-1,2,4,5-tetrazine)</i>
<i>DAAzF</i>	-	<i>3,3'-Diamino-4,4'-azofurazan</i>

<i>DAT</i>	-	<i>3,5-Diamino-1,2,4-triazole</i>
<i>DDT</i>	-	<i>Deflagration to detonation transition</i>
<i>DNAT</i>	-	<i>5,5'-Dinitro-3,3'-azo-1,2,4-triazole</i>
<i>DHT</i>	-	<i>3,6-Dihydrazino-1,2,4,5-tetrazine</i>
<i>DSC</i>	-	<i>Differential Scanning Calorimetry</i>
<i>DTNTO</i>	-	<i>2,4-Dihydro-2,4,5-trinitro-1,2,4-triazol-3-one</i>
<i>E_A</i>	-	<i>Activation energy</i>
<i>EBW</i>	-	<i>Exploding bridgewire</i>
<i>EED</i>	-	<i>Electro-explosive device</i>
<i>EFI</i>	-	<i>Exploding foil initiator</i>
<i>ERL</i>	-	<i>Explosives Research Laboratory</i>
<i>ESD</i>	-	<i>Electrostatic discharge</i>
<i>FOX-7</i>	-	<i>1,1-Diamino-2,2-dinitroethylene</i>
<i>FOX-12</i>	-	<i>N-guanylurea dinitramide (also known as GuDN)</i>
<i>GuDN</i>	-	<i>see FOX-12</i>
<i>H₂BTA</i>	-	<i>Bis(tetrazolyl)amine</i>
<i>HBT</i>	-	<i>5,5'-Hydrazinebistetrazole</i>
<i>HMX</i>	-	<i>1,3,5,7-Tetranitro-1,3,5,7-tetraazacylclooctane</i>
<i>HNS</i>	-	<i>Hexanitrostilbene</i>
<i>Hy5At</i>	-	<i>Hydrazinium 5-aminotetrazolate</i>
<i>MCE</i>	-	<i>Main charge explosive</i>
<i>MS</i>	-	<i>Mass Spectrometry</i>

NASA	-	National aeronautics and space administration
NG	-	Nitroglycerine
NG-N1	-	N-Nitro-2,3-dinitrooxypropan-1-amine
NMR	-	Nuclear Magnetic Resonance Spectroscopy
NNHT	-	2-Nitrimino-5-nitrohexahydro-1,3,5-triazine
NSI	-	NASA standard initiator
NTO	-	3-Nitro-1,2,4-triazol-5-one
PBX	-	Polymer bonded explosive
PE4	-	Plastic explosive number 4
PETN	-	Pentaerythritol tetranitrate
PM	-	Performance modifier
PPZ	-	General abbreviation for polyphosphazenes used here to represent poly[P-5,6-dinitratohex-1-oxy/P-2,2,2-trifluoroethoxyphosphazene]
RADHAZ	-	see RFI
RDX	-	1,3,5-Trinitro-1,3,5-triazacyclohexane
RFI	-	Radio frequency interference
SBASI	-	Single bridgewire Apollo standard initiator (original name for the NSI)
SCB	-	Semiconductor bridge
STP	-	Standard temperature and pressure
TAGDNAT	-	Bis(triaminoguanidinium)-3,3'-dinitro-5,5'-triazolate
TAG.HCl	-	Triaminoguanidinium hydrochloride

<i>TAGzT</i>	-	<i>Bis(triaminoguanidinium)-5,5'-azotetrazolate</i>
<i>TATB</i>	-	<i>2,4,6-Triamino-1,3,5-trinitrobenzene</i>
<i>XRD</i>	-	<i>X-ray diffraction</i>
ΔH_C	-	<i>Enthalpy of combustion</i>
ΔH_{Exp}	-	<i>Enthalpy of explosion</i>
ΔH_F	-	<i>Enthalpy of formation</i>
<i>K</i>	-	<i>Thermal diffusivity</i>
λ	-	<i>Thermal conductivity</i>
ρ	-	<i>Density</i>

“The first principle is that you must not fool yourself and you are the easiest person to fool.”

Richard P. Feynman, Nobel Laureate

1 Introduction

Explosives are well known for their use in the mining industry, in demolition and in munitions but they are also increasingly present in cars, life rafts and in every probe, satellite and shuttle sent into space. While this comes as a surprise to many, all of these applications share the same basic principle.

When explosives thermally decompose they release energy in the form of heat and gas. By confining this gas, depending upon the magnitude of the energy released, it is possible to apply the resulting shockwave or high-pressure gas in a safe and constructive manner.¹ For example, within a fraction of a second an explosive device can be applied to:

- Sever or perforate mechanical linkages or seals, as seen in the famous exploding bolts on the Apollo missions which were used to jettison used rocket motors and stages (Figure 1);²
- Ignite an explosive charge by the transfer of heat or by shock as seen in rocket motors, in airbags and life-raft inflators.³

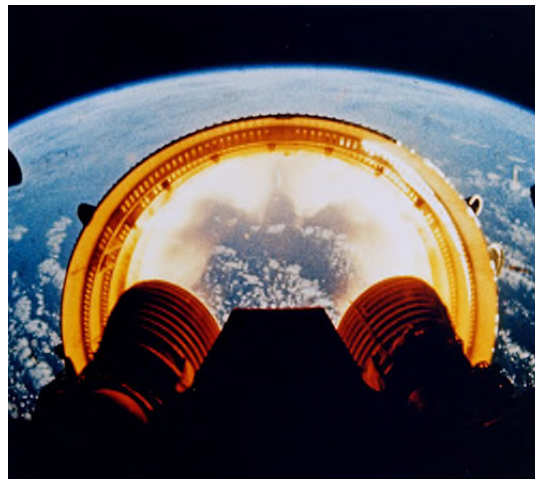


Figure 1: Saturn V rocket stage 1 separation demonstrating the use of exploding bolts

There is a collection of devices that apply explosives in this controlled manner. These devices are usually initiated by an electrical input, which has given rise to their classification as electro-explosive devices (EED). In general, these devices utilise

pyrotechnic compositions that are sensitive to the stimulus provided by an electric match or primer compound, this has given rise to the term pyromechanism.

These primer compounds are reliably ignited from a thermal stimulus, which originally would have been a burning fuse but has since been replaced by a heated electrical wire. The primer is capable of igniting readily from a thermal stimulus and prompting the reproducible ignition of the main explosive charge (see “Pyrotechnic Base Charge” in Figure 2). These squib devices, as they are known, have been in use as early as the 17th century, where they were applied to reliably ignite charges of gunpowder in mines. As gunpowder ignites erratically from a heat source, especially in the presence of moisture, it is therefore necessary to use a primer compound that induces consistent ignition of gunpowder upon actuation.

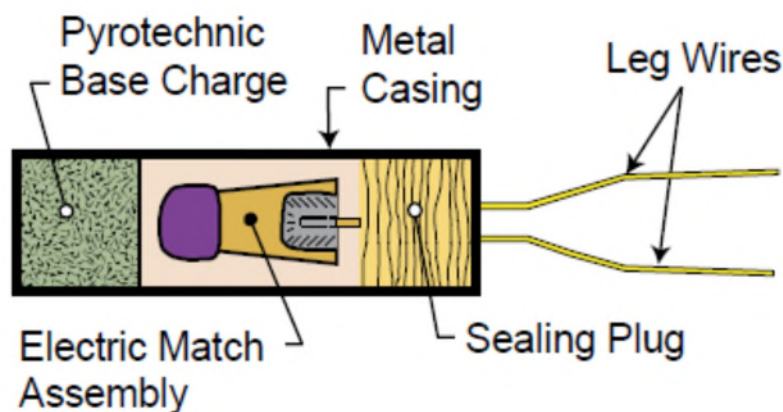


Figure 2: Early squib design⁴

These primer compounds tend to be sensitive, primary explosives and while they are very easily ignited with little energy, and so are useful in initiating other explosives, they display an unfortunate sensitivity to both intended and accidental stimuli. This means that while a hotwire may reliably initiate a primer composition; a fire, an accidental impact, electro-static discharge (ESD) or even friction may ignite that same composition. In a situation where that primer is being used to ignite a safer, more insensitive and generally larger charge of explosive, as with gunpowder in 17th century mines, the vulnerabilities of the primer become the vulnerabilities of the entire charge. Now an accidental impact or fire may cause not only the ignition of the primer but also

the main charge and in the case of the mining scenario, this may result in an unintended explosion that might risk the lives of all within the mine.

The safety of squibs has improved as the devices have been updated. This modernisation has mainly focussed on the replacement of the primer compositions with gradually less sensitive and less toxic compounds. However, contemporary devices still use relatively sensitive primer and pyrotechnic compounds and as long as this is the case, they pose a threat that may be made further safe by the incorporation of yet lower sensitivity compounds.

1.1 Aims of this study

It is the opinion of some researchers that it may be possible to improve the safety of current squib devices by replacing the toxic and sensitive compositions presently in use.⁵ Consequently, the aim of this project is to replace the sensitive primary explosive potassium picrate, in use in a hotwire-ignited squib, with an insensitive formulation. This composition must display equivalent sensitivity and performance to potassium picrate when ignited by a hotwire. This may be achieved by developing insensitive formulations that possess a high oxygen balance, fast burn rate or high nitrogen content and can be produced from readily synthesised or purchased compounds.

To understand the vulnerabilities of the existing squib designs and to be able to suggest improvements on the state-of-the-art, it is necessary to understand exactly how modern squibs work. The classification of squibs is rather broad and so it will be necessary, for the purposes of this project, to first introduce the various sub-types and then to concentrate on a particular generic device.

The thesis is structured as follows:

Literature Review

This review is designed to present the current status of squib technology and the advances that have been made to improve the safety of the devices while also indicating the areas where more improvements are necessary.

The Project

This chapter presents an existing squib device and details the project plan, which aims to improve the safety of this device by replacement of the existing explosive with a new and safer energetic formulation.

Down selection

This section is the second literature review of the thesis. Here a review of recently reported energetic materials, which display high performances, and suitable sensitivities are collated and scrutinised for their possible application in a novel squib formulation.

Results and Discussion

Here the practical science of the project is outlined and the results reported are used to show the rationale behind the decisions made in the direction of the research and ultimately the thesis conclusions. In some cases the experimental is included in this section to provide some insight into techniques which the reader may be unfamiliar with.

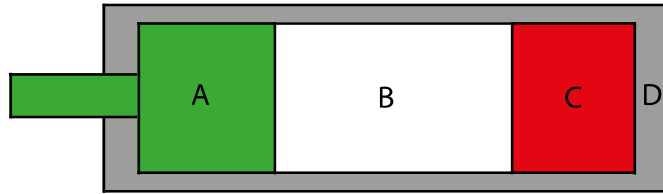
Conclusions

This chapter will attempt to provide a summary of the findings reported here. It will also highlight the limitations of the research and suggest improvements upon the current work and propose areas for further investigation.

Appendix

This section contains background information on the techniques used in the project and some A3 pull-out diagrams which are designed to provide information and clarity to the reader throughout the thesis.

2 Literature Review



	The Energy Input (A)	Energetic Materials (B)	Mechanical Output (C)	Body (D)
Low Energy, Sensitive Devices	<ul style="list-style-type: none"> • Hotwire • Thin Film 	<ul style="list-style-type: none"> • Primary Explosive • Primer Compound • Pyrotechnic Mixture 	<ul style="list-style-type: none"> • Valve • Piston 	<ul style="list-style-type: none"> • Pressure Resistant Casing
Low Energy, Reduced Sensitivity Devices	<ul style="list-style-type: none"> • Thin Film • Laser • Semiconductor Bridge (SCB) 	<ul style="list-style-type: none"> • Secondary Explosive 	<ul style="list-style-type: none"> • Cutter 	

Figure 3: Diagram of a generic non-detonable squib and legend

A generic squib can be described as consisting of an electrical input (A), an energetic material or composition (B) and an output (C) all of which are enclosed within a sealed body (D) (Figure 3). The variation in these components allows for squibs to be used in a wide range of applications. By varying the choice of energetic material, the design of the output assembly and the electrical input it is possible to generate varied responses over a wide range of response times.

This project will focus on the non-detonable squib sub-group that function through the fast generation of hot gas, which can be pressurised in an enclosed volume and released through a burst disc to affect the opening of a valve. This review of the literature will attempt to explain the theory and background of the squib, by assessing

the contributions of the individual squib components A-C, and building on this to suggest possible improvements upon the existing designs.

2.1 The Output of the Device

A typical squib may be actuated over a period of a few milliseconds (ms) or less and generate a high gas pressure on the order of several hundred megapascals (MPa).ⁱ This may be achieved with less than a gram of explosive and an electrical input current on the order of 5A.

Understandably, the nature of the required output heavily influences the design of the squib. This is seen in the development of the many different types of squib marketed by Leaffield Engineering Ltd (Figure 4).ⁱⁱ

Each of these devices is specifically designed to perform various tasks such as cutting, ignition, pulling, pushing and detonation, at different levels of intensity and at varying speeds. As such, each task-specific squib is available in several sub-types capable of delivering varying grades of output energy.

While this is one method of satisfying the various pyrotechnic applications, it requires the individual development of each device. Alternatively it is possible to use one standard squib and tailor the output depending on the required application. This is the method applied by NASA with respect to the NASA standard initiator (NSI).ⁱⁱⁱ

ⁱ Depending on the volume into which the gas is expelled.

ⁱⁱ Leaffield Engineering Ltd is a division of Chemring Energetics UK who are a company who specialise in explosives applications.

ⁱⁱⁱ Developed from the single bridgewire Apollo standard initiator (SBASI) as it was developed in 1966 for the Apollo missions and the Viking standard initiator.

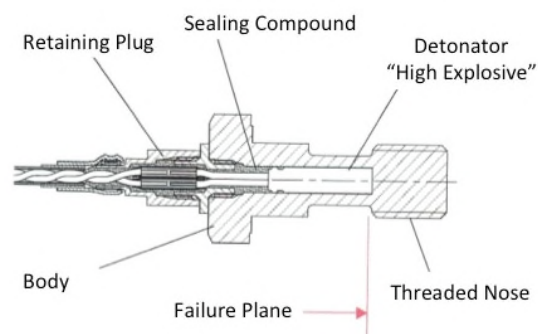
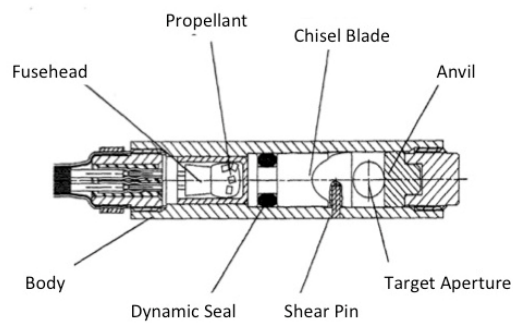
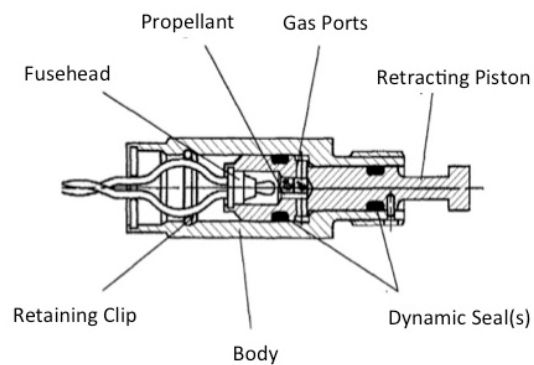
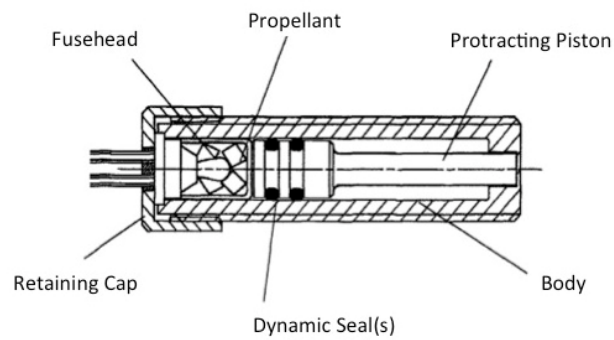


Figure 4: Typical examples of pyromechanisms (from top): protractor, retractor, cutter and exploding bolt^{iv}

^{iv} Pictures courtesy of Mr Mike West formerly of Chemring UK.

The NSI is a squib which was designed for the Apollo missions and has since become the standard initiator in space vehicles. It has been involved in a large number of critical applications such as the mixing of fluid propellants onboard satellites. NASA utilises the fast and reliable production of hot, high-pressure gas and hot metal particulates which are generated by the NSI. When mixing fluid propellant, the gas and heated metal particulates are focussed by the output assembly or “pyrovalve” to ignite a booster charge. This booster then propels a piston, which opens a flow path between the two liquid propellant components (

Figure 5Error! Reference source not found.). By relying on a common squib, the NSI, for all devices of this type NASA have been able to focus on optimising the reliability of the NSI which is now the gold standard in its field.^{1,6}

The significance of this is that the reproducibility of the squib assembly in all of these devices dictates the consistency and ultimately the success of the overall mechanism in which they are involved.

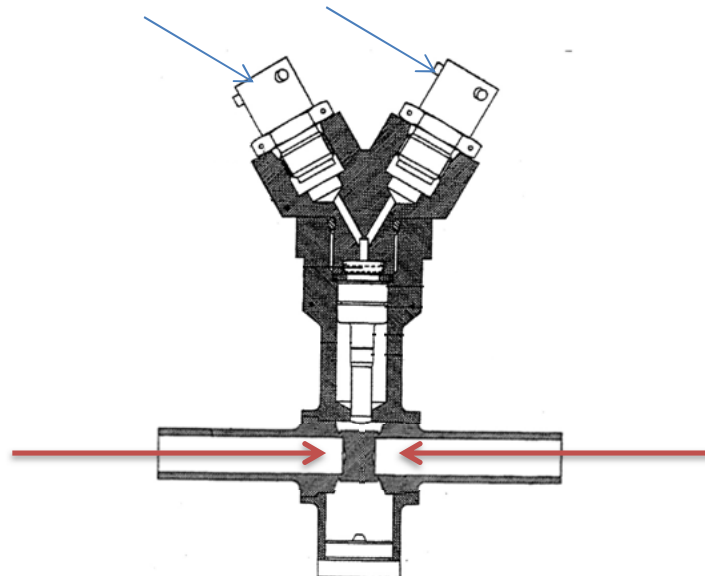


Figure 5: NASA Standard Igniter (NSI), highlighted by blue arrows, in use in a “normally-closed” Pyrovalve, the red arrows indicate the flow path which is blocked between two vessels (normally containing fuel and oxidiser components of a liquid rocket propellant) ^{7,v}

2.1.1 Summary

All of the design variants of a non-detonable, gas-generating squib follow the same basic principle. Upon the release of gas from the squib, the increase in pressure due to confinement in a given volume is focussed onto the end-face of a tool, be it a piston, cutting blade or other (Equation 1).

$$PV = nRT$$

Equation 1: The ideal gas law [P = pressure (N m⁻²), V = volume (m³), R = ideal gas constant (8.314 J K⁻¹ mol⁻¹) and T = temperature (K)]

This pressure can then be expressed as a force when applied over a moveable surface area (Equation 2).

$$F = PA$$

Equation 2: The force exerted by a squib [where F = force (N), P = pressure (Pa) and A = area (m²)]

In this way it is possible, if the required force is known, to define the necessary gas-pressure and hence the volume of gas that the squib must generate to be successful in its application.

2.2 The Energy Input

Squibs are often employed in critical, life-saving applications (such as the inflation of airbags, self-inflating life rafts and in the ignition of ejector seat propellants) where their output and response to the firing stimulus must be fast and reproducible.^{vi} To

^v It is common practice for two simultaneous NSI devices to be employed to reduce the opportunity for the loss of a mission due to a single squib failure. In this case, in the rare instance that one of the squibs may fail, the other is capable of actuating the piston or cutter itself and either halting or allowing flow between fluids A and B.

^{vi} NASA sets their acceptable failure rates for the Apollo missions as the following, “The pyrotechnic safety design reliability goal was established to be 0.9999 at the 95% confidence level.”²

understand how squibs can be manufactured to produce such a consistent response to the firing stimulus it is important to understand the ignition process.

2.2.1 Ignition

Ignition occurs when sufficient energy is provided to enable a material to sustain its own thermal decomposition i.e. “propagate”. The critical quantity of energy required to reach ignition is the activation energy (E_A) of that material’s thermal decomposition reaction. Importantly, the thermal decomposition of an explosive is always exothermic. Thus there is always a net increase in energy release,^{vii} which is proportional to the enthalpy (ΔH) of the explosive decomposition reaction (Figure 6).

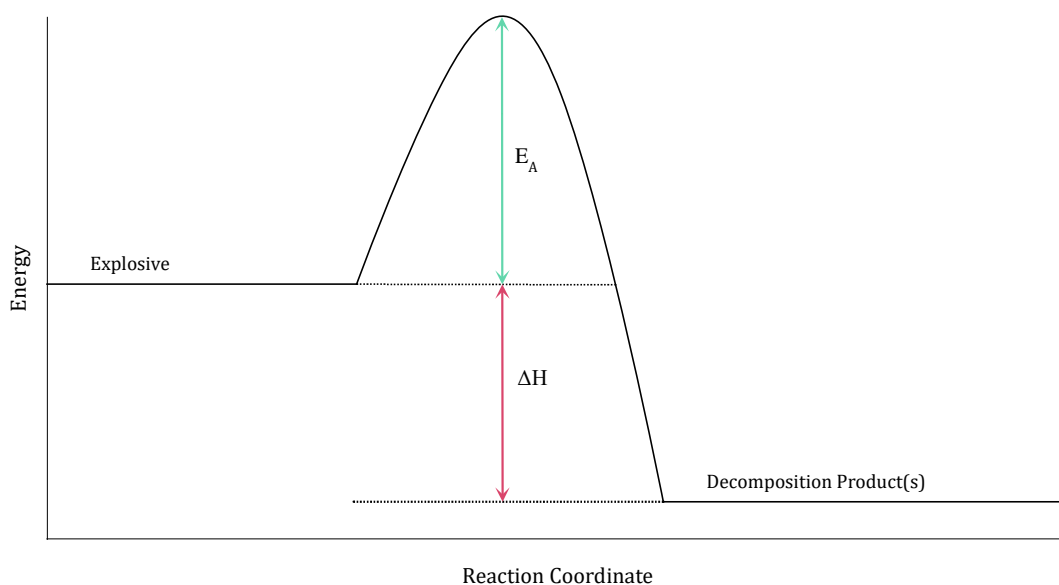


Figure 6: Illustration of activation energy (E_A) and enthalpy of decomposition (ΔH) (ΔH and E_A are expanded upon in Appendix 8.6)

As an initiating device, the primary purpose of a squib is to use an electrical stimulus to reliably affect ignition in an explosive charge. For this to occur in a fast and reliable way the squib must convert the electrical input into heat. The simplest example is given by the resistive heating of a length of wire (known as a “hotwire”).

As the energetic material absorbs heat, some thermal energy dissipates through the charge. For ignition to occur, the rate of absorption must be greater than the rate of

^{vii} Provided that heat losses are minimised.

dissipation. If this is achieved heat may build in the explosive, at a localised region near the hotwire.^{viii} The temperature can then increase until decomposition commences. At this point chemical bonds within the explosive molecule begin to break and exothermic decomposition begins. The resulting release of heat from the decomposition reaction surpasses the electrical input as the main source of thermal energy and propagates the reaction throughout the rest of the charge without need for any additional energy (Figure 7).

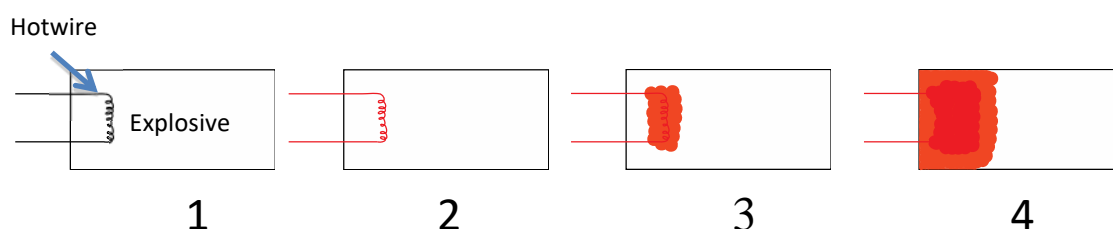


Figure 7: Illustration of ignition within a squib: 1) A simplified squib device 2) A current is applied to the hotwire causing it to heat up 3) The explosive material is heated by the hotwire 4) The explosive decomposes, heating the surrounding unreacted explosive and the reaction propagates

In a successful ignition event, the time lapsing from applying an electrical current to the hotwire until the complete ignition of the explosive can be as little as a few microseconds. Although the process can be exceedingly quick it is also highly complex and can be better understood by dividing it into two parts; the transfer of heat from wire to explosive and the propagation of the ignition. By looking at each part it is possible to observe factors that influence the rate and reliability of ignition. With this understanding it may then be possible to improve the means by which explosives are ignited in squibs.

2.2.2 Transfer of Heat from Wire to Explosive

An explosive must be provided with energy to induce it to ignite. In a squib this energy is provided in the form of heat from a hotwire. The rate of heat transfer from the

^{viii} Ignition theory is more fully described by Bowden and Yoffe in their 1952 monograph "Initiation and Growth of Explosion in Liquids and Solids."⁸

hotwire to the explosive directly influences the rates of ignition and actuation of the device. The initial transfer of heat in hotwire ignition occurs by thermal conduction and the rate is given by Fourier's Law (Equation 3).^{ix}

^{ix} Thermal conduction can be described as the transport of heat through a solid body by molecular vibrations.

$$\frac{dQ}{dt} = -\lambda A \frac{dT}{dn}$$

Equation 3: Rate of heat transfer according to Fourier's law [where Q = heat being conducted, t = time, λ = thermal conductivity (negative as heat is moving down a temperature gradient), A = surface area, T = temperature and n = distance into the sample normal to the surface]

Fourier defines the rate of heat transfer by conduction as being dependent upon the contact surface area of the explosive exposed to the hotwire and the substance's thermal conductivity (Equation 3). To improve the rate of conduction the squib design can be modified to allow more energetic material to be in direct contact with the hotwire by altering the hotwire geometry, this may increase the effective contact surface area and therefore the rate of heat transfer. However, improvement of the rate of heat transfer by altering the thermal conductivity is more complex.

The thermal conductivity of an explosive defines its ability to absorb heat and is a function of the material's thermal diffusivity (κ), specific heat capacity (C_p) and density (ρ) (Equation 4).^x

$$\lambda = \kappa C_p \rho$$

Equation 4: Thermal conductivity [where λ = thermal conductivity ($\text{J s}^{-1} \text{m}^{-1} \text{K}^{-1}$), κ = thermal diffusivity ($\text{m}^2 \text{s}^{-1}$), C_p = specific heat capacity ($\text{J kg}^{-1} \text{K}^{-1}$) and ρ = density (kg m^{-3})]

By referring to Equation 4 it is possible to increase the thermal conductivity of a material by increasing its density, which reduces the thermal diffusivity (the rate of heat transfer through a body or rate of heat dissipation). However an increase in density causes an increase in the energy required to heat the sample. This is due to the increase in the number of molecules per unit volume as density increases. This increases the volumetric heat capacity (C_v), which is highly relevant in EEDs as the explosive charge is generally ignited within an enclosed body. The volumetric heat capacity denotes the energy required to increase the temperature of a given volume by a single degree (Equation 5).

^x Specific heat capacity is the energy required to heat 1 kg of a material by 1 °C.

$$C_v = C_p - P \frac{dV}{dT}$$

Equation 5: Volumetric heat capacity [where C_v = volumetric heat capacity, C_p = specific heat capacity ($\text{J kg}^{-1} \text{K}^{-1}$), T = temperature (K) and P = pressure (N m^{-2})]

Therefore while an increase in density of the explosive may result in a greater rate of heat transfer, more energy would be required to increase the temperature and therefore achieve ignition. This would be counterproductive in a device where the input energy was limited by design. For an adequate quantity of the explosive to be rapidly heated to decomposition a compromise is to be found between higher density of the explosive around the hotwire and the required input energy. While the initial absorption and transfer of heat occurs by conduction and therefore is proportional to density, the efficiency of convection, which is suggested to be responsible for the spread of heat in fast burning decompositions, is dependent upon the porosity of materials and so is negatively influenced by high density solids.

2.2.3 Propagation of Ignition

Once the initial transfer of energy from the hotwire to the explosive has taken place and the decomposition of the explosive has begun, conduction is surpassed as the primary method of heat transfer. The product of an explosive decomposition is, often, a mixture of hot gases. It is this hot gas, which can transfer heat throughout the explosive charge by convection and eventually increase the burning rate.

Convection is the transfer of heat facilitated by the movement of a fluid. In the case of an explosive decomposition the fluid is a mixture of heated decomposition gases. As the decomposition reaction in an EED is confined within a body, the decomposition gases are trapped and so pressure increases as more gas is produced. The hot and pressurised decomposition gas is forced around and eventually through the unburned, pristine explosive, increasing the effective reaction surface area. The increase in

surface area results in a dramatic increase in the reaction rate.^{xi} This is observed as an increase in the burning rate of the explosive and the rate of the burning surface regression is described by Vieille's law (Equation 6).

$$r = aP^n$$

Equation 6: Vieille's law [where r = burn rate, P = pressure, n = pressure exponent and a = burn rate coefficient (a and n are unique values which are determined experimentally for every material)]¹²

The increase in pressure influences not only the burning surface area but also the method of heat transfer and eventually the method of ignition (as shown in Table 1).

Type of Burning	Typical Speed of Burning Propagation (m s ⁻¹)
Conductive Burning	0.01
Convective Burning	100
Compressive or Erosive Burning	700-2000
Detonation	>2000

Table 1: Decomposition regimes in ascending order of pressure and propagation rate ^{13,14,15}

It is important to understand that as pressure increases it influences the burning rate by forcing hot gas into pores and voids in the explosive. At a critical point the pressure increase can be sufficient enough that the explosive can be ignited by high-pressure induced shock-compression of the material rather than conductive or convective heating. This marks the transition from fast burning (deflagration) to detonation (DDT).^{xii}

^{xi} It is also possible to increase the surface area by using a granular explosive with a small particle size and indeed this is also employed to modify the burning character of propellants and explosives.^{9,10,11}

^{xii} The progression of fast-burning to detonation is known as a deflagration to detonation transition (DDT) and is a feature of some explosive devices not featured in this review. It should be noted that the rate of transition between the burning regimes is dependent upon multiple variables from explosive particle size to the degree of porosity.

In a device, such as a fast-response gas-generating squib, where the energetic output is required almost immediately (sub-millisecond (ms)), the fastest possible burning rate is desirable but the transition to detonation is not. Fortunately DDT is only possible if there is a sufficient quantity of explosive to allow the progressive increase in burn rate. In this scenario the critical diameter of the explosive or composition is referred to. The critical diameter is the minimum diameter of an explosive charge which may sustain detonation at a given density and within a given level of confinement.¹² This diameter can be used to advise the dimensions of the explosive charge if detonation is, as in this case, undesirable as an output of the EED.

2.2.3.1 Summary

To prepare an explosive for optimum ignition by hotwire, efforts should be made to increase the density around the ignition stimulus and the thermal contact to optimise heat transfer by conduction. However a degree of porosity elsewhere is necessary to permit convection of the hot decomposition gases and to encourage the higher burning rates reported in the literature.

2.2.4 Methods of Ignition

The principles of ignition are key to understanding and improving upon the ignition methods used in EEDs. The simple concept, which lies at the heart of most devices, is that a relatively small input energy should be sufficient in delivering the desired explosive or pyrotechnic output. This section will present a selection of devices which fulfil this concept. However due to a shortage of publications specialising in purely deflagrating devices this section will also use examples of several types of detonator.

2.2.4.1 Low-Energy Ignition

The predominant form of electrical initiator in non-detonable squibs was, and to some extent still is, the hotwire. In these devices the application of a current through a bridgewire in contact with the explosive induces the resistive heating of a wire, the heat is transferred to the explosive by conduction as described in the last section (see Section 2.2.2). For successful ignition the required increase in explosive temperature is rather modest, in the case of an energetic material such as pentaerythritol tetranitrate

(PETN) the temperature of an adequate volume should be increased to approximately 300 °C.¹⁶ Historically this method of ignition has been applied to sensitive and easily initiated explosives such as mercury fulminate, PETN and lead styphnate. On the whole these materials are being phased out due to their high susceptibility to accidental ignition (and toxicity due to lead content etc.).^{17,18}

The hotwire device applies James Prescott Joule's first law in its design. Joule's first law dictates that the application of a current to a length of wire will release energy in the form of heat proportional to the square of the current, the resistance of the wire and the duration of the electrical pulse (Equation 7).^{xiii} Thus the bridgewire of a hotwire device can be viewed as a resistor and by increasing its resistance it is possible to increase the heat released to the explosive (Figure 8).¹⁹

$$Q = I^2 R t$$

Equation 7: Joule's first law discovered in 1841 [where Q = heat (J), I = current (A), R = electrical resistance (Ω) and t = time (s)]

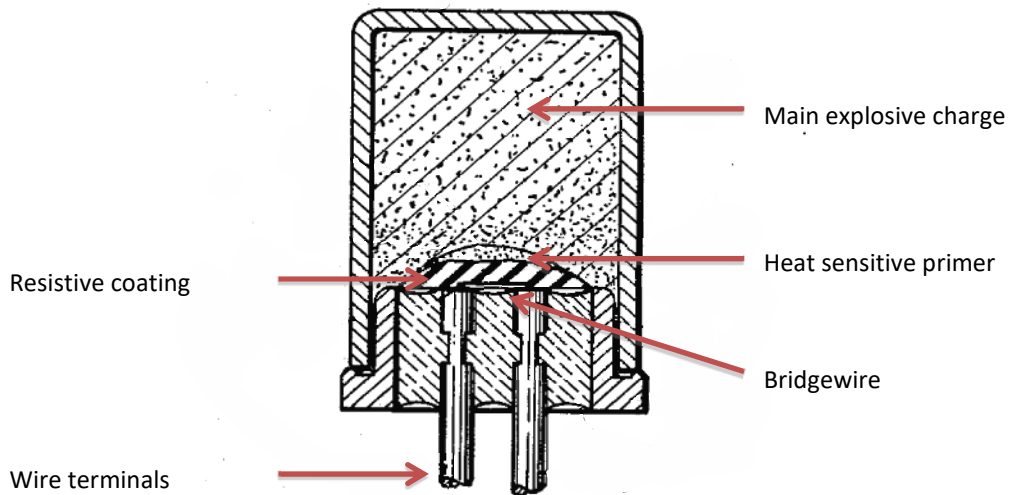


Figure 8: Example of a squib applying resistive coating to increase the resistance of the bridgewire¹⁹

^{xiii} Heinrich Lenz discovered Joule's first law independently in 1842.

The hotwire ignition method has been proven to be successful in the initiation of primary explosives in squibs and other EEDs. However as the working environment, in which squibs have been applied, has become more crowded with electrical equipment, a failing in their design has materialised. “Stray” electromagnetic radiation such as radio waves and electrostatic discharge (ESD) from electrical equipment and operators has the potential to induce a current in the hotwire circuit and stimulate ignition.^{20,21,22}

The response to the threat of accidental ignition by electromagnetically induced currents (known as RFI or RADHAZ) and ESD was divided. One answer was to increase the minimum current and voltage necessary to ignite the explosive. This involved establishing the 1 A/1 W rule which dictated that an EED must not be actuated when exposed to 1A or 1W over a predetermined time period. In some areas this was achieved by the inclusion of safety resistors, attenuators or filters in the firing circuit (Figure 9). These all served to increase the voltage required to draw a firing current over the bridgewire. In a device where the available voltage and current are not limited, this provided a solution to the RFI and ESD problem.

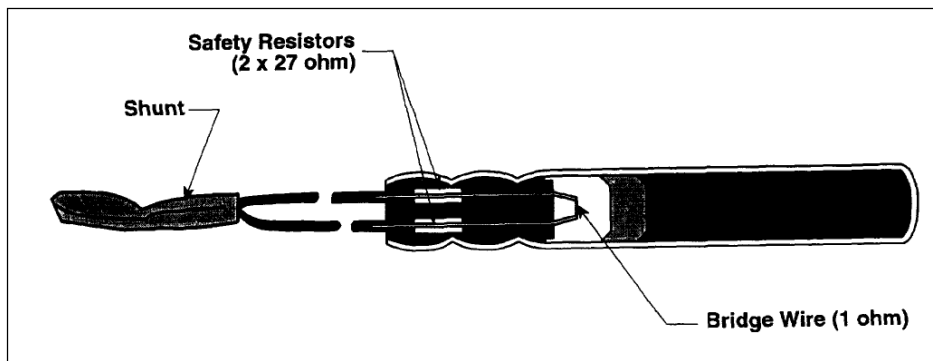


Figure 9: “Resistorised” electric detonator²³

However the limit of 1 A meant that although issues with RFI were avoided, sensitive primary explosives were still employed to assure reproducible ignition in these low energy devices.

2.2.4.2 High-Energy Ignition

Detonators have developed away from hotwire ignition of explosives to direct high-energy shock initiation of the explosive charge. In use, the hotwire detonator is

sensitive to accidental ignition due to its design and the sensitive explosives that it employs.^{xiv} The exploding bridgewire (EBW) detonator and exploding foil (EFI) or “slapper” detonator are preferable in terms of safety. These devices are capable of producing a shockwave without the use of a primary explosive. EBW and EFI are capable of inducing ignition without the need to progress through conductive and convective processes as hotwire devices must (Table 1).

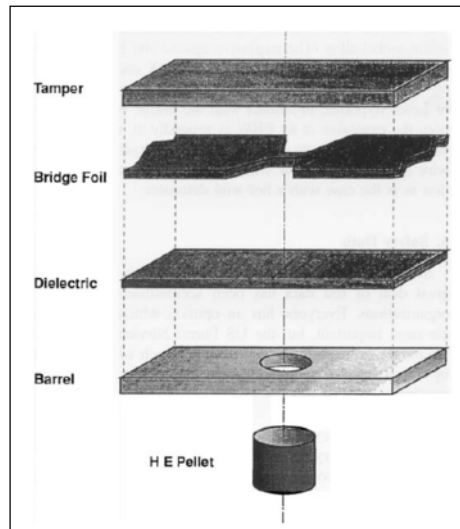


Figure 10:An exploded view of an EFI device²⁴

These high-energy devices operate by resistively shattering a bridgewire (EBW) whose resultant plasma shock initiates an explosive charge, or in the case of an EFI, propelling a plastic (labelled as the dielectric in Figure 10) projectile with the force of a vaporised foil bridge (EFI see Figure 10). The shockwave generated in both cases can be used to bring a charge of secondary explosive to detonation. The shockwave may even be utilised to ignite material that is not in direct contact with the bridgewire or foil. By igniting an explosive over an air gap rather than by direct contact it is possible to avoid any corruption of the explosive by premature heating of the bridgewire.²⁵

The EBW and EFI function through the swift application very large voltages by capacitors, when compared to that of a hotwire device, on the order of several

^{xiv} Although detonators utilising sensitive materials such as lead azide are still commonly used.

thousand volts in some cases.^{23,24} However due to the length of time which EBW and EFI function over (in the order of μs) they use approximately the same amount of energy as a hotwire device (Equation 8).

$$E = Pt$$

Equation 8: Relationship of energy and power [where E = energy (J), P = power (W) and t = time (s)]

It is this application of a short, intense burst of energy, which is used to bring explosives such as PETN, RDX and HNS to detonation. This method of ignition has only seen successful application with materials that are reliably shock initiated. As such EBW and EFI devices only apply compounds which are capable of DDT within the given volume. As the transition to detonation is not the desired output for a non-detonable, gas-generating squib it may be possible to use EBW and EFI as high-energy alternatives to hotwire ignition.

	Hotwire	Exploding Bridgewire (EBW)	Exploding Foil Initiator (EFI)
Current (A)			
Threshold	1	200	2000
Operating	5	500	3000
Voltage (V)			
Threshold	20	500	1500
Energy (J)			
Threshold	0.2	0.2	0.2
Power (W)			
Threshold	1	100000	3000000
Function Times (μs)			
Typical	1000	1	0.1

Table 2: Comparison of input current, voltage, energy, power and response times in a typical hotwire, EBW and EFI device²⁴

This may reduce the vulnerability of the EED to accidental ignition by removing electrical hazards and allowing the use of an insensitive secondary explosive fill. Unfortunately EBW and EFI are expensive devices, as they require costly additional hardware capable of delivering high power and high voltages over an extremely limited time. As such these devices are only suitable for applications deemed to warrant their price.²³

2.2.5 Alternative Ignition Systems

Whilst modern hotwire devices use low currents to reliably ignite sensitive explosives, EBW and EFI apply extremely high currents to detonate insensitive explosives (see Table 2). These approaches seem to leave a region, which is fairly underdeveloped in the literature, where insensitive explosives are merely ignited by moderate currents.

2.2.5.1 The Semiconductor Bridge (SCB)

The most modern developments in ignition mimic the EBW and EFI in their quick release of energy to the explosive charge. Unlike the EBW and EFI this energy release is not capable of directly initiating to detonation^{xv} and does not require the extremely large voltages which are common in high-energy detonators.

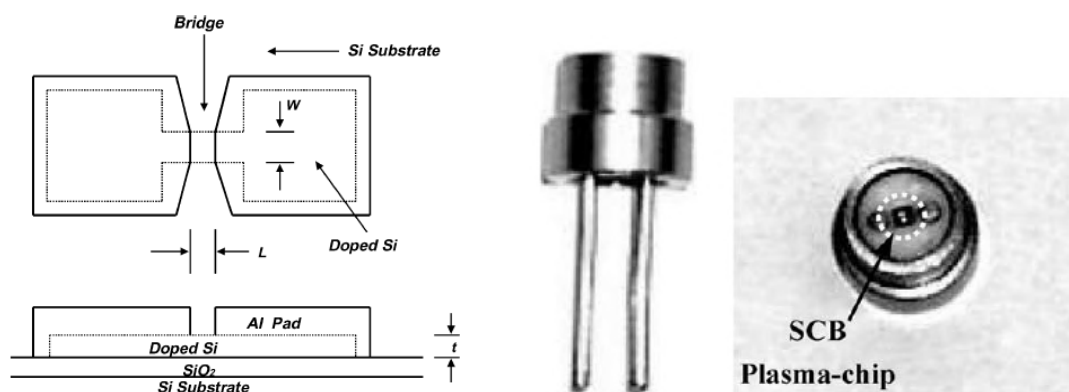


Figure 11: Diagram of Semiconductor Bridge [where $L = 20 \mu\text{m}$, $W = 90 \mu\text{m}$ and $t = 2 \mu\text{m}$] on the left and on the right 2 photographs of the entire header assembly^{27,28}

The SCB is a relatively new form of ignition mechanism that emerged around 30 years ago.²⁹ It uses a minute bridge of semiconducting material (Figure 11), which upon application of the firing current is vaporised into a plasma and induces ignition of the explosive. The temperatures of the plasma have been reported in the excess of 5000°C and can be generated on a μs timescale (Table 3) allowing the fast and reproducible ignition of energetic compositions such as boron/potassium nitrate, titanium subhydride/potassium perchlorate and thermites.^{23,30,31,32,33} Although the SCB

^{xv} Not yet reported in the open literature, however there is some proof of success in unpublished results from T.A Baginski.²⁶

represents a higher energy ignition than hotwire devices, it is fired with relatively modest currents and voltages (Table 3).

	Hotwire	SCB
Threshold		
Current (A)	3.5	14
Pulse Length (μ s)	2000	15
Energy (mJ)	24.5	2.8
Bridge Resistance (Ω)	1	1
No fire		
Current (A)	1	2.2
Power (W)	1	4.8
Function time at threshold (μ s)	>2000	50

Table 3: Differences between a SCB and hotwire when igniting a pyrotechnic in a generic hotwire and SCB device³⁴

The real ingenuity in the SCB is that it is capable of acting as a resistor at low currents and therefore is less susceptible to RFI or ESD and can be tuned to initiate at specific voltages, Figure 12 shows the measurement of a current in an SCB which is designed to be actuated only by voltages greater than or equal to 500 V. This reduces the need for electrical protection of the device from RFI as required in hotwire devices.

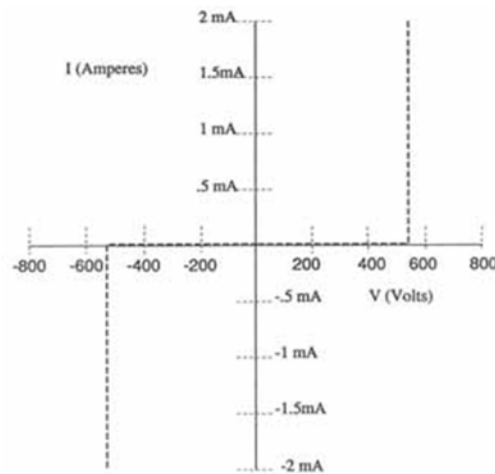


Figure 12: Graph of voltage vs. current over an SCB, which cannot be initiated with a potential less than 500 V³⁰

2.2.5.2 Laser Ignition

Successful ignition of secondary explosives (PETN, HNS, RDX) has been reported using lasers, however these cases have used laser driven flyer plates to shock initiate the explosive charges.³⁵ The laser driven flyer operates by utilising the plasma generated upon the laser ablation of a metal foil to propel a projectile or flyer into an explosive charge. This approach is analogous to the high energy EBW and EFI in bridgewire ignited EEDs and involves a high-energy shock initiation of the explosive charge.

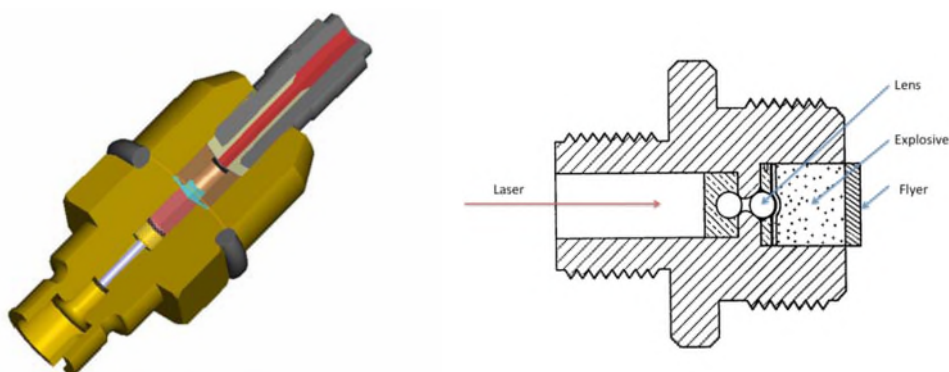


Figure 13: Examples of laser-driven-flyer detonators^{35,36}

The main technological challenge, in terms of laser initiation, has been in the attempts at low energy laser ignition. This involves the direct laser ignition of an energetic material and the efficient absorption and translation of laser light into heat is essential if it is to be achieved. In practice the absorption of laser light has been made possible through the use of additives in explosive samples which absorb the laser energy and translate that to the surrounding composition.^{xvi,37,38} Much of the current work in laser initiation is involved in reducing the power of the laser required and successfully initiating more insensitive secondary explosives (eg. polymer bonded HMX ignition).^{39,40}

^{xvi} This is usually achieved by including either a dye that absorbs efficiently at the laser wavelength or a reflecting material that effectively increases the sample length and therefore opportunity for absorption of the energy (Figure 14). Unfortunately the addition of such dopants can, in some circumstances, have the undesirable effect of compromising the hazard properties of the insensitive explosive material.

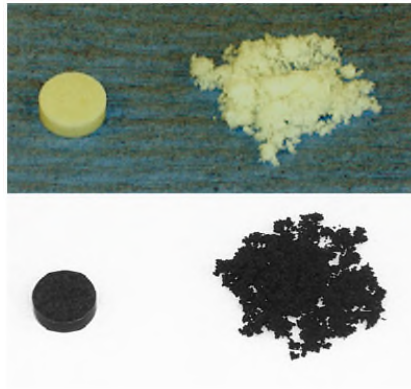


Figure 14: Insensitive explosive formulation of n-guanylurea dinitramide (GuDN) and an energetic binder (top) and the same composition after laser sensitisation with carbon black (bottom)³⁹

2.2.6 Ignition Overview

While it is possible to safely ignite an explosive charge in a fast and reproducible manner, using an EBW or EFI, this method is expensive and may be considered as somewhat excessive. Even as an expensive alternative, EBW and EFI pose a much safer ignition option than the majority of hotwire ignited devices which still seem to rely on sensitive primaries or pyrotechnic compositions.⁴¹ The development of laser and SCB ignition systems offers a more elegant solution, which may lead to the fast and reproducible ignitions of insensitive formulations. However, the current focus in SCB devices remains upon the ignition of pyrotechnics and laser ignition has not yet been fully accepted by the industry due to problems with its efficiency and the perceived complexity of the technology.

While advances in methods by which explosives can be ignited may lead to the development of safer EEDs, the fundamental issue of impact, friction and ESD sensitivity determines the choice of energetic composition used.

2.3 Energetic Materials

For a safe, low sensitivity and fast-acting EED the correct choice of explosive is as important as the ignition stimulus if not more so. While it is possible to mitigate some of the potential hazards associated with a particularly successful but sensitive energetic material it is also possible to greatly reduce the hazard by choosing a less sensitive and therefore safer compound.⁴²

2.3.1 The Explosive

The energy that is released upon actuation of a squib is liberated from the explosive compound stored within the device upon ignition. As the choice of explosive influences the nature of the burning or detonation phenomena it is necessary to choose an energetic material which is capable of delivering the desired output.

2.3.2 Combustion Chemistry

The energy of a conventional explosive is released through an oxidation reaction, which occurs during the thermal decomposition of the material. The result of the oxidation reaction is the exothermic formation of CO₂, H₂O, N₂ and other relevant oxides. It is the formation of these gaseous products (H₂O is a gas at the temperature of the reaction) and the heat released upon their formation that causes their expansion and is used to affect work in squib applications.

The composition of the reaction products depends on the quantity of oxygen present within the explosive composition. Stoichiometric combustion of a CHNO-based explosive results in the formation of CO₂, H₂O and N₂. This can only be achieved experimentally through the ignition of an explosive which has a stoichiometric proportion (or greater) of oxygen in its structure (see Figure 15) or by igniting an oxygen-deficient explosive in an atmosphere of oxygen. Both of these experiments result in the maximum exothermic output possible from the oxidation of the explosive. This value of energy is known as the enthalpy of combustion (ΔH_C).

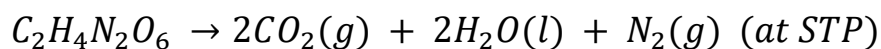


Figure 15: Stoichiometric decomposition reaction of ethylene glycol dinitrate (EGDN), which exhibits a neutral oxygen balance ($\Omega = 0\%$)

The majority of explosives in use contain less oxygen in their structure than is necessary for complete anaerobic combustion. Thus the energy released upon anaerobic combustion is usually less than ΔH_C . This means that upon decomposition the extent of the combustion reaction and therefore the level of energy released depends upon the quantity of oxygen present in the explosive or formulation.

$$\Omega = \frac{[(d - (2a) - (b/2)) \times 1600]}{MW} \%$$

Equation 9: Calculation of oxygen balance (Ω) [where a = the number of carbon atoms in the explosive, b = hydrogen atoms, d = oxygen atoms and MW = molecular weight of the compound]⁴³

This proportion of structural oxygen is represented as the oxygen balance (Ω), which is an expression of the percentage of oxygen present in the material with respect to the quantity required for complete combustion (Equation 9).

It is more efficient to use the maximum quantity of available energy from an explosive and as such it is preferential to use a material with a high oxygen balance. However, it has been observed that, as the oxygen balance of an explosive is increased the hazard characteristics of the material display increasing sensitivity.⁴⁴

Nevertheless, most explosives in existence possess a negative oxygen balance and due to this values for the enthalpy of explosion (ΔH_{Exp}) are generally lower than values for the enthalpy of combustion. This is because the formation of lower oxides such as CO in an incomplete combustion does not release as much energy as is released during a complete combustion due to the formation of highly exothermic products such as CO₂

and H₂O.^{xvii} This affects the quantity of heat released in the reaction, which is significant as heat directly influences the magnitude of the squib output. The greater the heat the higher the gas pressure evolved.

The effect of this increased pressure can be calculated using the ideal gas law (Equation 1) or at high pressures using a more advanced equation of state (EoS) which considers the contribution of intermolecular interactions such as the Virial EoS (Equation 10).

$$PV = RT + \frac{B}{P} + \frac{C}{P^2} \dots$$

Equation 10: The Virial equation of state [where P = pressure (N m⁻²), V = volume (m³), R = ideal gas constant (8.314 J K⁻¹ mol⁻¹), T = temperature (K), B = the first Virial coefficient (describing interactions between two bodies) and C = the second Virial coefficient) describing interactions between three bodies]. The ellipses show that the equation can be considered as an infinite series.]

In addition to affecting the quantity of heat in the reaction the oxygen balance influences the number of moles of decomposition gas formed. As previously mentioned a higher oxygen balance will result in more oxides of carbon (CO and CO₂) and less solid C, importantly this increases the number of moles of gas that are formed. Thus by increasing the oxygen balance in carbon-based (as opposed to nitrogen-based) explosives it is possible to maximise the number of moles of gas and the temperature of the decomposition reaction. Accordingly, to optimise the output energy from an explosive material in a gas-generating squib, oxygen balance is an essential factor which must be considered and maximised where possible.

2.3.3 Explosives in Use

Due to the unfortunate loss of life and damage to infrastructure in some high profile accidents,^{5,45} making explosives safer to handle has become the focus of much of the research in energetic materials science (e.g. investigation of reduced sensitivity RDX

^{xvii} This is a generally accepted simplification of the relationship between Ω , heat released and the expansion of hot gases. To fully understand the relationship between heat and isochoric gas pressure it is necessary to also consult the heat capacities of the product gases as well as the heat losses to the surfaces of the combustion chamber.

and the development of polymer bonded explosives (PBX)).^{46,47} This research may be undermined if the insensitive compositions developed are then placed in applications where the primer charge is a sensitive primary material. In explosive trains an acceptor charge is only as safe and insensitive as the ignition compound employed.^{xviii} Unfortunately many early devices were designed with the ease of ignition and reproducibility as a higher priority than safety. This led to the use of many sensitive compounds and formulations that would now be considered as hazardous primary explosives and avoided if at all possible. These compounds, such as lead azide, zirconium:potassium perchlorate and mercury fulminate represent many of the problems posed by the materials traditionally used in hotwire-ignited devices. Many of the compositions contain heavy metals such as lead and oxidisers such as potassium perchlorate, which are known to pose a toxicological threat. Additionally the impact, friction and ESD sensitivity of the vast majority of these compounds is either empirically proven to be hazardous or is known to be hazardous but has not been quantified by modern characterisation methods.

2.3.4 New Materials and Methods for their use

A squib must successfully translate an input stimulus into a fast and reproducible output. This has, too often, been achieved through the use of sensitive and therefore intrinsically unsafe energetic materials.

The current trend of either low-energy ignition of sensitive materials or high-energy ignition of insensitive compounds may be challenged by an alternative strategy.

For instance, in a gas-generating device it may be possible to start with an insensitive material, which is capable of generating the requisite gas pressure but is not easily ignited by low energy means. This material may be adapted by the addition of components, which alter the composition's response to a hotwire stimulus without

^{xviii} The primary ignition device can be isolated mechanically from the explosive train. Safe and Arm units are effective safety devices but are only an option in applications that are afforded both the budget and volume required for their deployment.

interfering with the insensitive nature of the formulation. This method may show promise in sensitising an otherwise safe and insensitive compound to low-energy thermal ignition. This type of “focussed corruption” has been seen in explosive science previously; Bowden and Yoffe’s classic experiments involving the addition of grit to explosive samples successfully sensitised compounds to impact.⁸ The addition of grit was shown to enable the translation of kinetic energy to thermal energy by increasing the number of localised hotspots generated through friction. This strategy is motivated by the fact that many materials are capable of the performance required in gas-generating squibs but lack the sensitivity to be applied as the primary ignition compound.

In this way it may be possible to design an energetic composition for use in a squib using the method more commonly applied when designing rocket propellants.

2.3.5 Adapting Formulations

When developing a propellant it is traditional to begin with a desired performance target or energetic output. A compound can then be chosen to achieve this target; however this material will generally have to be adapted in some way to satisfy all of the performance criteria.

Normally a fuel, such as a carbon-based polymer with suitable physical properties is chosen and combined with an oxidiser. The addition of an oxidiser will increase the heat of the decomposition reaction by enhancing the oxidation of the carbon-based polymer. This will lead to an increase in the rate of reaction and the number of moles of gas released. The result of this is generally observed as an increase in the specific energy of the composition. In rocket motors this adaptation is applied not only to affect the specific energy and impulse but to also to modify the burn rate and the effect of pressure on the burn (pressure exponent). Enhancement of the burn rate has traditionally been achieved by the addition of various metal salts, which have been referred to as decomposition catalysts or burn rate modifiers.^{48,49,50} This is of interest to squib and EED development, as any explosive formulation employed in a fast-acting device must have a high and reproducible burning rate.

This method of performance enhancement may be applicable to insensitive formulations for application in squibs. By starting with an insensitive explosive material (the main charge) which has the potential to provide the energetic output, it might be possible to increase the material's susceptibility to ignition through the addition of burn rate modifiers or similar.

In propellant science it is common to use metal salts as these burn rate modifiers or "performance enhancers", however given the reported environmental toxicity of the most common metal salts (CuO and $\text{Cu}(\text{NO}_3)_2$ are acutely toxic to the aquatic environment) used in burn rate modification this project will initially look elsewhere for formulation components. Instead organic materials, which pose less of a threat to the environment and are consumed within the decomposition reaction will be preferred.

By choosing low sensitivity energetic additives which possess either a positive or near neutral oxygen balance, a high burning rate or similar performance enhancing characteristics suitable for use in a squib, it might be possible to modify the behaviour of a formulation while preserving its insensitivity to accidental ignition.

In the first case compounds such as N-nitro-2,3-dinitrooxypropan-1-amine (NG-N1), ammonium nitrate and ammonium dinitramide (ADN) display relatively high oxygen balances and therefore high heats of explosion,^{12,51} clean combustion, efficient gas generation and reasonably low sensitivity. In some cases the compounds possess low melting points that serve by absorbing possible ignition energy and utilising it to change the phase from solid to liquid rather than to initiate decomposition.⁵¹ These materials are relatively rare in the literature and some exhibit problematic properties such as hygroscopicity which have hampered their use. However, their addition to an insensitive formulation may serve to increase the heat of the initial decomposition reaction, due to their highly exothermic products, and increase the rate of propagation through the spread of heat by conduction and convection. This may increase the effectiveness of a low-energy thermal ignition stimulus such as a hotwire in successfully igniting a composition of insensitive explosive.

The latter suggestion of adding compounds exhibiting a high burn rate may boost the rate of any initial decomposition reaction achieved by a low-energy stimulus. In other words, the fast burning of one component in a formulation mixture may trigger the decomposition of the surrounding explosive material. This in turn might allow for propagation of the ignition through the sample.

Materials such as bis(triaminoguanidinium)-3,3'-dinitro-5,5'-azo-1,2,4-triazolate (TAGDNAT), triaminoguanidinium azotetrazolate (TAGzT), and 3,6-bis(1H-1,2,3,4-tetrazol-5-amino)-s-tetrazine (BTATz) are all credited with high burn rates.⁵²⁻⁵⁴ These materials represent a new trend in energetic compounds as they rely upon their positive heat of formation and decompose to form primarily N₂^{xix} rather than oxides of carbon. As with substances possessing a high oxygen balance, solid materials which have very high nitrogen contents can display high sensitivity to impact, friction and electrostatic stimuli, the effect is not solely dependent upon nitrogen content and is heavily influenced by the structural characteristics of the compound as seen with the highly sensitive 1,1'-azobis(tetrazole).⁵⁵ It is also true that the decomposition of high nitrogen compounds can have the undesirable formation of cyanide containing products such as HCN.⁵⁶

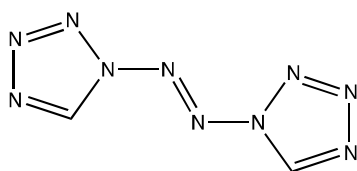


Figure 16: 1,1'-Azobis(tetrazole)⁵⁵

The most pragmatic solution may be found between these two strategies. The extremes of highly positive oxygen balanced carbon-based explosives and fast-burning, high-nitrogen energetic materials are capable of providing efficient gas generation. However these substances often trade safety for performance and are generally

^{xix} The adiabatic explosion temperature is lower than that observed from the decomposition of standard carbon based explosives, however temperatures still regularly exceed 1000 °C upon ignition.

impractical. A material, which consists of a minimum proportion of carbon, may utilise a small quantity of intramolecular oxygen to form CO and CO₂ and so produce heat to expand the decomposition gases while relying on the formation of molecular nitrogen for the majority of the gas generation.

In short a composition of two or more low sensitivity materials combined in order to enhance the hotwire sensitivity and evolution of hot gas may provide the required performance while remaining safe. It should be said however, that when formulating with explosive materials in an attempt to achieve a combination of desirable features, a mixture of the components' undesirable properties is also a possible outcome. This is due to the fact that studies on the properties of these compounds, when pure, reveal results which are a product of a large number of factors including intermolecular interactions. By adding an additional component, and depending on the proportion in which it is added, these intermolecular interactions and the behaviour of the solid may be effected either positively or negatively and can lead to a change in the physical characteristics of the mixture relative to the pure components.

2.3.6 The Obstacles to Novelty

Innovation in the field of energetic materials science is evident from the large number of publications regularly issued in the literature. However there is a disparity between the level of innovation and the application of these novel ideas. These ideas seem to rarely graduate from the laboratory to large-scale production and as such the majority of explosives in use have been for at least 80 years.

Most commonly applied explosives are not the products of multi-step novel syntheses and are usually fairly simple compounds. 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) is one of the most common and widely used explosives in production. RDX is neither the most powerful or safest explosive available and has been in production since WWII. Its attraction is that it is very easy to synthesise and involves only a one-step high-yielding (90%) synthesis from readily available and cheap starting materials (see Figure 17).

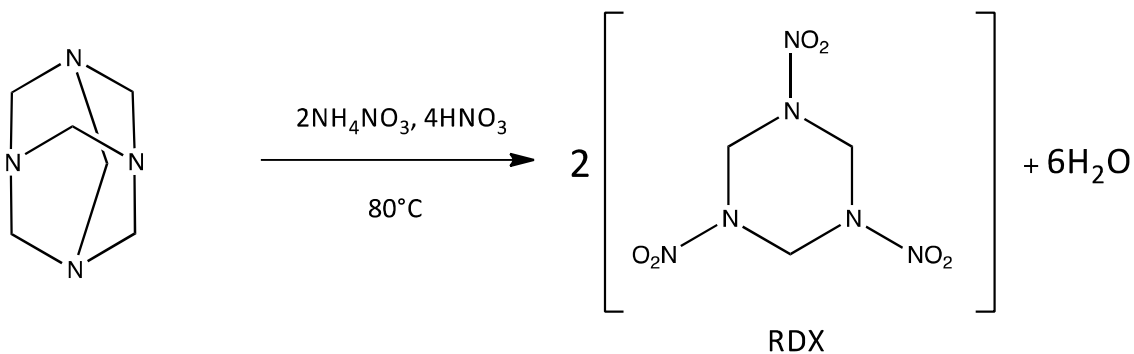


Figure 17: The K process for the synthesis of RDX⁵⁷

This is the main obstacle to any improvement in the field of energetic materials. There is no shortage in the development of new and promising energetic compounds. There is, however, a severe lack in the application of these new and promising developments. This is due to the inherent risk involved when developing a novel material, not only financially but also practically. The scale up of a chemical product is sufficiently challenging without including the unknown quantity of a novel energetic material whose properties and synthesis may behave differently on a larger scale. Explosives syntheses which progress in a safe and reproducible manner in the laboratory may prove potentially lethal on the industrial scale.

3 The Project

3.1 The Current Device

This project focuses upon a generic squib, which is currently in use, and aims to improve the safety of this device without any deleterious effect on its required performance, as shown below (Table 4).

Output	Pressure Rise	10 MPa – 120 MPa within 0.5ms
	Peak Pressure	120 MPa – 165 MPa
Reliability and Maintainability	Reliability	0.998 with a 70 % confidence level (equivalent to 600 firings without failure)
	Maintainability	The squib shall require no maintenance
Environment	Normal Operating Temperature	-40 °C to 70 °C
	Maximum Rates of Temperature Change	+16 °C to -10 °C per hour
	Maximum Temperature Cycles per Lifetime	80
Lifetime	Duration	32 years
Input	All-Fire Current	>6 A
	No-Fire Current	1 A/1 W
	Maximum Firing Current Duration	50 ms
Safety	Input	1 A/1 W safe over 20 minutes at 70 °C
	Self-Ignition Temperature	>250 °C
	ESD	25 kV from a 500pF capacitor through a 500 Ω resistor

Table 4: Explosive specific performance criteria outlined in the legacy squib technical requirement report⁵⁸

The project squib is an EED that is expected to produce a high-pressure gas over a short period of time, approximately 150 MPa in 500 μ s (when tested in a 0.25 cm³ bomb). This device utilises a hotwire-type ignition stimulus, which is comprised of a

thin-film of a nickel-chromium alloy.^{xx} The squib itself consists of a metal body, which contains an aluminium bursting disc and plastic propellant cup (see Figure 18). The chosen energetic material is pressed into the propellant cup and the header assembly (which contains the thin-film) is pressed onto it. The header is located by a compression and load ring and held in place by a locking ring. Upon ignition and propagation of the decomposition reaction, pressure builds within the squib and bursts the aluminium septum; this allows the release of a stream of high-pressure gas.

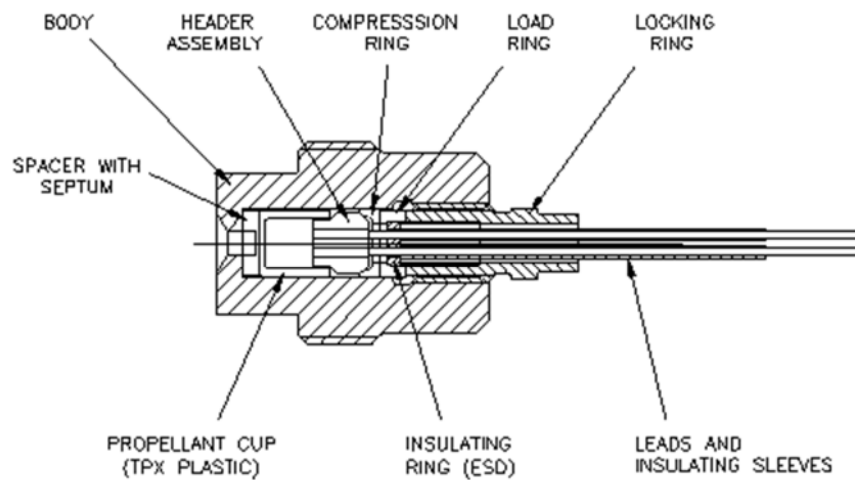


Figure 18: The project squib^{xxi}

The squib is ignited by means of a 6 A all-fire current and is a 1 A/1 W safe device. Therefore it can be defined as a low-energy EED. Due to the low energy ignition stimulus it is unsurprising that the material currently in use is a primary explosive, potassium picrate, and that yet more sensitive primers such as lead styphnate have been coated directly onto the bridgewire. It is the use of this primary explosive and primer, which this project will endeavour to replace.

^{xx} The thin-film is a slight adaptation of the original hotwire ignition stimulus that uses a film of nickel-chromium alloy (nichrome) rather than a wire to quickly and efficiently generate high temperatures.

^{xxi} This diagram is available as a pull-out diagram for reference throughout the thesis, see Pg 141.

3.2 Project strategy

The project was planned as a chemical study and as such the primary focus of the thesis was the replacement of the sensitive energetic material, potassium picrate, with an insensitive formulation while attempting to maintain the squib performance.⁵⁹

The device was previously researched in combination with alternative explosive materials by Leaffield Engineering Ltd. Leaffield produced trial reports on the testing of the squib with a variety of energetic fills. They produced these results by firing the squib into a closed vessel adapted to fit a pressure transducer. This setup allowed for the measurement of both the pressure output and rise time. Due to the success of this apparatus it was decided that the Leaffield experimental setup would be replicated for this project (see Figure 19).

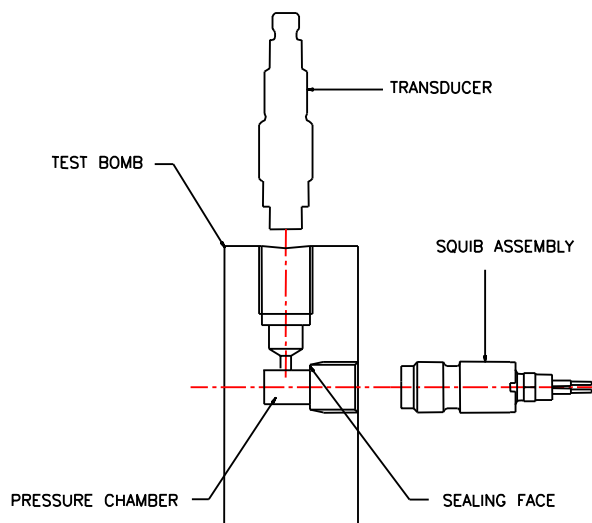


Figure 19: Leaffield experimental setup

The initial task in improving the generic device was to choose promising insensitive compounds that may be formulated and tested within the squib. By starting with one insensitive but poorly ignited material, which would form the majority of the compositions (and would be referred to as the main charge explosive (MCE)), it was possible to enhance the ignitability and overall output by combination with small proportions of more ignitable or high performance materials (these will be referred to as performance modifiers (PM)). By using small proportions of these PMs it was

possible to formulate an effective squib composition, which remained insensitive to impact, friction and ESD.

Insensitive energetic materials are relatively common in the literature and so it was necessary to scrutinise the published compounds. Energetic materials that displayed promising performance and were either readily synthesised or available for purchase were considered for use as PMs in combination with the MCE.

The suggested PMs were tested for chemical compatibility in a 50:50 wt % composition with the MCE and the same formulation was then tested for its sensitivity to impact, friction and ESD. Providing no signs of decomposition were observed in either test, compositions of each PM were prepared with the MCE in ratios of 9 to 1, 8 to 2 and 7 to 3 by weight (where the largest proportion of each formulation was always the MCE). These rather crude formulation ratios were chosen to maximise any observable impact the PM may have on the MCE ignition and decomposition. If chemical incompatibility or excessive sensitivity to impact, friction or ESD was detected an alternative PM would be chosen from the literature and the process of evaluation in composition with the MCE would be repeated.

The chemically compatible and low sensitivity compositions were then physically tested for their efficacy as alternative squib fills. The physical testing involved measuring the pressure generated by the ignition and propagation of each prepared composition within a closed vessel. This test enabled comparison of the composition's gas generating ability, ease of ignition and to a lesser extent burn rate. A flow diagram summarising this process is presented on the next page (Figure 20).

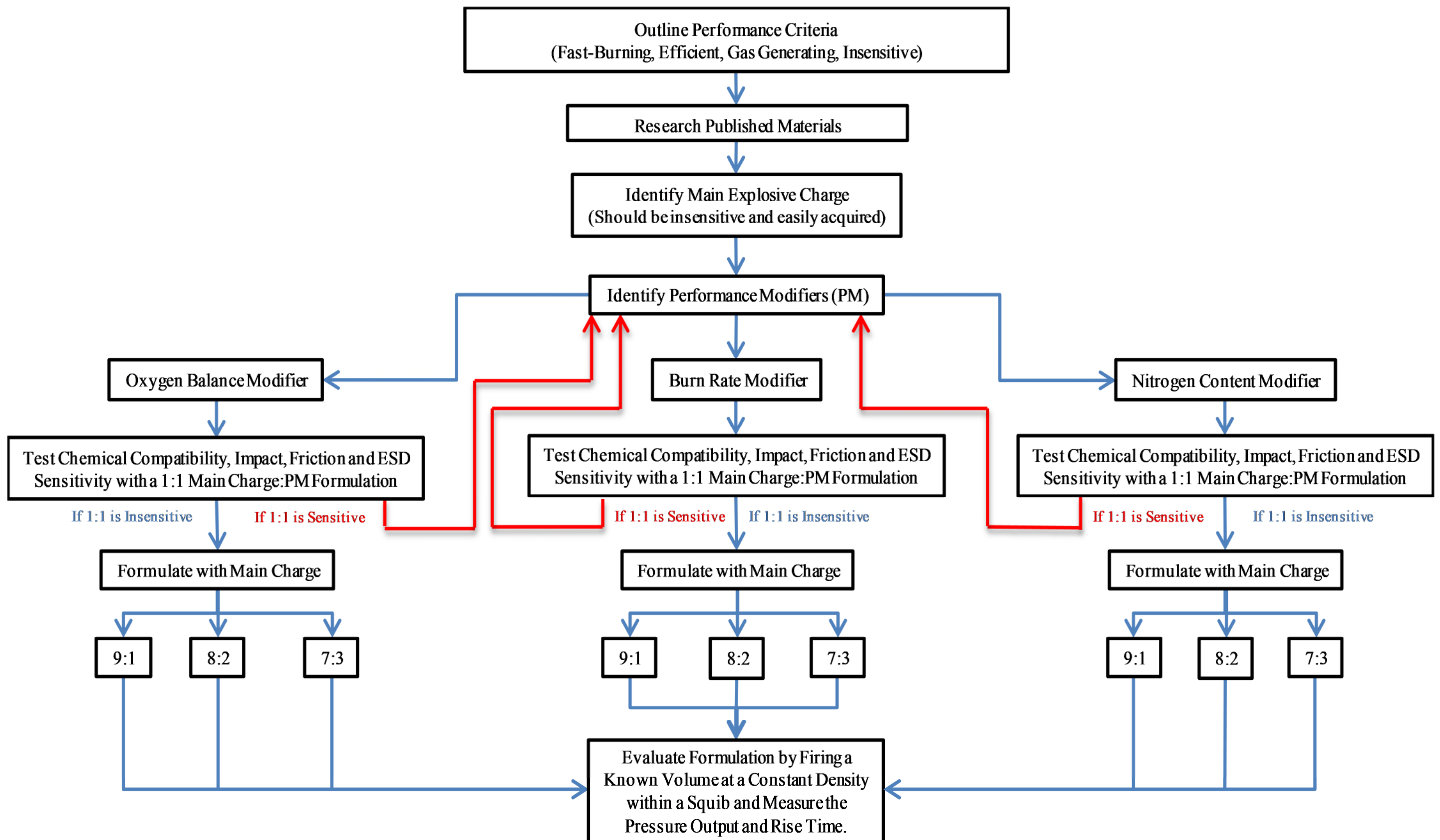


Figure 20: Project outline

4 The Down Selection of Energetic Materials

The project squib uses an energetic material that is ignited rapidly from thin-film hotwire stimulus, generating a large volume of gas in a short period of time while remaining stable for approximately 30 years. It is unfortunate that the explosive material is synthesised from a hazardous and toxic precursor (picric acid), displays impact sensitivity and has the potential to detonate.⁵⁹

4.1 Formulating the Ideal Explosive

The ideal explosive for the squib application is a material that is rapidly ignited from a hotwire stimulus whilst resisting decomposition by any other means. This ideal compound would be insensitive to all undesirable stimuli, chemically stable and capable of remaining unchanged within the squib body over the course of an approximate 32 year operational lifetime. It would also be preferable if the compound were the product of a cheap and simple chemical synthesis.

Unfortunately, no such material has yet been published. Instead an amalgam of low sensitivity explosives may provide a formulation that displays the majority of the “ideal explosive’s” performance characteristics.

The combination of compounds to provide an “ideal explosive” is not a recent idea and in fact most well-known explosive materials are formulations. Substances such as, gunpowder, dynamite and the famous RDX based formulation, composition C-4 (C4) are all formulated from a combination of components. For example, dynamite and C4 employ the same basic concept in their development. The explosive deployed in each is hazardous and relatively easily ignited. In the case of dynamite, Nobel soaked hazardous nitroglycerine onto an inorganic substrate known as kieselguhr, a type of clay. C4 is a more modern development and utilises polyisobutylene as the desensitising substrate to improve the hazard properties and to enhance the physical characteristics of RDX (C4 is similar in texture to a clay and can be safely moulded by hand). In both formulations the non-explosive or inert material (binder) reduces the potential for hazardous ignition by mitigating any internal heating caused by friction

between explosive particles. In layman's terms the polymer or clay acts as a protective barrier around the explosive crystals. Thus an ideal material is produced with much of the explosive performance of the neat energetic compound and greatly improved hazard properties.

This modern class of explosive formulation, which includes composition C-4 (C4) and its British analogue plastic explosive number 4 (also known as PE4), are known as plastic explosives. Plastic explosives and their more modern equivalent, polymer bonded explosives (PBX), are widely used in larger charges where the effect of adding a small proportion of inert polymer is insignificant. However, on the small and exacting scale of a squib device, the dilution of the explosive content of the formulation does not seem an efficient method of approach. Any reduction in the proportion of the explosive present will lead to a subsequent reduction in the energetic output of the device. Furthermore, the act of desensitising an effective but sensitive explosive by combining it with a polymeric binder, as seen in PBXs and dextrinated lead azide, does not remove the potential risk.⁴² Desensitising a sensitive compound merely shifts the hazard from the EED to the formulation laboratory where the neat sensitive explosive is combined with the binder. It is the opinion of the author that, to enhance the low sensitivity and safety of a squib device, the manufacture and preparation of the device, including the handling of explosive materials, should be without any of the hazards that are mitigated in the finished article.

The converse approach to desensitising an effective but sensitive explosive compound is to sensitise an insensitive compound. This approach avoids the hazards associated with sensitive primary explosives (impact, friction and electrostatic sensitivity) and focuses upon tailoring a safe and insensitive explosive to suit a low energy thermal ignition, as seen in the project squib.

This approach involves the selection of a low sensitivity explosive compound that, while relatively safe, is not readily ignited by a heated bridgewire. The compound is then adapted to respond to a thermal stimulus through the addition of suitable insensitive energetic materials. The combination of new materials should be

implemented in a manner in which the impact, friction and ESD hazard properties of the explosive are uncompromised.

The method of adapting the formulations should focus on altering measurable properties of the composition with respect to the pure explosive, which may then be tested for their effect on low-energy ignition.

For example

The addition of a small proportion of a low-melting point wax (A) to an explosive (B) which produces a formulation (C) may reduce the overall melting point of C with respect to the melting point of B. Thus upon testing C for its ease of ignition, any improvement or deterioration, with respect to the ignition of B, may be attributed in some small part to the change in net melting point.

The properties that are the focus of the formulations should be features commonly detailed by energetic materials scientists. An effective squib formulation should efficiently release energy from a small mass and be easily ignited, burn quickly and completely over a short time period. This would suggest that properties such as the burn rate, heat of formation, thermal conductivity, temperature of decomposition, oxygen balance and nitrogen content might be of interest in the development of a successful squib formulation (section 2.3).

Unfortunately, properties such as burn rate, thermal conductivity and heat of formation are not regularly featured in the publication of novel energetic compounds.

In general this is due to the relatively large mass of synthesised material that is required for their experimental measurement.^{xxii}

This introduces a limitation in the study as, for any effect to be truly meaningful, there should be a wide range of formulations tested and compared. The process of synthesising multiple novel compounds to facilitate the production of a variety of formulations is ambitious in the duration of a PhD project. Rather, materials that have been developed and published may be considered and applied. This may reduce the period of the required synthesis and allow for more time to be focussed on developing and testing the formulations. Hence by relying on published materials the project is ultimately biased by the characterisation data that is, or is not, featured in the literature.

It should also be noted that the methods used for determining the impact, friction and ESD sensitivity of explosive materials have developed considerably since the first synthesis of potassium picrate. Therefore it is only possible to compare the hazard properties of materials, which have been characterised using the same methods.^{xxiii} Unfortunately potassium picrate has not been hazard characterized by modern methods and so cannot be directly compared to newly developed compounds. Instead, to give a sense of perspective to the hazard properties of the researched materials the widely used explosives RDX and HMX will be used as references. The materials will be

^{xxii} Strand burning requires a substantial mass of energetic material for each experiment and is usually repeated several times to increase the accuracy of the result.¹² This is also the case for the determination of a material's heat of formation, which, uses less material but requires multiple experiments to increase the accuracy of results (it is usually given as a calculated value instead). The reporting of thermal conductivity is slightly different, as there seems to be very little tradition of recording what would seem an important factor in ignition. A Scopus[®] search using the keywords "thermal conductivity explosive" yields 215 results with only a handful referring to explosives, most of which are either the commonly used RDX or HMX.

^{xxiii} Historically the measurement of impact and friction data has been carried out in a variety of different methods which has inhibited comparison. The majority of results presented here have been measured using the American type 12 or German BAM apparatus; more information on these techniques is included in Appendix 8.11.2.

ranked by their sensitivity being greater than, less than or equal to the reference explosives.

There is a fundamental issue when comparing the sensitivities of compounds, which have been synthesised and characterised in a variety of laboratories using a variety of experimental techniques. As Zukas notes, “The apparatus and procedure vary from laboratory to laboratory. No two machines are precisely the same. Even those nominally the same can be different in subtle ways.”⁶⁰ Thus the results from different laboratories have the potential to vary. This is emphasised by the variation in results given by a selection of impact tests shown in Table 5. Here each laboratory was asked to rank the materials tested in order of increasing impact sensitivity utilising the methods and apparatus employed in their institution.

Order of Insensitiveness	US Navy NOL*	Picatinny Arsenal	US Bureau of Mines	NY Bureau of Explosives	BAM	Rotter (Fol#)
1	TNT	TNT	TNT	TNT	TNT	TNT
2	Tetryl	HMX	HMX/RDX	Tetryl	RDX	RDX
3	RDX	RDX/Tetryl	Tetryl	RDX	Lead Azide	HMX
4	HMX	PETN	PETN/Lead Azide	PETN	PETN/Tetryl	PETN
5	PETN	Lead Azide	-	Lead Azide	-	Lead Azide
6	Lead Azide	-	-	-	-	-

Table 5: TNT, Tetryl, RDX, HMX, PETN and Lead Azide listed in order of insensitiveness at different locations (*Naval Ordnance Laboratory, #Figure of Insensitiveness)⁶⁰

The variation in Table 5 is striking, especially when PETN and lead azide, a secondary and primary material respectively, are considered. Consequently, the hazard data taken from the literature must be treated as a guide to the nature of the characterised compounds rather than a strict definition. Regardless, a material that is to be combined in an explosive formulation will require retesting to ascertain the hazard properties of the composition as a whole.

With these caveats aside it is possible, by reviewing published insensitive energetic compounds, to populate a list of materials which may enhance or modify a formulation’s oxygen balance, nitrogen content, melting point, temperature of

decomposition etc. without compromising the formulation's insensitivity to impact, friction and ESD. In order for a material to qualify for testing it must also be readily synthesised or purchased.

4.2 The Process of Elimination

In the course of the down selection several hundred publications, reporting the development and characterisation of novel low sensitivity explosives, were reviewed and entered into a Microsoft Excel[®] spread sheet. The spread sheet was used to visually rank the properties of compounds against each other and the selected baselines of RDX and HMX. A simple "traffic light" system was used to clearly define each property of the researched materials. Thus if a material displayed a reduced sensitivity to impact with reference to the baseline it would be coloured green, if the material was equally sensitive to the baseline it would be coloured amber and if the material was even more sensitive to impact than the baseline (and therefore highly undesirable) it was coloured red. This allowed for a simple and highly valuable and visual assessment of all of the properties of the researched materials with respect to the RDX and HMX baselines although significantly the population of the spread sheet was a substantial and labour intensive task (Figure 21 on next page and the full table is included in the supporting information disk included).

Evaluation of the recently published novel and low sensitivity energetic materials highlighted three main categories of compound which had the potential to enhance the formulations and provide the project with PMs. These were low sensitivity compounds which exhibited a high burn rate, high oxygen balance or high nitrogen content.

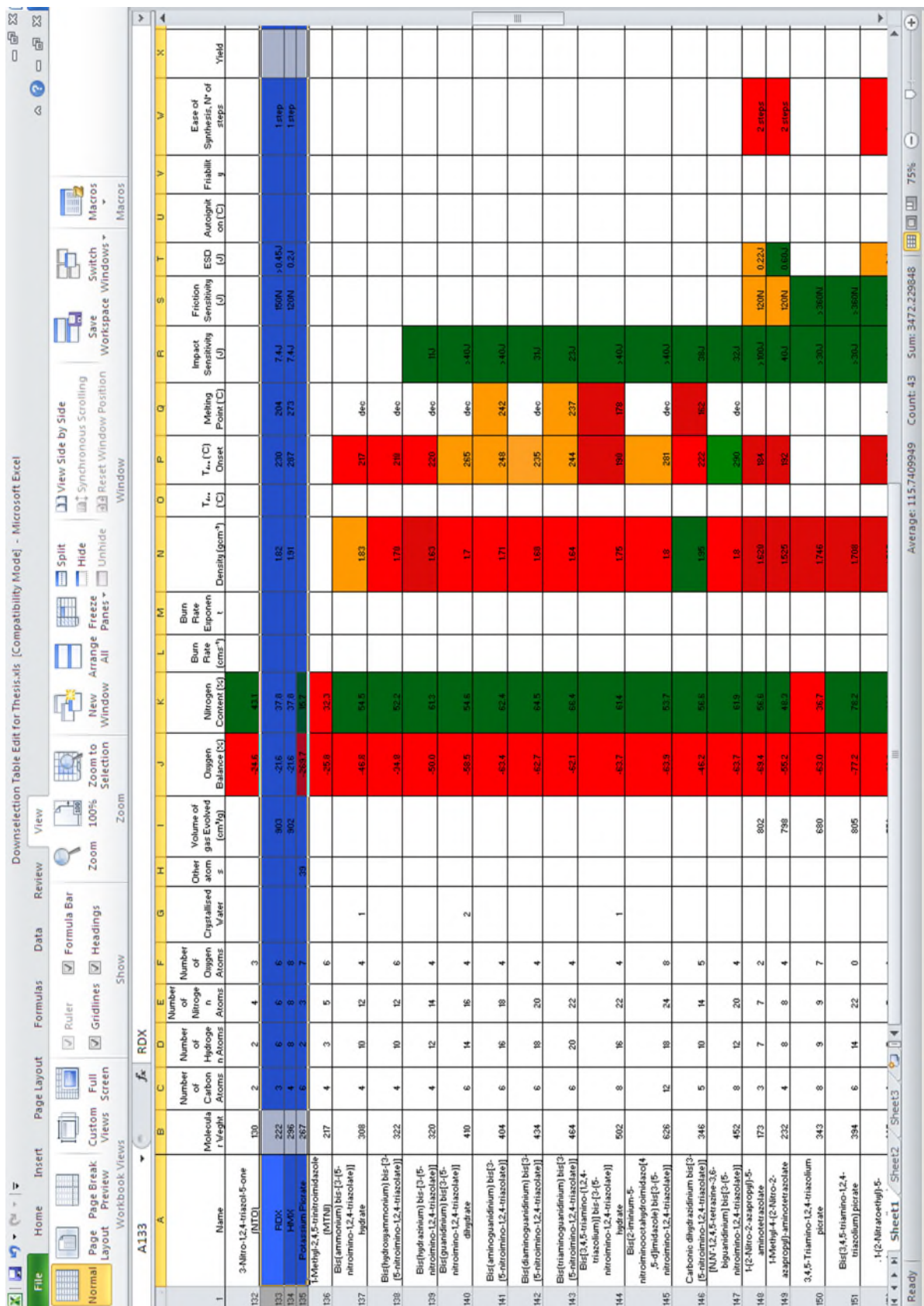


Figure 21: Screenshot of the down selection process

4.3 Burn Rate Enhancement

A high burn rate is a priority for any fast-acting squib composition. However as burn rate can be related to pressure (as described by Vieille's Law Pg 15) it is important that any fast burning material researched burns quickly within the desired pressure regime. Initially the squib is a small confined volume and upon ignition internal pressure rises dramatically. At approximately 100 MPa^{xxiv,61} the squib septum bursts, increasing the volume and reducing the reaction pressure (see pull-out diagram Pg 127). Thus, due to the variable internal conditions, a compound whose burn rate is highly dependent upon pressure may not be suitable. Instead a successful squib formulation may profit from a low value pressure exponent (n) and high value pressure coefficient (a) (Figure 22). This would result in a high burn rate that was minimally dependent on internal pressure.

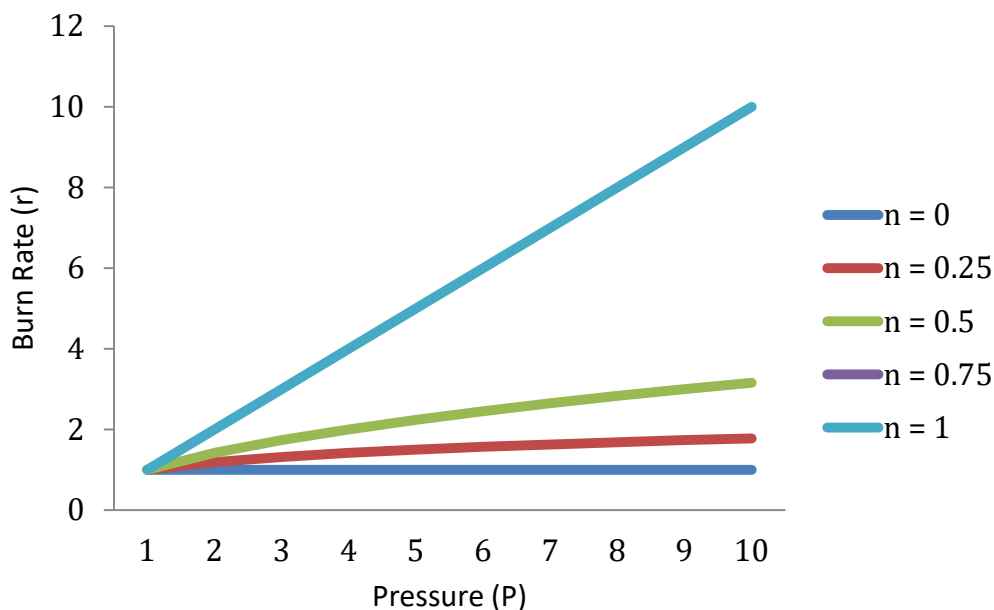


Figure 22: The pressure exponent in Vieille's law (using arbitrary units and where a is constant throughout)

Unfortunately, there are few insensitive materials published with fully characterised burn rates (r), pressure exponents (n) and coefficients (a) and consequently the

^{xxiv} 100 MPa is approximately 1000 times atmospheric pressure (0.1 MPa = 10^5 Pa = 1 bar).

number of materials reported in this review of the recent literature is limited. The shortage of data is understandable due to the multiple variables that can influence burn rate such as particle size, pellet density, vessel pressure, sample purity etc. However, it was still possible to identify materials that were highlighted in the literature for their prominently high burn rates (Table 6).

Compound	Tdec ¹ (°C)	IS ²	FS ³	ESDS ⁴ (J)	Burn Rate (r)	a ⁵	n ⁶
Bis(triaminoguanidinium)-3,3'-dinitro-5,5'-triazolate (TAGDNAT)	202	9.3 J [§]	157 N [§]	0.125	6.79 (@6.9 MPa)	-	-
Bis(triaminoguanidinium)-5,5'-azotetrazolate (TAGzT)	181	6.1 J [§]	98 N [§]	0.0625	4.89 (@6.9 MPa)	-	0.67
3,6-Bis(1H-1,2,3,4-tetrazol-5-ylamino)-1,2,4,5-tetrazine (BTATz)	264	32 cm*	36 kg*	0.36	4.59 (@6.9 MPa)	0.58	0.49
3,3'-Azobis(6-amino-1,2,4,5-tetrazine) (DAAT)	252	70 cm*	>36 kg*	>0.36	-	-	-
3,3'-Diamino-4,4'-azofurazan (DAAzF)	315	320c m*	>36 kg*	>0.36	-	-	-
3,3'-Diamino-4,4'-azoxy furazan (DAAF)	220	>320 cm*	>36 kg*	>0.36	-	0.03 1	0.71
3,6-Dihydrazino-1,2,4,5-tetrazine (DHT)	160	65 cm*	>36 kg*	>0.36	-	0.14	0.75
RDX	230	7.4 J (28-30 cm)	150 N (32 kg)	>0.45	-	-	-
HMX	287	7.4 J (23 cm)	120 N (12 kg)	0.2	2.11 (@6.9 MPa)	-	0.84

Table 6: Comparison of selected fast-burning materials and the reference materials, RDX and HMX (1temperature of decomposition, 2impact sensitivity, 3friction sensitivity, 4ESD sensitivity, 5burn rate coefficient, 6burn rate exponent, *comparable values measured using a drop height or weighted friction technique, § comparable values measured using BAM apparatus)^{12,53,61-72}

4.3.1 Bis(triaminoguanidinum)-5,5'-azotetrazolate (TAGzT)

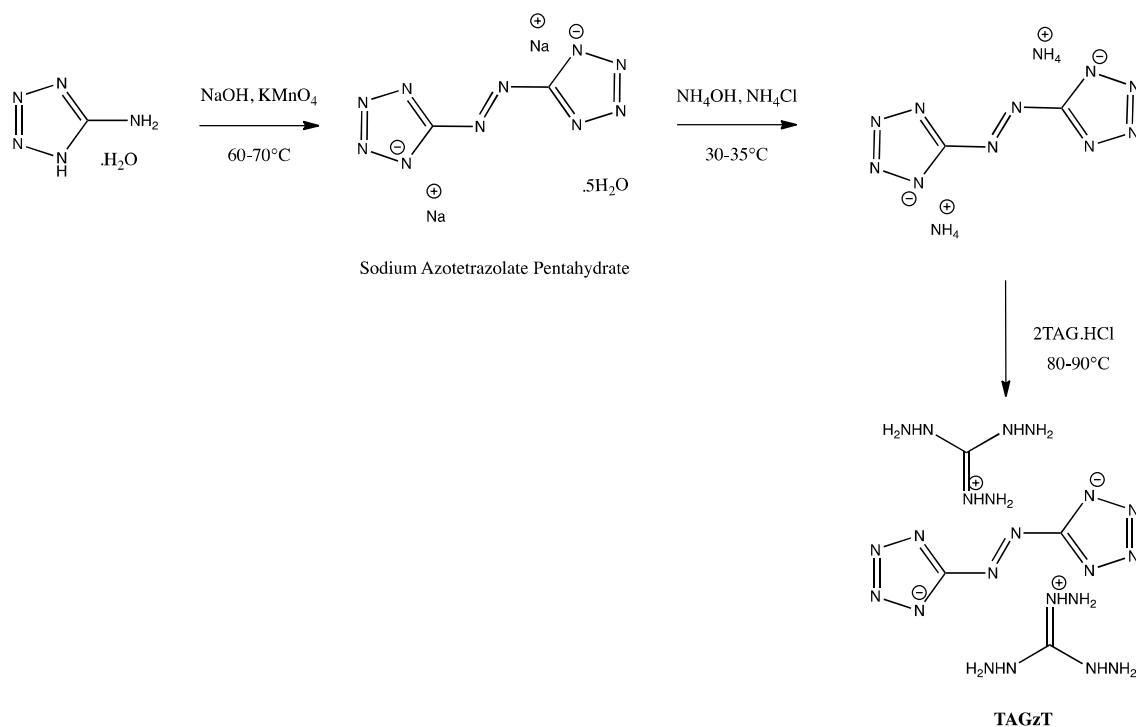


Figure 23: Synthesis of TAGzT from 5-aminotetrazole monohydrate via sodium azotetrazolate pentahydrate^{57,73}

TAGzT is a fast-burning compound synthesised from the oxidative coupling of 5-aminotetrazole (Figure 23). It has been shown to improve the burning rate of compositions of RDX while reducing the temperature of the combustion and barrel erosion.⁷⁴ Unfortunately the impact, friction and ESD sensitivity of the material is quite substantial and would therefore pose a threat in handling.⁶²

4.3.2 3,6-Bis(1H-1,2,3,4-tetrazol-5-ylamino)-1,2,4,5-tetrazine (BTATz)

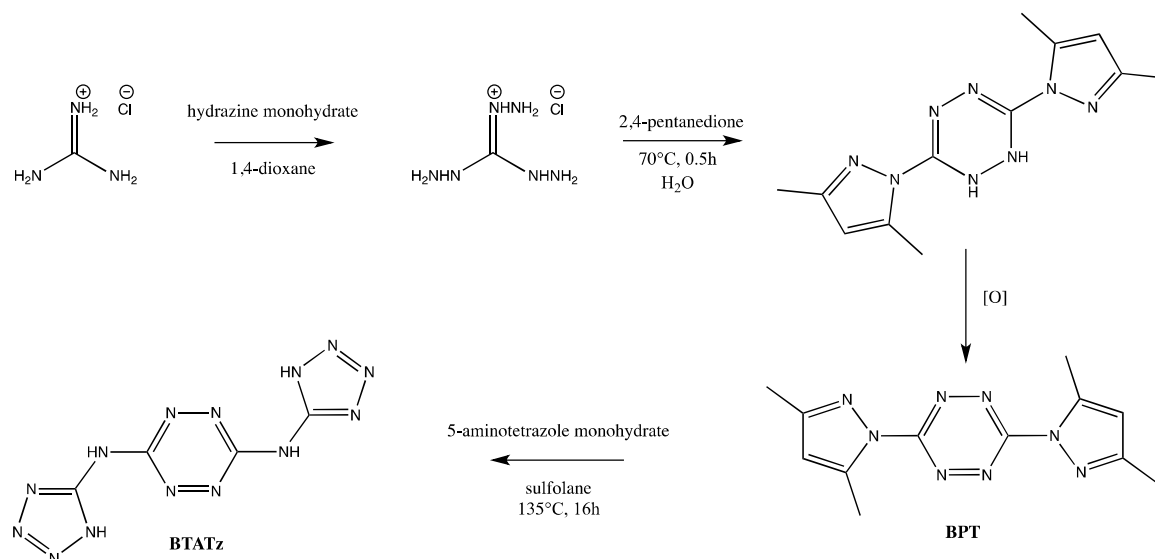


Figure 24: Synthesis of BTATz and BPT^{64,65}

BTATz is a heavily referenced fast burning explosive which was first synthesised by Chavez, Hiskey and Naud at Los Alamos.⁷⁵ It shows some sensitivity to impact but low sensitivity to friction and ESD and is readily synthesised in a 4-step synthesis (Table 6).^{64,65} This synthesis involves the production of 3,6-bis(3,5-dimethyl-1H-pyrazol-1-yl)-1,2,4,5-tetrazine (BPT) which is a common intermediate in the syntheses of both DAAT and DHT (Figure 24).

4.3.3 3,3'-Azobis(6-amino-1,2,4,5-tetrazine) (DAAT)

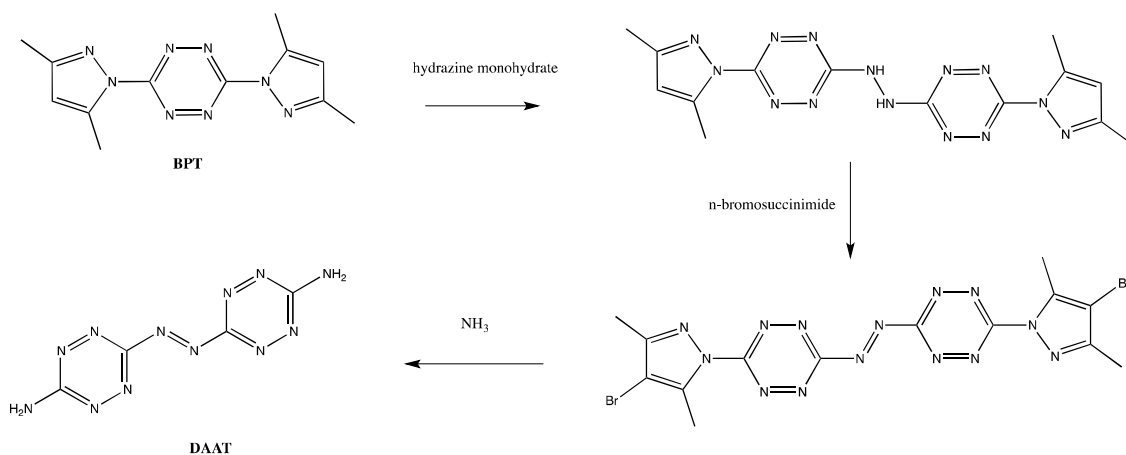


Figure 25: Synthesis of DAAT from BPT^{65,76}

DAAT comprises two tetrazine rings connected by an azo linkage and consists of more than 70% nitrogen. DAAT's slight sensitivity to impact (Table 6), although an improvement on HMX and BTATz, does not represent a sound investment when it is considered that it is the product of a 6-step synthesis.

4.3.4 3,6-Dihydrazino-1,2,4,5-tetrazine (DHT)

DHT was first synthesised in 1963 and is the product of a 5-step synthesis involving the toxic reagent hydrazine (Figure 26).^{65,66} Therefore it is surprising that it continues to be published in the recent literature as a viable fast-burning material.^{54,77} The compound displays low sensitivity to impact, friction and ESD and decomposes at 160 °C (Table 6).

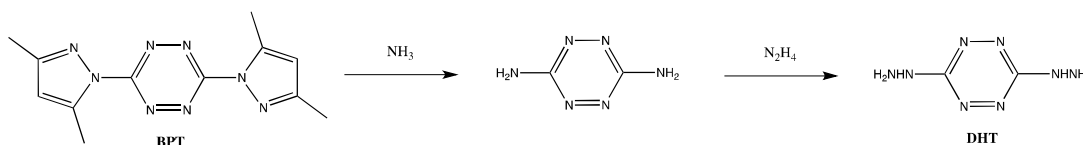


Figure 26: Synthesis of DHT from BPT^{65,66}

4.3.5 3,3'-Diamino-4,4'-azoxyfurazan (DAAF)

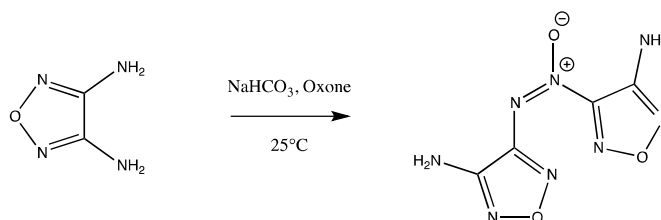


Figure 27: Synthesis of DAAF^{70,78}

DAAF is a compound that is receiving substantial interest due to its 1-step synthesis from 3,4-diamino-1,2,5-oxadiazole. This updated synthesis improves on the Solodyuk process which used H₂SO₄ and 30 % H₂O₂ to oxidise the starting material and produced a mixture of products.^{xxv} The new route uses Oxone, a much safer oxidising medium, which is a combination of potassium sulfate, bisulfate and peroxymonosulfate. This

^{xxv} This oxidizing mixture whose active species is peroxymonosulfuric acid is very similar to "Piranha solution" or "Caro's Acid" and is known to be potentially explosive.⁷⁹

results in the precipitation of 84 % of the pure product.⁷⁰ The only drawback is that the starting material 3,4-diamino-1,2,5-oxadiazole is very expensive (approx. £30/g).⁸⁰

4.3.6 3,3'-Diamino-4,4'-azofurazan (DAAzF)

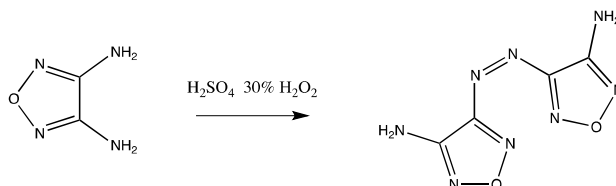


Figure 28: Solodyuk synthesis of DAAzF⁷²

DAAzF is the azo-bonded analogue of the azoxy compound DAAF. As such it can be synthesised by the 2-step reduction of DAAF or in 1-step from the Solodyuk process involving H_2SO_4 and H_2O_2 . The Solodyuk process involves an extraction step as DAAF and DAAzF are both formed.⁷² Although DAAzF is more thermally stable (see Table 6), DAAF is likely to be more favourable due to the ease of its synthesis.

4.3.7 Bis(triaminoguanidinium)-3,3'-dinitro-5,5'-triazolate (TAGDNAT)

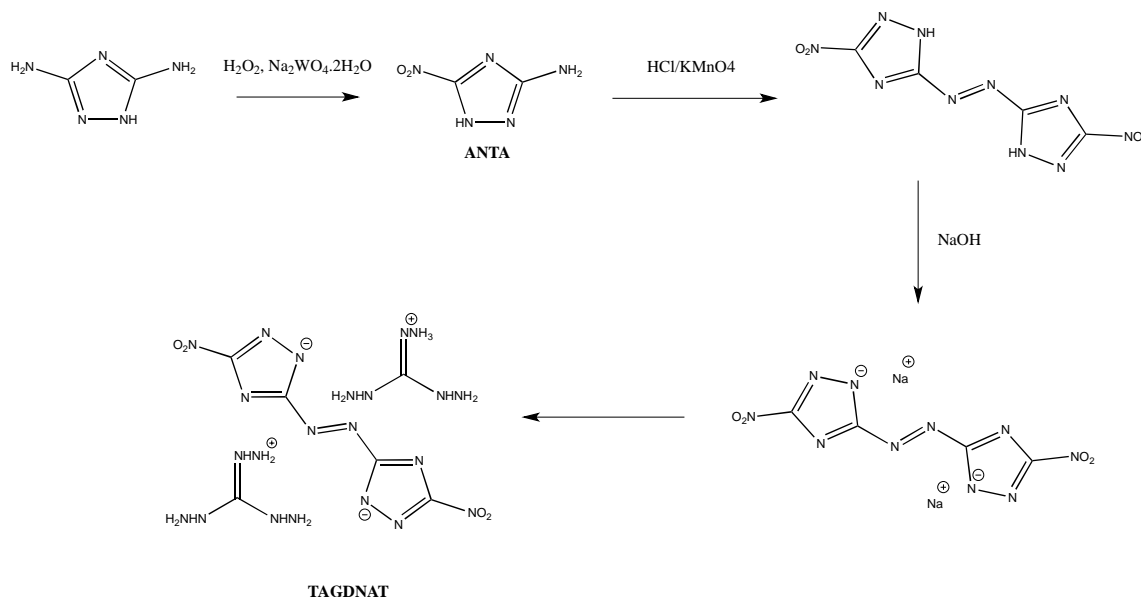


Figure 29: Synthesis of TAGDNAT via ANTA^{53,63}

TAGDNAT has been reported to possess “one of the fastest low-pressure burning rates (at 6.9 MPa) measured”⁵³ and displays low sensitivity to impact and friction though sensitivity to ESD (see Table 6). The synthesis is achieved in 4 steps from 3,5-diamino-

1,2,4-triazole and proceeds via the explosive intermediate 3-amino-5-nitro-1,2,4-triazole (ANTA). The synthesis of TAGDNAT has the potential to provide the project with an additional insensitive explosive (ANTA) and the greatest potential for enhancement of the squib formulation due to the prominence of the neat compound's burn rate. Therefore it was selected for synthesis as a possible formulation ingredient.

4.4 Oxygen Balance Enhancement

Low sensitivity oxygen-rich energetic materials are rare in the literature. In some cases it has been observed that as the oxygen balance of a compound is increased the hazard properties are negatively influenced. Although this has been shown to be true with some compounds it can be a misleading generalisation. Explosives with high oxygen balances tend to contain a large number of nitro (NO_2) or nitrate ester (ONO_2) groups. These are usually products of substitution reactions that replace either protons or hydroxyl groups, which are involved in hydrogen bonding. Thus increasing the number of $-\text{NO}_2$ and $-\text{ONO}_2$ groups may eventually lead to a reduction in hydrogen bonding. It is this reduction in hydrogen bonding which has the potential to reduce the thermal stability of the compound and perhaps increase sensitivity.

Name	O ₂ Balance (%)	N ₂ Content (%)	T _{dec} (°C) (Onset) ¹	IS ²	FS ³	ESDS ⁴ (J)
2,4-Dihydro-2,4,5-trinitro-1,2,4-triazol-3-one (DTNTO)	21.8	38.2	264	80 cm [*]	25 kg [*]	-
Ammonium nitrate (AN)	20.0	35.0	210 (169.6)	-	-	-
3,6-(Bistrinitroethylamino)-1,2,4,5-tetrazine (BTAT)	-3.7	38.7	184	6 J [§]	160 N [§]	0.2
1-Nitramino-2,3-dinitroxypropane (NG-N1)	-7.1	24.8	173	14 J [§]	96 N [§]	1.1
Ammonium dinitroguanidine (ADNQ)	-9.6	50.6	197	10 J [§]	252 N [§]	0.4
Ammonium 5-nitrotetrazolate-2N-oxide (ANTX)	-10.8	56.8	173	7 J [§]	120 N [§]	0.25
RDX	-21.6	37.8	230 (204)	7.4 J [§] (28-30 cm [*])	150 N [§] (32 kg [*])	>0.45
HMX	-21.6	37.8	287 (273)	7.4 J [§] (23 cm [*])	120 N [§] (12 kg [*])	0.2

Table 7: Comparison of low sensitivity oxygen-rich compounds and the reference materials, RDX and HMX (¹temperature of decomposition, ²impact sensitivity, ³friction sensitivity, ⁴ESD sensitivity, ^{*}comparable values measured using a drop height or weighted friction technique, [§]comparable values measured using BAM apparatus,^{12,43,51,68,81–83})

By reviewing the literature it was possible to identify 6 compounds (5 synthetic targets and 1 commercially available), as shown in Table 7, with somewhat reduced sensitivity to impact, friction and ESD, which possess uncommonly high oxygen balances.

4.4.1 2,4-Dihydro-2,4,5-trinitro-1,2,4-triazol-3-one (DTNTO)

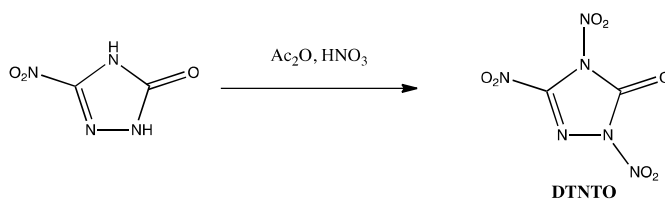


Figure 30: Synthesis of DTNTO from NTO⁶⁸

DTNTO represents the highest oxygen-rich ($\Omega = 21.8$) and low sensitivity compound in the literature (Table 7). The reported synthesis is a 1-step procedure from 3-nitro-1,2,4-triazol-5-one (NTO), an existing low sensitivity explosive (Figure 30). Attempts to replicate this synthesis were recently carried out at Cranfield University and were

entirely unsuccessful when following the published procedure. For this reason DTNT will not be considered.

4.4.2 Ammonium nitrate (AN)

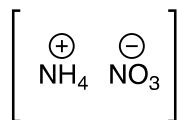


Figure 31: Ammonium nitrate (AN)

AN has been used in explosive formulations since its discovery in 1654 by Glauber.⁴³ The compound has been referred to as a “tertiary explosive” due to the requirement for considerable impetus to induce detonation.¹² As a material which decomposes by deflagration rather than detonation and can be commercially purchased, ammonium nitrate is a particularly apt choice for a fast-burning gas-generating composition. Unfortunately AN is notoriously hygroscopic and is known to “cake” when exposed to air. While this may not be an issue once confined within the sealed squib, formulation of a highly hygroscopic compound introduces an undesirable level of complexity.

4.4.3 3,6-(Bistrinitroethylamino)-1,2,4,5-tetrazine (BTAT)

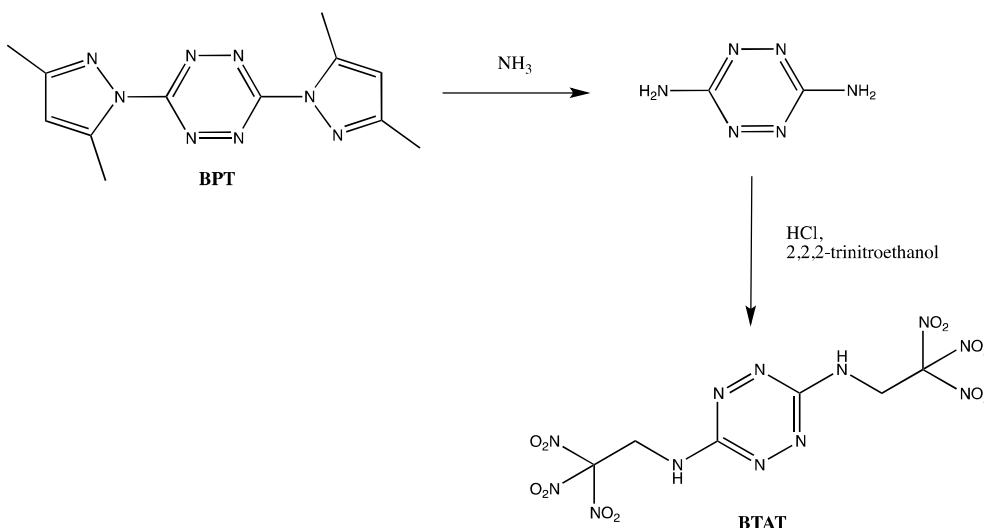


Figure 32: Synthesis of BTAT⁸¹

BTAT is the combination of the oxygen rich, 2,2,2-trinitroethanol and the nitrogen rich, 3,6-diamino-1,2,4,5-tetrazine.⁸¹ This means that the 12 atoms of oxygen present can

be utilised to oxidise the 6 atoms of carbon and hydrogen per mole. As such the compound is only slightly oxygen deficient and displays roughly the same level of sensitivity to impact, friction and ESD as HMX while not as thermally stable. This does not represent a substantial improvement in sensitivity when considering that it is the product of a 5-step synthesis (not including the 2-step production of 2,2,2-trinitroethanol).⁸⁴ In addition the final step, published by Göbel et al, does not have a reported yield.⁸¹

4.4.4 N-Nitro-2,3-dinitrooxypropan-1-amine (NG-N1)

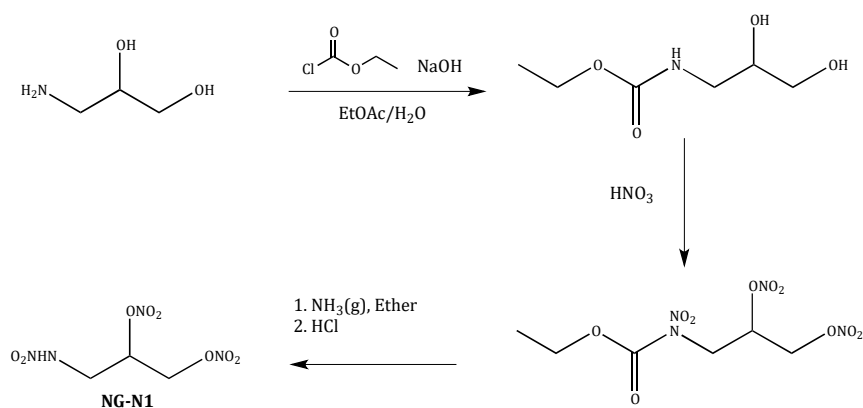


Figure 33: Synthesis of NG-N1⁵¹

NG-N1 is a nitramine derivative of the famous explosive nitroglycerine (NG). Whereas NG suffers from high sensitivity and a low boiling point (65 °C) NG-N1 is a low sensitivity explosive which possesses a high oxygen balance (-7.1). This is achieved by the replacement of just one of the nitrate ester groups in the NG structure with a primary nitramine. It is suggested that the acidic proton which resides on the nitramine group is responsible for increasing NG-N1's stability through hydrogen bonding.⁵¹ The combination of a relatively high oxygen balance with low sensitivity has led to NG-N1 gaining some interest as a possible plasticiser for insensitive munitions.⁸⁵

4.4.5 Ammonium dinitroguanidine (ADNQ)

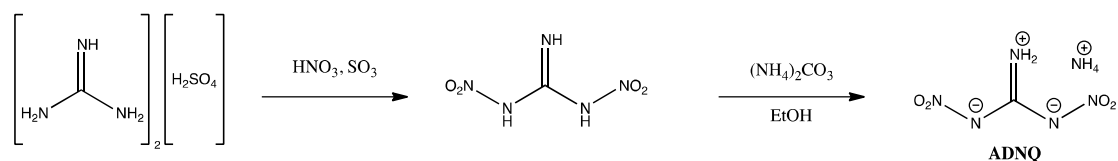


Figure 34: Synthesis of ADNQ⁸²

ADNQ is synthesised in 2 steps from the readily available starting material guanidinium sulfate.^{82,86} The compound displays a reasonable level of thermal stability (197 °C), low impact, friction and ESD sensitivity and is synthesised in 2 steps with a yield of 86 %.

4.4.6 Ammonium 5-nitrotetrazolate-2N-oxide (ANTX)

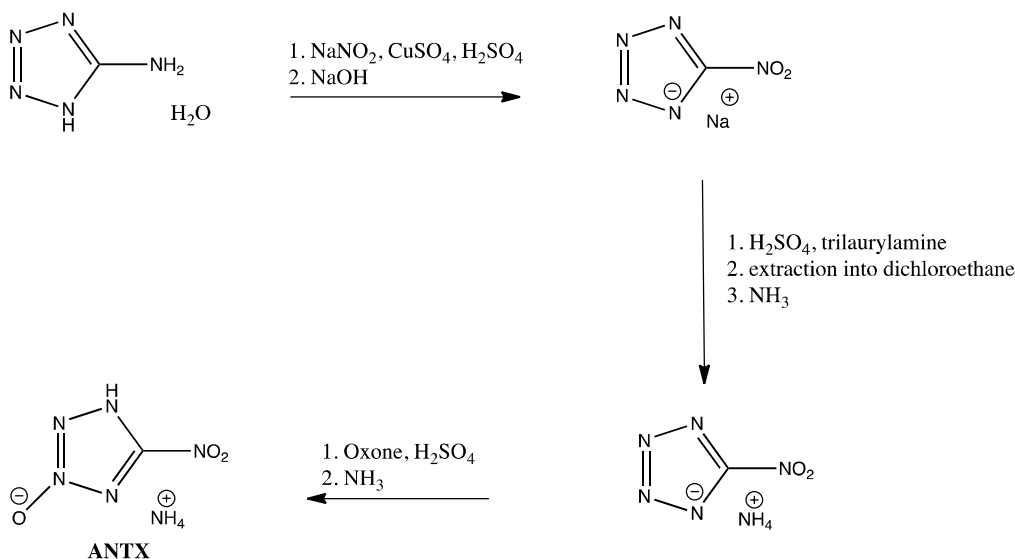


Figure 35: Synthesis of ANTX^{83,87}

ANTX displays moderate sensitivity to impact, friction and ESD and as such does not represent an advance in terms of safety when compared to RDX and HMX. The synthesis does not seem directly compatible with an industrial scale up. The process involves a diazotisation reaction whose intermediates can be sensitive explosives if inadvertently isolated and the preparation of a tertiary alkylamine salt, which is commonly a solution to poor organic solubility (this is observed in similar compounds in the literature, e.g. 3,5-dinitro-1,2,4-triazole).⁸⁸

4.5 Nitrogen Content Enhancement

The recent trend in low sensitivity energetic materials has been focused mainly around the output from a small number of researchers focused upon high-nitrogen compounds. Promising compounds in this field display low sensitivity and high-energy output which is delivered from their highly positive heats of formation.

By reviewing the literature it was possible to identify 6 (5 synthetic targets and 1 commercial product) of the most nitrogen-rich compounds in the literature (Table 8). The success of high-nitrogen content compounds is highlighted by the presence of TAGzT in both Table 8 and Table 6 which emphasises the potential energetic output that these materials may be capable of.

Name	O ₂ Balance (%)	N ₂ Content (%)	ΔH_f (kJmol ⁻¹)	T _{dec} (°C) ¹ (Onset)	IS ²	FS ³	ESDS ⁴ (J)	Yield
5-Aminotetrazole (5AT)	-85.4	82.4	324*(g)	207	-	-	-	-
Hydrazinium 5-aminotetrazolate (Hy5AT)	-75.2	83.8	373.2*	186	100 J [§]	>360 N [§]	3	-
5-Aminotetrazolium 5,5'-azotetrazolate (5ATzT)	-57.1	83.3	-	170 (134)	178 cm*	180 psig*	0.326	72 %
5,5'-Hydrazine bistetrazole (HBT)	-57.1	83.3	414*	208	>30 J [§]	~108 N [§]	-	71 %
Bis(triaminoguanidinium)-5,5'-azotetrazolate (TAGzT)	-72.7	82.4	257.0	195 (181)	25c m*	98 N [§]	0.0625	63 %
Bis(tetrazolyl)amine (H ₂ BTA)	-57.5	82.4	648.0	250	10 J [§]	>360 N [§]	2	89 %
RDX	-21.6	37.8	67	230 (204)	7.4 J [§] (28-30 cm*)	150 N [§] 135 psig* (32 kg*)	>0.45	-
HMX	21.6	37.8	75	287 (273)	7.4 J [§] (23 cm*)	120 N [§] (12 kg*)	0.2	-

Table 8: Comparison of nitrogen-rich compounds and the reference materials, RDX and HMX
 (*calculated value, (g) calculated heat of gas-phase formation, ¹temperature of decomposition,
²impact sensitivity, ³friction sensitivity, ⁴ESD sensitivity, *comparable values measured using a drop
 height or weighted friction technique, [§]comparable values measured using BAM apparatus,
[†]comparable values measured in psig = pound-force per square inch gauge)^{12,62,67,89-94}

4.5.1 Hydrazinium 5-aminotetrazolate (Hy5AT)

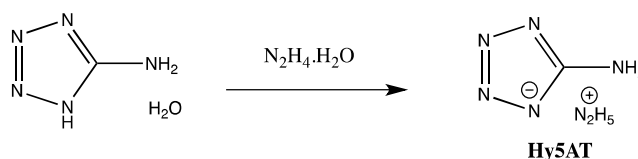


Figure 36: Synthesis of Hy5AT⁹²

Hydrazinium 5-aminotetrazolate (Hy5AT) is synthesised in 1 step from the commercially available compounds 5-aminotetrazole monohydrate (5AT.H₂O) and hydrazine hydrate. While hydrazine hydrate is a toxic reagent the ease of the synthesis and the high levels of insensitivity in the product (the compound has been reported to resist detonation even when initiated via detonator and booster assembly) make Hy5AT an intriguing prospect, which has been suggested for use in rocket propellants.⁹² It may be suggested that Hy5AT does not represent a suitable improvement on the inert but nitrogen-rich starting material 5AT (Table 8). However as 5AT is only commercially available as a monohydrate and as such must be dried before use, direct synthesis of Hy5AT from 5AT.H₂O avoids the drying stage, increases the product's enthalpy of formation and the nitrogen content.

4.5.2 5-Aminotetrazolium 5,5'-azotetrazolate (5ATzT)

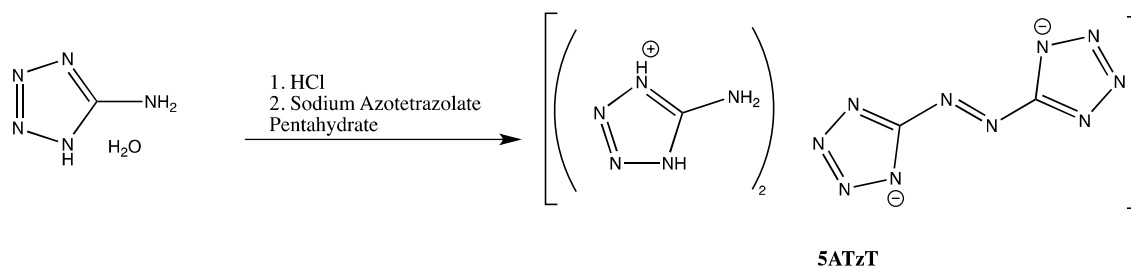


Figure 37: Synthesis of 5ATzT^{73,93}

5ATzT is an elegant combination of 3 moles of 5-aminotetrazole which displays reduced sensitivity to impact, friction and ESD when compared to RDX. The compound utilises the amphoteric nature of the 5AT moiety and employs the heterocycle as both cation and anion in a highly energetic salt which also comprises the prominent azotetrazole unit.^{73,93}

4.5.3 5,5'-Hydrazinebistetrazole (HBT)

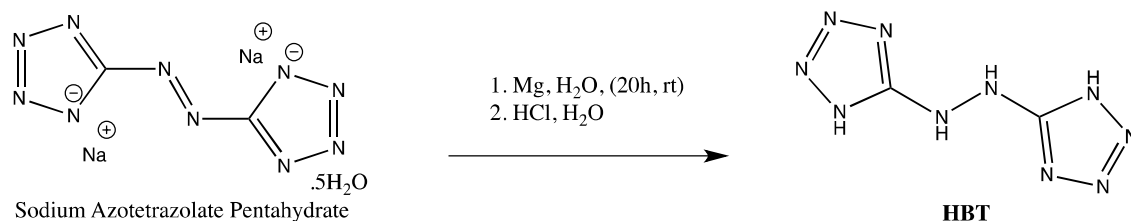


Figure 38: Synthesis of HBT^{94,95}

The reduction of 5,5'-azobistetrazole results in the protonation of the azo bond and the formation of 5,5'-hydrazinebistetrazole. While HBT is a promising compound with a well-defined critical diameter (>8 mm⁹⁵), its synthesis from sodium azotetrazolate pentahydrate seems wasteful as it should, in theory, result in the reduction of the product's molar enthalpy of formation. Although this cannot be confirmed due to a lack of experimental data, the situation is analogous to the relationship between 4,4',6,6'-tetraazido-2,2'-hydrazo-1,3,5-triazine and 4,4',6,6'-tetraazido-2,2'-azo-1,3,5-triazine which vary in ΔH_f by 418 kJ mol⁻¹ in favour of the azo compound.⁹⁶

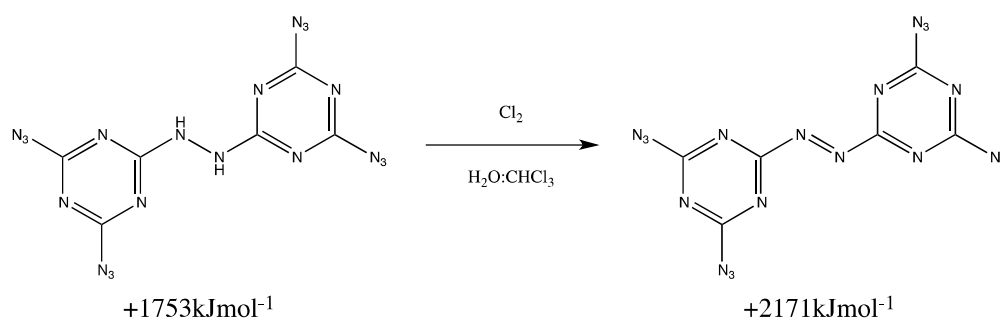


Figure 39: Synthesis of 4,4',6,6'-tetraazido-2,2'-azo-1,3,5-triazine (right) from 4,4',6,6'-tetraazido-2,2'-hydrazo-1,3,5-triazine (left) showing the respective molar enthalpies of formation⁹⁶

4.5.4 Bis(tetrazolyl)amine (H₂BTA)

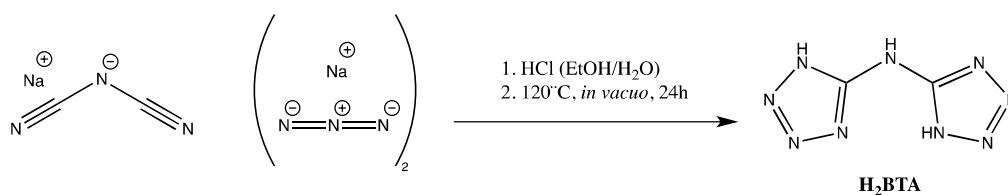


Figure 40: Synthesis of H₂BTA^{97,98}

H₂BTA.H₂O is synthesised in 1 step by the condensation of 2 moles of sodium azide with 1 mole of sodium dicyanamide in the presence of acid and dried in an evacuated oven to achieve anhydrous H₂BTA. The involvement of sodium azide in the synthesis, although a common component in airbag gas generators, introduces an obstacle to large-scale synthesis due to the compound's acute toxicity. However H₂BTA displays a low level of insensitivity to impact, friction and ESD and a high thermal stability making it a highly desirable nitrogen-rich compound (Table 8).

As with many of the novel energetic materials reported here H₂BTA is a member of a larger family of salts that make use of the acidic nature of the tetrazole ring and combine nitrogen-rich cations. Consequently two members of the H₂BTA family possess higher nitrogen content but unfortunately have not yet been subject to hazard characterisation.

4.6 Main Charge Selection

The choice of the MCE, the compound that will form the basis of all the proposed squib formulations, is profoundly different from that of the performance enhancing compounds. To implement the previously outlined strategy of sensitising an insensitive material the project requires an insensitive explosive which may be sourced in sufficient quantity, consistent purity and reproducible particle size. Thus any promising MCE should ideally be commercially available. A table of possible MCEs is shown below.

Name	Oxygen Balance	Nitrogen Content (wt %)	Tdec ¹ (°C)	IS ²	FS ³	ESD ⁴ (J)
N-Guanylurea dinitramide (GuDN)	-19.13	47	215	159 cm [§]	>350 N	>3.125
1,1-Diamino-2,2-dinitroethylene (FOX-7)	-21.61	38	215	20-40 Nm ^a	>550 N	4.5
3-Nitro-1,2,4-triazol-5-one (NTO)	-24.6	43	270	>120 Nm ^a	no reaction at 353 N	
3-Amino-5-nitro-1,2,4-triazole (ANTA)	-43	54	227	>177 cm [#]	16.8 kg [#]	no reaction
Triaminotrinitrobenzene (TATB)	-55.8	33	384	50 Nm ^a	no reaction at 353 N	
2-Nitrimino-5-nitrohexahydro-1,3,5-triazine (NNHT)	-42	44	230	95 cm [*]		
RDX	-21.6	38	230	7.4Nm ^a 33 cm [*] 38 cm [§]	150 N	>0.45
HMX	-21.6	38	287	7.5 Nm ^a 32 cm [#]	120 N 11.6 kg [#]	0.2

Table 9: Comparison of main charge explosives and reference materials, HMX and RDX (*impact sensitivity testing at the US Bureau of Mines for NNHT and RDX carried out with a 2kg dropweight⁹⁹, ^acomparable impact values quoted by Meyer¹², [#]dropweight and friction sensitivity data published by Simpson et al ¹⁰⁰, ¹temperature of decomposition, ²impact sensitivity, ³friction sensitivity, ⁴ESD sensitivity, [§] impact sensitivity published by Östmark et al^{101,102}

Compounds such as 2-nitrimino-5-nitrohexahydro-1,3,5-triazine (NNHT) and 3-amino-5-nitro-1,2,4-triazole (ANTA) are noteworthy materials, which display the required

level of insensitivity for the squib project, however these compounds are not commercially available. This situation may change in the future as NNHT has been recently considered for scale-up by QinetiQ but at present these materials will not be considered for the project.¹⁰³

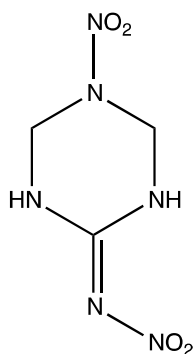


Figure 41: 2-Nitrimino-5-nitrohexahydro-1,3,5-triazine (NNHT)

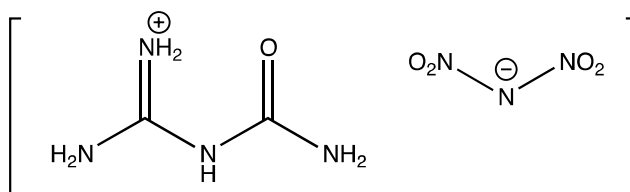


Figure 42: N-Guanylurea dinitramide (GuDN)

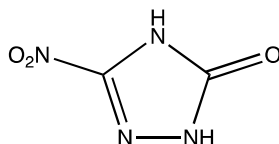


Figure 43: 3-Nitro-1,2,4-triazol-5-one (NTO)

Conversely, materials such as 1,1-diamino-2,2-dinitroethene (FOX-7, Figure 44), n-guanylurea dinitramide (GuDN) and 3-nitro-1,2,4-triazol-5-one (NTO) are commercially available (see Figure 42 and Figure 43). GuDN, an insensitive propellant, and NTO, an insensitive high explosive, are both currently employed in a number of applications including gas-generators in commercial airbags as a replacement for NaN_3 .^{104,105} While FOX-7 seems to be gaining more interest from military based research as a safe replacement for RDX due to its high stability and performance.¹⁰⁶

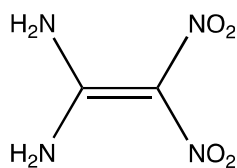


Figure 44: 1,1-Diamino-2,2-dinitroethene (FOX-7)

FOX-7 and TATB are chemically similar in that they feature both primary amines and nitro groups. These functional groups are known to conjugate to allow delocalisation of electrons across the molecule and yield several resonance structures thus leading to a greater level of stability.¹⁰⁷ Unfortunately both these compounds also display poor solubility in most organic solvents and require highly polar, and therefore difficult to remove, solvents to dissolve them.

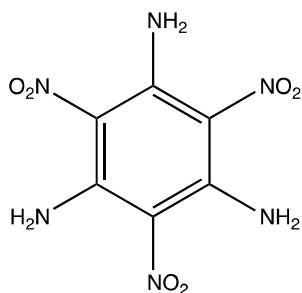


Figure 45: 1,3,5-Triamino-2,4,6-trinitrobenzene (TATB)

The thermal stability of NTO and 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) (thermal decompositions at 270 °C and 384 °C respectively, Table 9), while desirable from a hazard perspective, may lead to a reduction in the ignitability of a squib formulation when compared to a composition based on the slightly less thermally stable compound such as GuDN (215 °C). While this may lead to the preparation of a formulation with an auto ignition temperature below the desired 250 °C (Table 4), the main charge may then be substituted for a more thermally stable compound. It is the aim of this project to prove the ignitability of a low sensitivity formulation in the generic squib and, if achieved, this result may then be optimised to realise all of the outlined performance criteria.

4.7 Conclusions of the Down Selection Process

The down selection process has provided the project with an insensitive MCE in GuDN, a low sensitivity and fast-burning performance enhancer in TAGDNAT, a low sensitivity and oxygen rich additive in NG-N1 and a highly insensitive and nitrogen rich compound in Hy5AT.

The selection of GuDN was influenced not only by its insensitive nature but also by its moderate thermal stability and commercial availability in a number of well-defined particle size ranges.

TAGDNAT compares favourably to other fast burning materials in the literature. A combination of its low sensitivity, synthesis and the characterisation of its high burn rate made it the clear choice over alternatives such as TAGzT and DAAF.

NG-N1 has been selected to increase the oxygen balance of a range of squib formulations. Although DTNTO, BTAT and ammonium nitrate possess more positive oxygen balances each material has disadvantages associated with their synthesis or physical properties that reduce their appeal. NG-N1 represents the most oxygen rich compound in the literature with a short synthesis and which is not reported to display hygroscopicity.

Hy5AT is the most insensitive high nitrogen compound highlighted in the down selection literature review. Due to its simple 1-step synthesis it represents an obvious choice as a nitrogen content modifier for the squib formulations.

This concludes the review of published energetic materials. The following chapters will focus upon the synthesis of the three performance enhancers, TAGDNAT, Hy5AT and NG-N1 and their combination with GuDN in novel squib formulations to be tested.

4.7.1 Polyphosphazenes

In addition to using reported materials as PM compounds there was also the opportunity to employ chemical substances previously researched at Cranfield

University which could be made available to the project and might enhance the ignitability of the MCE.

Poly[P-5,6-dinitratohexan-1-oxy/P-2,2,2-trifluoroethoxyphosphazene] (PPZ) has been previously published in combination with the chosen MCE, GuDN.³⁹ Polyphosphazenes are a part of a family of energetic binders which can be combined with an explosive to both improve the physical characteristics such as impact and friction sensitivity while also contributing to the decomposition reaction.¹⁰⁸ These binders differ from the majority of compounds in use as they incorporate a phosphorus nitrogen backbone (Figure 46) which leads to the formation of the highly exothermic decomposition products, phosphoric acid (H_3PO_4 $\Delta H_f = -1299 \text{ kJ mol}^{-1}$) and hydrofluoric acid (HF $\Delta H_f = -335 \text{ kJ mol}^{-1}$). Thus upon the decomposition of the PPZ its enthalpy is far greater than the enthalpy of other carbon-based energetic binders previously reported.^{109,108} It is for this reason that PPZ was included as the third PM compound as upon successful ignition it has the potential to release sufficient energy to bring the MCE to its temperature of decomposition.

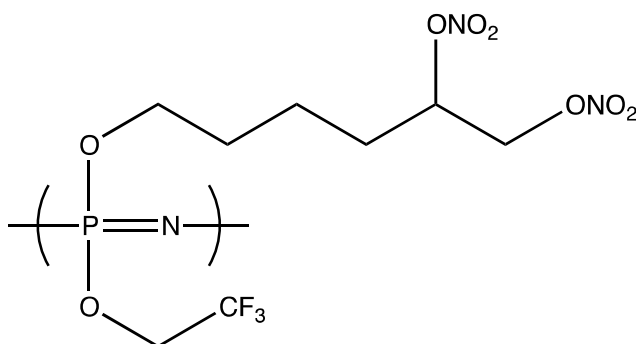


Figure 46: Poly[P-5,6-dinitratohexan-1-oxy/P-2,2,2-trifluoroethoxyphosphazene]

5 Results and Discussion

The investigation into novel squib formulations was conducted by first identifying possible performance modifying compounds (PM) in the literature. These were then synthesised or purchased and combined with GuDN (MCE), an insensitive propellant, which was chosen to form the basis of the formulations. Providing that the compositions remained insensitive to friction, impact and ESD they were pressed into a squib and ignited by bridgewire. The pressure generated from each squib was measured using a closed bomb fitted with a piezoelectric electric gauge and plotted against time from the firing pulse. The following chapter is divided into 4 parts, which present the work involved in each section of the project:

- | | | |
|-----|---|-------------------|
| 5.1 | - | Synthesis |
| 5.2 | - | Formulation |
| 5.3 | - | Squib Preparation |
| 5.4 | - | Squib Firing |

5.1 Synthesis

5.1.1 Synthesis of Bis(triaminoguanidinium)-3,3'-dinitro-5,5'-azo-1,2,4-triazolate (TAGDNAT)

Fast-burning compounds were reviewed in the previous chapter as a means of improving the performance of the MCE. Bis(triaminoguanidinium)-3,3'-dinitro-5,5'-azo-1,2,4-triazolate (TAGDNAT) (**8**, Figure 47) was chosen due to its high performance and reported use in fast-burning formulations.¹¹⁰

The use of heterocyclic compounds as burn rate modifiers stems from their inherent positive heats of formation. In some cases these positive heats of formation are present in the heterocyclic starting materials such as 3,5-diamino-1,2,4-triazole (**1**) (heat of formation = +81.1 kJ mol⁻¹)¹¹¹. The explosive performance can be increased by introducing oxygen with the addition of a nitro group to form 3-amino-5-nitro-1,2,4-triazole (**5** - ANTA).¹¹² The synthesis of 5,5'-dinitro-3,3'-azo-1,2,4-triazole (**6** -DNAT) takes this a step further by coupling two equivalents of **5** through an azo-linkage to form a highly endothermic compound (>+400 kJ mol⁻¹). In the case of **6** and other similar heterocyclic compounds it is possible to deprotonate the rings and form stable salts with nitrogen rich cations e.g. triaminoguanidinium. These cations unlike their metal analogues are capable of improving the hydrogen bonding and therefore the stability and insensitiveness of the explosive.⁶² The inclusion of cations such as triaminoguanidinium has the added benefit of increasing the percentage of nitrogen in the explosive substance, this is particularly useful when synthesising explosives for the purpose of gas generation.

A study of the literature gave the proposed synthetic route to TAGDNAT (**8**) as shown in Figure 47.¹¹³

5.1.2 Synthesis of 3-Amino-5-nitro-1,2,4-triazole (**5** – ANTA) by the oxidation of 3,5-Diamino-1,2,4-triazole (**1** – DAT)

The synthesis of **5** as described in the literature is a 4-step procedure. It involves the formation of a potentially explosive diazonium salt⁶³ and requires the extraction of a highly insoluble intermediate **2**, by either continuous liquid-liquid extraction or

synthesis of a salt of the intermediate with a tertiary alkyl amine.^{88,113} An alternative method was found in the work of Kofman et al⁵⁹ which provided a more convenient and efficient single step synthesis and avoided these time consuming steps.

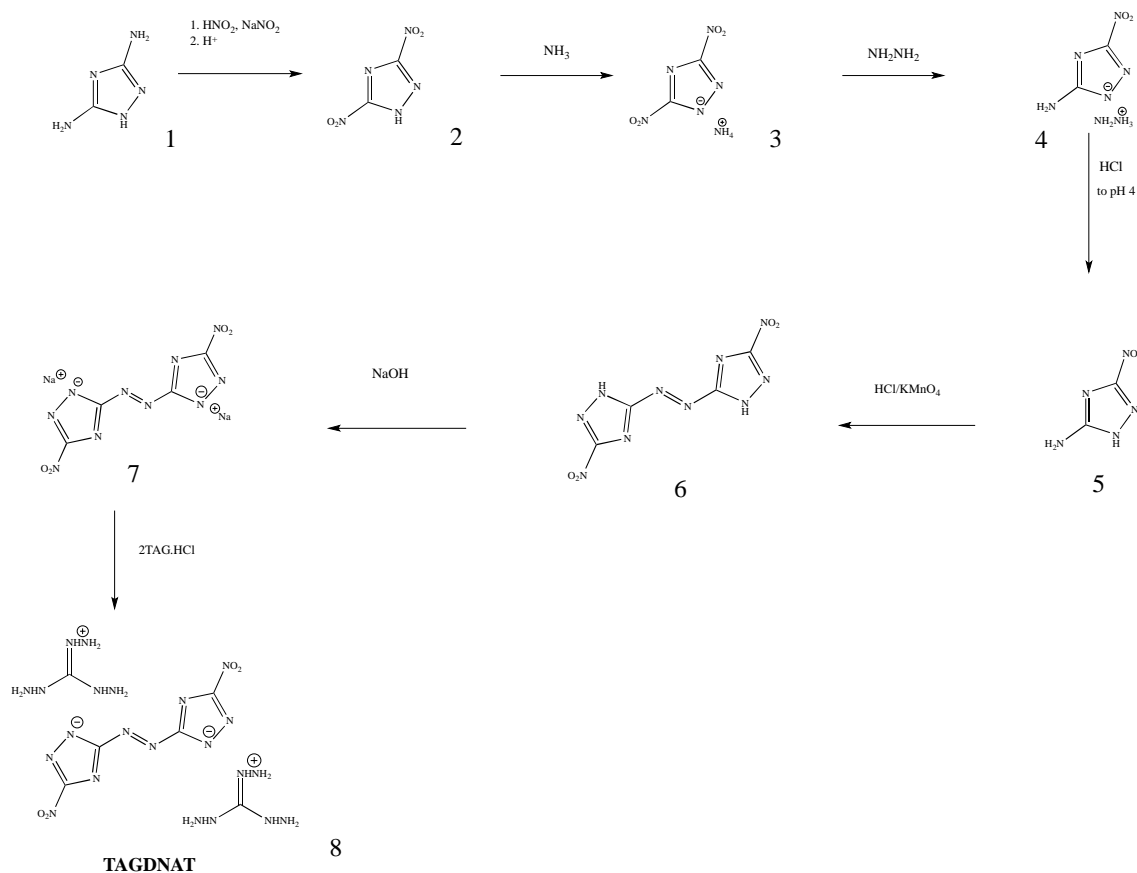


Figure 47: Published route to TAGDNAT (8)

The alternative synthetic route developed is shown in Figure 48, and involved the direct synthesis of **5** from the commercially available starting material **1**. In practice the synthesis of **5** was achieved in high reproducible yields of up to 60 %.⁵⁹

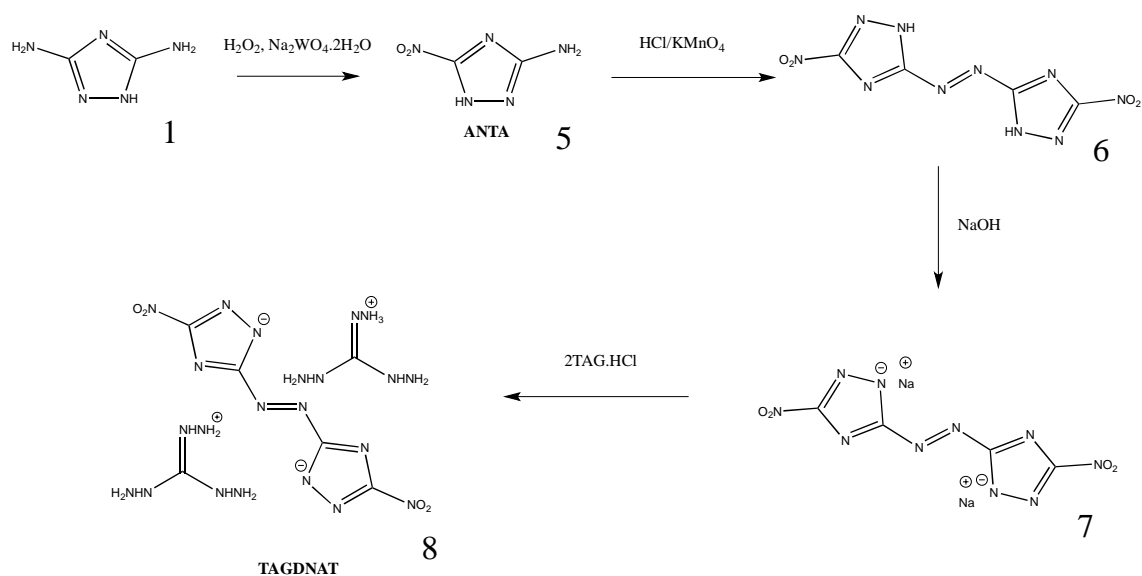


Figure 48: Alternative synthetic route to TAGDNAT (8)

5.1.3 Synthesis of 5,5'-Dinitro-3,3'-azo-1,2,4-triazolate (6 – DNAT)

Upon the successful isolation of **5**, two moles of the compound were oxidised in the presence of permanganic acid. The mechanism of the amine oxidation and subsequent azo-coupling of **5** by reaction with potassium permanganate and hydrochloric acid was not available in the published literature although it has been suggested that it may progress via the formation and consequent condensation of nitroso derivatives of the amine with an unreacted amine of **5** (as shown in Figure 49).

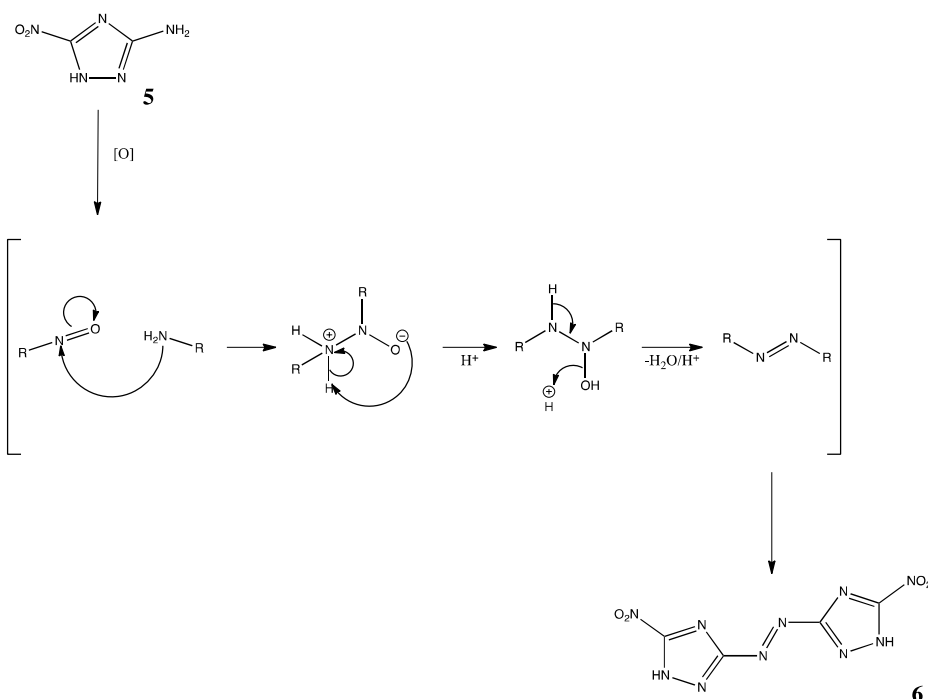


Figure 49: Oxidative Coupling Mechanism proposed by Michael Hiskey (R = 5-nitro-1,2,4-triazole)¹¹⁴

In practice this synthesis was not as productive as the literature suggested, yielding 15 % as opposed to the reported 70.6 %.¹¹⁵ The reaction was repeated several times to amass a sufficient quantity of **6** and the final step of the synthesis was carried out.

5.1.4 Formation of TAGDNAT

The metathesis reaction of triaminoguanidinium hydrochloride (TAG.HCl) and **6** to form **8** involved the deprotonation of 1 equivalent of **6** with excess NaOH at 80 °C before the addition of 2 equivalents of TAG.HCl. Upon cooling the reaction mixture the product is described as freely precipitating from the aqueous solution. These conditions suggest that the displacement of the sodium cations from the deprotonated DNAT by triaminoguanidinium is a favourable process. However upon replication of these conditions no product was observed to precipitate. As the by-product of the preparation was most likely sodium 5,5'-dinitro-3,3'-azo-1,2,4-triazolate, an uncharacterised and possibly sensitive explosive, the aqueous reaction mixture was acidified to regenerate the starting material, **6**, and the residues disposed of as explosive waste.

It was thought that the use of excess NaOH might have resulted in the failed synthesis of **8** by deprotonating the triaminoguanidinium cation thus removing any competition to the sodium cation.

The reaction conditions were altered accordingly and instead a stoichiometric proportion of 2 equivalents of NaOH were added to deprotonate 1 equivalent of **6**. Upon the addition of 2 equivalents of TAG.HCl a precipitate was immediately observed. The yield again was substantially reduced from the reported figure, 15 % rather than 85 %.

In total the combined yield of the reported synthesis of **8** is 39 %. The combined crude yield achieved in replicating the synthesis was 1 % which was never successfully characterised by NMR. As it was estimated that approximately 5 g of performance enhancing compound would be required for the squib formulations, this yield would suggest that approximately 500 g of starting material would be required. This may have been plausible if the intermediate products **5** and **6** were non-explosive. However the laboratory guidelines for synthesis of explosives limit isolation of no more than 1 g of explosive per reaction, which would dramatically increase the number of required syntheses. Consequently a replacement for **8** was investigated.

5.1.5 Synthesis of Hydrazinium 5-Aminotetrazolate (Hy5At)

As a high-nitrogen explosive Hy5At provides an alternative to TAGDNAT although its burn rate has not been characterised. As opposed to TAGDNAT the synthesis of Hy5At is a reproducible and high yielding one-step process. The only pertinent issue observed with the compound is its chemical incompatibility with electrophiles. The highly basic hydrazinium ion was observed to attack the carbonyl of acetone upon exposure during work up. This was observed by the formation of 5-aminotetrazole and the evaporation of hydrazone in the rotary evaporator (see Figure 50). By limiting the exposure of Hy5At to non-electrophilic solvents such as ethanol, methanol and water it was possible to eliminate the decomposition of the salt.

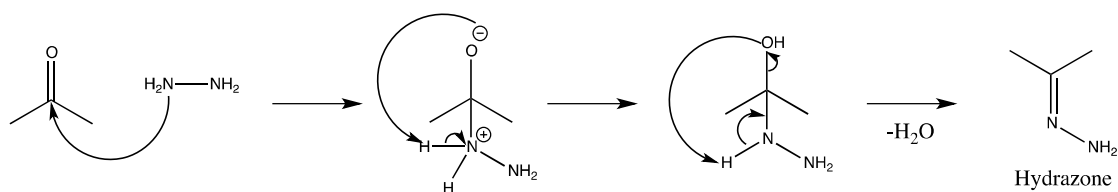


Figure 50: Formation of hydrazone from hydrazine and acetone.

5.1.6 Synthesis of N-Nitro-2,3-dinitrooxypropan-1-amine (NG-N1)

The synthesis of NG-N1 was successfully reproduced with similar yields to the reported preparation (combined yield $\approx 30\%$). However a slight discrepancy in the extraction of the final product was observed.

During the final stages of the synthesis of NG-N1 it was observed, while drying the solvent-wet crystalline solid at 50°C by rotary evaporation, that some impurities were present. The product, NG-N1, was present in the base of a round-bottomed flask in its molten phase but white/translucent crystals had formed around the flask neck and the rotary evaporator stem (Figure 51).



Figure 51: Ethyl carbamate crystals observed adhering to the stem of the rotary evaporator during the drying of NG-N1

The presence of these crystals suggested the sublimation and deposition of an impurity that had cooled and condensed upon the glass above the level heated by the rotary evaporator. Some of these crystals were removed from the flask and an NMR spectrum was collected (Figure 94). The presence of a proton signal typical of an amide

suggested that the impurity present was most likely to be ethyl carbamate^{xxvi}, the expected by-product (

Figure 93: ^1H of NG-N1 (contaminated with ethyl carbamate) in DMSO- d_6 (see Figure 94, Figure 95 and Figure 96 for individual spectra of NG-N1 and ethyl carbamate)

^{xxvi} This was confirmed by comparison of the unknown impurity's ^1H and ^{13}C NMR spectra with that of ethyl carbamate synthesised from ethyl chloroformate and ammonia gas (Figure 95).

). This was unanticipated as the prescribed work-up procedure was specifically designed to remove this compound.⁵¹

It was proposed that scaling-up the reported procedure might have reduced the efficacy of the extraction process that involved repeated solvent-solvent extractions. Purification of NG-N1 from ethyl carbamate was investigated by several means. Exhaustive solvent-solvent extraction and column chromatography were successful in purifying NG-N1 but proved to be excessively time consuming processes. Klapötke et al had reported that NG-N1 might be recrystallized from DCM and this was investigated as a means to improve the sample purity. It was observed that crystals grown from DCM were often poorly formed and instead chloroform was investigated as the recrystallizing solvent. The crystals grown from a supersaturated chloroform solution were recovered as pure acicular NG-N1 crystals (Figure 52, Figure 96 and Figure 97). This process was repeated for the remaining NG-N1 syntheses as the method of purification.



Figure 52: NG-N1 recrystallised from chloroform (scale shown on the right hand side)

5.1.7 Purity of PM compounds

The synthesised PM compounds were analysed by Differential Scanning Calorimetry (DSC) and NMR spectroscopy. These techniques provided measured values for the compound's melting point, decomposition temperature and chemical shift values for the hydrogen and carbon in their structure. These values were compared against the

literature values and indicated that the syntheses were successful and that the materials produced were of high purity (> 95 %) (all values presented in Appendix 8.6 and 8.8). Each synthesised compound was combined in one batch so that no variations would be observed between products synthesised in different procedures.

5.2 Formulations

Each formulation was prepared using a solvent evaporation method. This section presents the experimental procedure employed before then discussing the finer details concerning formulation of energetic compositions.

5.2.1 Experimental Procedure for the Preparation of the Novel Squibb Formulations

Stock solutions of the PMs were prepared in suitable organic solvents, dichloromethane (DCM), ethanol and tetrahydrofuran (THF). In the preparation of each formulation, a pre-determined volumetric aliquot of the PM solution was added to a 150ml round bottomed flask and the solvent removed by rotary evaporation and vacuum desiccation until a constant mass was achieved (X mg Table 10). The solid was then redissolved in a GuDN non-solvent and a proportionate mass of dry GuDN (Y mg Table 10) was suspended in the resultant solution. The suspension was dried for 1.5 h at 50 °C by rotary evaporation and vacuum desiccation for 12h at room temperature. The total mass of the formulation (Z mg Table 10) was weighed to confirm complete solvent evaporation.

Composition	Performance Modifier (PM)	Solvent	PM Mass (X mg)	GuDN Mass (Y mg)	Overall Mass (Z mg)	X (wt %)	Y (wt %)
1	N/A	N/A	N/A	1000	1000	0	100
2	NG-N1	DCM	118	1062	1178	90	10
3	NG-N1	DCM	201	804	1008	80	20
4	NG-N1	DCM	283	661	943	70	30
5	Hy5At	Ethanol	102	918	1013	90	10
6	Hy5At	Ethanol	203	811	1011	80	20
7	Hy5At	Ethanol	302	705	1009	70	30
8	PPZ	THF	90	810	903	90	10
9	PPZ	THF	183	734	917	80	20
10	PPZ	THF	295	689	989	70	30

Table 10: Composition masses, chosen solvents for each performance modifier and the relevant ratios

5.2.2 Particle Size and the Method of Formulation

Upon the completion of the synthesis of the PMs, NG-N1 and Hy5At, the method for combining them in novel squib formulations with the MCE, GuDN, was investigated. In addition to the synthesised additives an energetic polymer, PPZ (see section 4.7.1), which was made available to the project and had been previously studied in the laboratory was also included in the formulation-testing plan.

In general, explosive formulations are prepared by either dissolving the additive in a solvent, which the main explosive charge is insoluble in, and removing the solvent by evaporation or addition of the additive whilst molten. Addition of a dissolved compound is a simpler process, providing that suitable solvents are available, and although Hy5At and NG-N1 both possess low melting points (118 °C and 65 °C respectively) and so would be suitable for molten addition or melt casting, solvent evaporation was preferred.

Formulation by solvent evaporation involves the dissolution of the PM in a solvent that GuDN is insoluble in (section 5.2.1). By doing this GuDN may be suspended in a solution of the PM and upon removal of the solvent a homogeneous coating of the additive may be achieved on the particles of GuDN. Thus the dimensions and range of particles of GuDN, which are coated, should loosely define the particle size and range of the novel formulation and therefore the surface area and burn rate.

Accordingly a source of GuDN with a defined particle size range was acquired from Eurenco, a Swedish explosives manufacturer. Eurenco offered four grades of GuDN, each designed to satisfy a variety of burn rates (Figure 53).

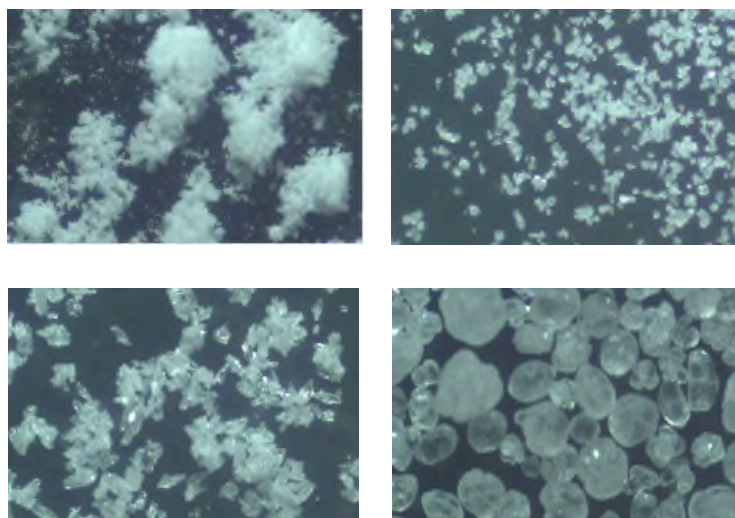


Figure 53: GuDN batches viewed at the same magnification by light microscopy (clockwise from top-right; class 1 (20-50 μm), class 2 (80-150 μm), class 4 (250-400 μm) and gun propellant grade (10-25 μm))¹¹⁶

As a successful squib formulation should possess a high burn rate it seemed logical that the smallest, and therefore largest surface area and fastest burning, particle range should be selected for use as the MCE. However, upon closer inspection of the GuDN grades it was observed that the smallest particle range 10-25 μm (gun propellant grade) was in fact formed by the agglomeration of smaller particles (see Figure 54). Thus these particles could break up into smaller particles or equally agglomerate into larger fragments over time.

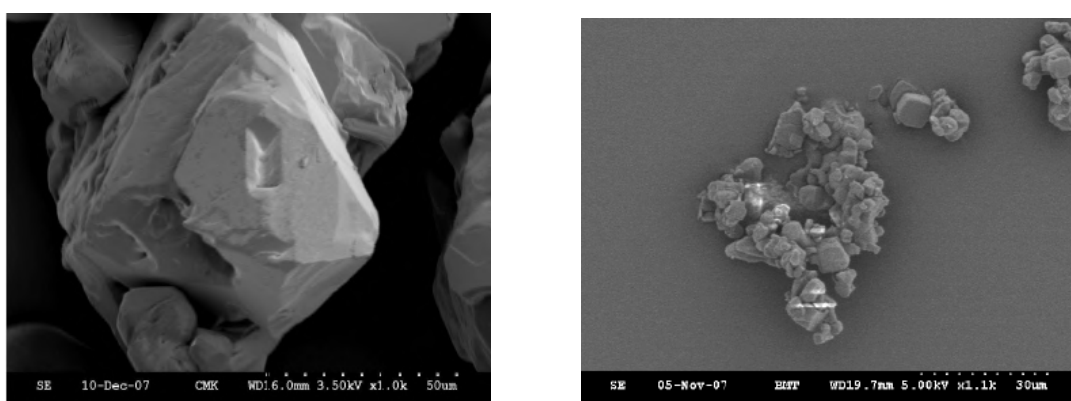


Figure 54: Scanning electron micrographs of GuDN class 1 (left) and gun propellant grade (right) respectively¹¹⁶

Due to the relationship between burn rate and particle size this degradation of the particle size range could have had the effect of altering the burning properties of the formulation over time and thus would not be suitable for a formulation required to satisfy a prolonged shelf-life. Consequently a slightly larger particle size, class 1 (20-50 μm), was selected (Figure 54). The grains of GuDN in this grade were formed by recrystallisation and therefore were less likely to break or agglomerate over time.

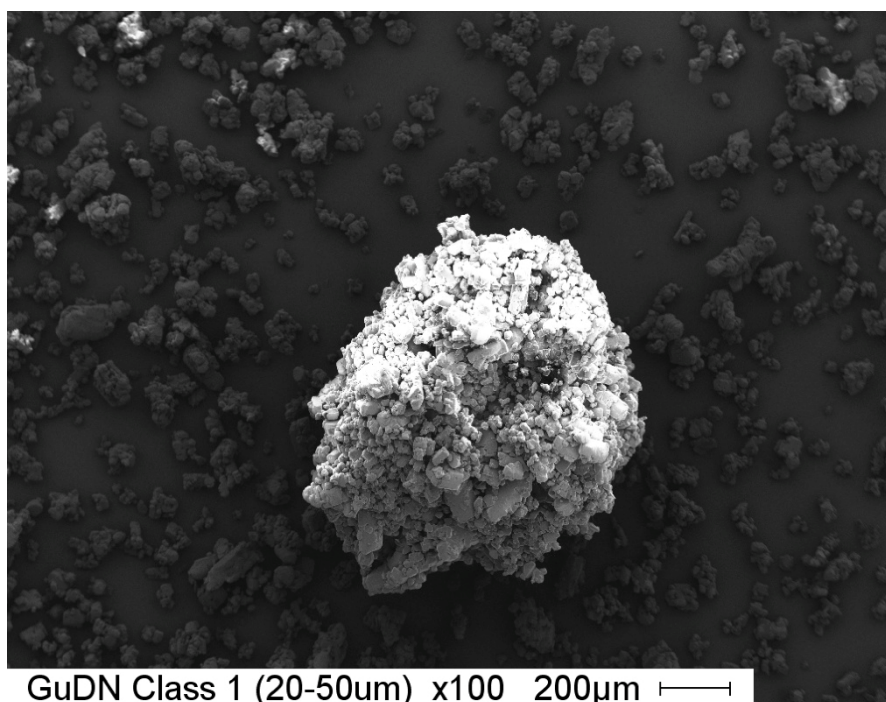


Figure 55: Large agglomerate of Class 1 GuDN (20-50 μm) after transport of the sample from Sweden to the UK

Nevertheless it was necessary to re-sieve the graded GuDN to remove larger agglomerates that had likely formed during transport from Sweden to the UK (see Figure 55).

This sample of GuDN was used as the basis for all of the formulations tested. Furthermore, by reducing the possibility of inconsistent particle size across all of the novel formulations it was possible to neglect the effect of surface area as a reason for any observed ignition and/or propagation improvements of the compositions.

5.2.2.1 Chemical Compatibility and Small Scale Hazard Characterisation

Prior to the combination of chemicals in a formulation it is necessary to assess the potential reactivity between components. Therefore each proposed formulation was first evaluated for chemical compatibility by hazard testing a 100 mg 1:1 composition of GuDN and each of the additives, NG-N1 and Hy5At.^{xxvii} The 1:1 formulations were then subject to small-scale testing (Table 11). The small-scale testing used involved experiments designed to elucidate the impact, friction, ESD and thermal sensitivity of each formulation.

Experiment	NG-N1:GuDN	Hy5At:GuDN
Direct Impact: Steel Hammer on Steel Anvil	0/10 events	0/10 events
Glancing Blow: Steel Hammer on Steel Anvil	0/10 events	0/10 events
ESD: 0.45J	0/3	2/3
Isothermal Storage for 1h@100C	no change	no change
Isothermal Storage for 24h@rt	no change	no change
Temperature of Decomposition by DSC (°C) (onset)	174 (159)	201(185)

Table 11: Small-scale hazard characterisation of 1:1 formulations of GuDN with NG-N1 and Hy5At (Appendix 8.3)

Both formulations displayed insensitivity to impact and friction and reasonable thermal stability.

However upon testing the 1:1 GuDN composition with Hy5At, some sensitivity to ESD was detected. There was some speculation over this result as there was no decrease in the mass of the tested sample (as would be expected if the sample had decomposed). The spark test strips, which are used in the small-scale hazard characterisation of formulations, are thought to expose the compositions to a harsher environment than is necessary and in effect do not represent a fair test. Upon passing the 0.45 J spark through the sample it is thought that the air within the compound is heated up and

^{xxvii} PPZ was previously hazard characterized at Cranfield University by Dr James Padfield in combination with GuDN.³⁹

may result in some melting of the composition. It is this melting which is suggested to provide a false positive in the ESD test (Appendix 8.8).

This observed false positive is not recorded in the large-scale ESD tests, which apply the same spark of 0.45 J but through a wider and deeper sample of composition. Consequently composition 7 which consists of 70 % GuDN with 30 % Hy5At was tested using the large-scale ESD test strips and was shown to be insensitive to 0.45 J when tested 3 times. No evidence of melting was observed.

With the knowledge that the 1:1 compositions displayed low sensitivity to impact, friction and ESD it was possible to progress with the preparation of all the proposed novel formulations.

5.2.2.2 Homogeneity

The homogeneity of the compositions was analysed by NMR, DSC and SEM. As the compositions were not UN classified it was not possible to acquire CHN or chromatographic mass spectroscopy (MS) analysis which may have provided a more definite quantitative assessment of each mixture.^{xxviii}

Each of the additives was included in formulations at 10, 20 and 30 % with respect to GuDN content (see Table 12).

^{xxviii} CHN and MS are provided by an external contractor however it is University policy to transport only UN classified explosives and formulations. UN classification requires a large quantity of sample (grams) for hazard characterisation and as such was not feasible on the scale of this project (<1 g).

Formulation Number	Percentage GuDN (%)	Performance Modifier	Percentage Performance Modifier (%)
1 (Control)	100	N/A	N/A
2	90	NG-N1	10
3	80	NG-N1	20
4	70	NG-N1	30
5	90	Hy5At	10
6	80	Hy5At	20
7	70	Hy5At	30
8	90	PPZ	10
9	80	PPZ	20
10	70	PPZ	30

Table 12: List of novel squib formulations

5.2.2.2.1 Nuclear Magnetic Resonance Spectroscopy^{xxix}

As the project dealt with organic energetic materials, all of the components included in the novel formulations were readily analysed by ^1H nuclear magnetic resonance spectroscopy. Therefore, when dealing with mixtures of more than one material it was possible to interpret the homogeneity of the binary systems by assessing the spectral integral ratios of the signals. The accuracy of this method would be affected by the variation in the resolution of the proton signals attained from the various energetic molecules and as such the data can only be considered as a qualitative indication but nonetheless a valuable one. Unfortunately the ^1H peaks observed for Hy5At overlapped with the peaks observed for GuDN and so it was not possible to discriminate the integrals of these peaks. This meant that while the formulations containing PPZ and NG-N1 with GuDN could be evaluated, the Hy5At compositions were not directly assessable by ^1H NMR spectroscopy.

^{xxix} Refer to Appendix 8.6 for a brief introduction into NMR theory.

Three random 5mg samples of compositions 2-4 and 8-10 were dissolved in deuterated dimethyl sulfoxide (DMSO- d_6). By taking three samples it was hoped that some insight could be gained into the homogeneity of the formulations by assessing the spread in the data calculated from the variation in the integral ratios of each composition. This method is used commonly to define the relative proportions of impurities in synthesised organic products.

Initially it was necessary to choose a proton signal on GuDN, PPZ and NG-N1, which was distinct from all other signals so that the most accurate approximation could be made. For GuDN the chosen proton was the secondary amine proton on the guanylurea moiety found at 9.6 ppm and this was integrated from 10 – 9.1 ppm. With NG-N1 the methine proton at position 2 on the propyl chain, which is found at 5.6 ppm was selected and integrated from 5.8-5.4 ppm. Finally for PPZ the 2H methylene signal found at approximately 3.9 ppm was chosen and integrated from 4-3.7 ppm (Figure 56).

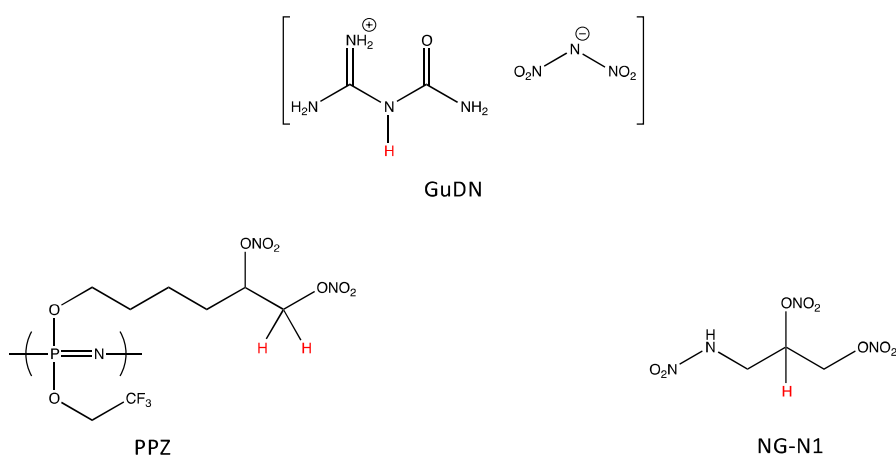


Figure 56: GuDN (1H), PPZ (2H) and NG-N1 (1H) with highlighted protons used in ascertaining the homogeneity of the formulations by NMR.

Composition	NMR Integral Ratios			Performance Modifier Integral Percentage (wt %)	Weighed Percentage (%)	Spread*
	GuDN 1H (10 - 9.1 ppm)	NG-N1 1H (5.8 - 5.4 ppm)	PPZ 2H (4.0 - 3.7 ppm)			
2	1	0.042	-	4.3	-	-
2	1	0.071	-	7.1	-	-
2	1	0.046	-	4.7	-	-
Average	1	0.053	-	5.4	10	1.5
3	1	0.0879	-	8.7	-	-
3	1	0.1286	-	12.2	-	-
3	1	0.1925	-	17.2	-	-
Average	1	0.1363	-	12.7	20	4.3
4	1	0.2987	-	24.4	-	-
4	1	0.2227	-	19.4	-	-
4	1	0.2529	-	21.5	-	-
Average	1	0.2581	-	21.9	30	2.5
8	1	-	0.0956	8.6	-	-
8	1	-	0.2348	18.8	-	-
8	1	-	0.1438	12.4	-	-
Average	1	-	0.1581	13.3	10	5.1
9	1	-	0.3614	26.2	-	-
9	1	-	0.4041	28.5	-	-
9	1	-	0.3913	27.8	-	-
Average	1	-	0.3856	27.5	20	1.1
10	1	-	0.7512	42.5	-	-
10	1	-	0.5336	34.4	-	-
10	1	-	0.5594	35.5	-	-
Average	1	-	0.6147	37.5	30	4.4

Table 13: Percentages of NG-N1 and PPZ in random samples of compositions 2, 3, 4, 8, 9 and 10 measured by NMR (*spread calculated using standard deviation calculation as outlined in Appendix 8.10)

The calculated ratios are presented in Table 13 and show that the homogeneity of the formulations is quite low and is most likely due to the fact that they were the product of a small-scale method which did not employ any techniques such as mechanical

mixing to ensure homogeneity. Improving homogeneity would be essential if any of the selected compositions was to be considered as a possible replacement for potassium picrate in a reliable squib application.

5.2.2.2.2 Differential Scanning Calorimetry^{xxx}

Differential scanning calorimetry (DSC) provided an additional indication of the consistency of the composition ratio and thus the sample homogeneity. This was achieved by comparing three repeat DSC experiments for each formulation. By comparing the measured melting and decomposition temperatures it was possible to achieve a qualitative assessment of the sample homogeneity. Repeated DSC experiments of a homogenous formulation should yield repeatable melting and decomposition temperature values and so any variation observed may be taken as an indication of inhomogeneity.

Composition	Mean Endotherm (°C)	Spread from the mean	Mean First Exotherm (°C)	Spread from the mean	Mean Second Exotherm (°C)	Spread from the mean
1 (GuDN)	-	-	228.9	1.8	-	-
2	63.6	0.4	174.7	0.6	220.5	1.8
3	64	0.9	174.3	0.4	215.9	1.7
4	63.6	0.6	209.3	3.8	-	-
5	107.5	0.8	206.8	0.3	-	-
6	107.2	1.0	207.4	1.5	-	-
7	106.7	0.7	203.1	0.7	-	-
8	-	-	216.3	5.4	-	-
9	-	-	211.2	2.0	-	-
10	-	-	210.9	2.0	-	-
NG-N1	64.5	-	184.6	-	-	-
Hy5At	109.5	-	236.8	-	-	-
PPZ	-	-	193	-	-	-

Table 14: Standard deviation in repeated DSC measurements of the novel squib formulations (spread from the mean calculated as outlined in Appendix 8.10)

^{xxx} Refer to Appendix 8.8 for more details on DSC and the DSC thermograms used to construct Table 14.

As shown in Table 14 the endotherms and exotherms of the majority of the formulations show little spread from the mean value, with the most blatant exceptions being compositions 8, 9 and 10. As the PM in these compositions was PPZ, a polymeric additive, it is understandable that the compound may have aggregated differently when compared to the comparatively small molecular additives, NG-N1 and Hy5At.

While it should be noted that this method of evaluating homogeneity is highly dependent on the precision of the calorimeter and that a certain degree of spread in the data was to be expected; these results do indicate that there is a degree of inhomogeneity in the formulations as observed in the NMR measurements previously outlined although the extent of spread in the data and therefore implied inhomogeneity is not equivalently assessed. This could imply that these methods are not viable for quantifying homogeneity or simply that more replicates are required to increase the accuracy and precision of the tests.

5.2.2.2.3 Scanning Electron Microscopy (SEM)^{xxxi}

SEM can be a highly biased means of analysis as the scientist has the choice of which images to publish or omit. As such SEM was used to probe the squib compositions for obvious signs of inhomogeneity such as segregation or agglomeration rather than provide a conclusive evaluation. Of the samples tested, the compositions containing Hy5At, were the most readily interrogated. This was due to the acicular crystal shape of Hy5At, which is clearly observed in contrast with GuDN particles which are ostensibly spherical (see Figure 57 and Figure 57).

^{xxxi} See Appendix 8.9 for a brief introduction into SEM.

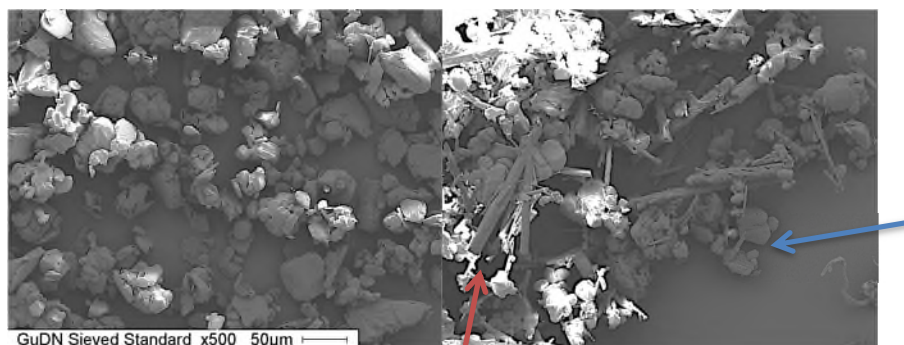


Figure 57: Composition 1 (pure GuDN, on the left) and Composition 7 (GuDN:Hy5At 7:3, on the right). Composition 7 displays acicular "needle shaped" crystals presumably of Hy5At (red arrow indicates a needle shaped crystal and blue arrow highlights typical spherical GuDN particles present in both)

Of all the samples analysed by SEM, compositions 2, 3 and 4 yielded very little information as it was difficult to distinguish between crystals of GuDN and NG-N1.^{xxxii} Similarly compositions 8, 9 and 10 showed little as the polymeric additive PPZ made it effectively impossible to observe individual particles without resorting to more complex methods of analysis (Figure 58 and Section 5.2.2.2.4). Therefore SEM was used primarily to study compositions 5, 6 and 7.

^{xxxii} NG-N1 is observed as an acicular crystal when recrystallized from chloroform but is observed as an amorphous solid when allowed to solidify from an evaporating solution. Thus NG-N1 is most likely in this amorphous state in the formulations as no acicular crystals were observed in any of the SEM micrographs of compositions 2,3 or 4.

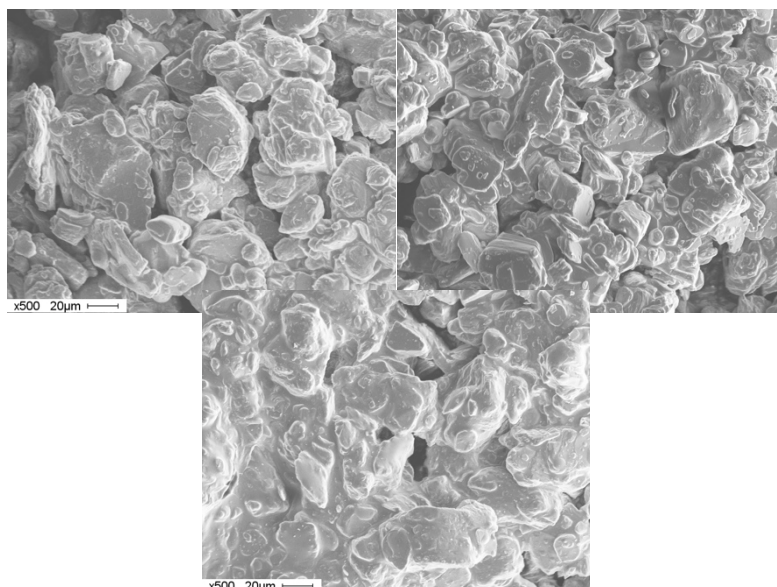


Figure 58: SEM micrographs showing from top left (clockwise): composition 8, composition 9 and composition 10

In the samples analysed there was very little evidence of agglomeration of the needle shaped Hy5At crystals. The micrograph shown in Figure 59 displayed the only evidence of agglomeration observed. Here acicular crystals appear to occupy most of the image and to have coalesced into a larger structure. While this does not prove inhomogeneity in the samples, it does indicate that the solvent evaporation method used might not prevent aggregation and that a more efficient method would be preferable if this work was to be repeated such as large-scale formulation including mechanical stirring.

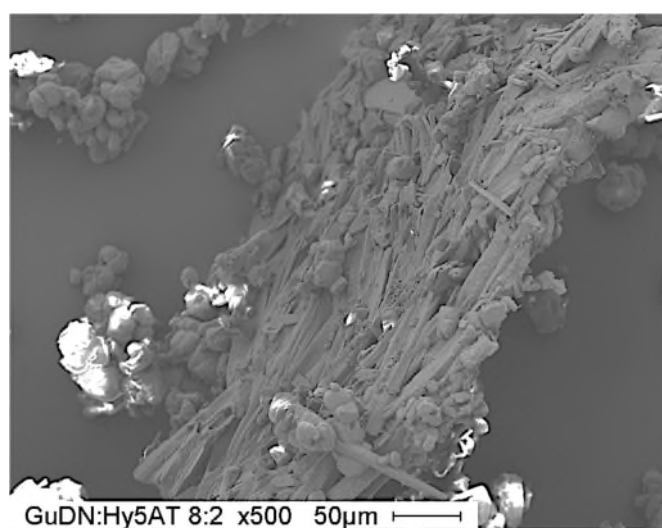


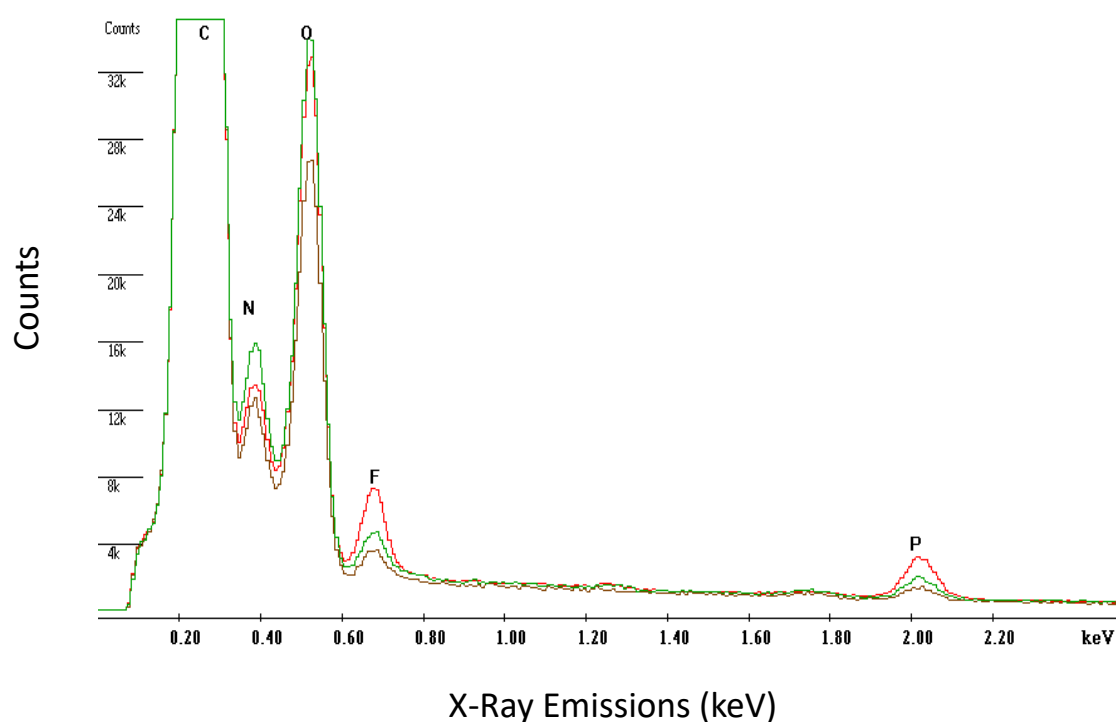
Figure 59: SEM micrograph of composition 6 which seems to show a Hy5At agglomerate.

5.2.2.2.4 Energy Dispersive X-Ray Spectroscopy (EDX) ^{xxxiii}

As with DSC, scanning electron microscopy (SEM) equipped with EDX provides a qualitative insight into the homogeneity of a formulation. EDX uses the electron beam of the SEM to excite x-ray emission from the test sample. By measuring the x-ray emissions it is possible to identify the elements present by their unique x-ray emission spectra. Upon researching EDX and its possible use in evaluating the distribution of each PM upon GuDN it was evident that meaningful results would only be likely when testing compositions 8, 9 and 10 due to the elemental variation in the additive, PPZ, which contains P and F, with the C, H, N and O based MCE, GuDN. This was fortunate as the SEM micrographs of compositions 8, 9 and 10 yielded very little information on their own due to the coating of PPZ which obscured the identification of individual GuDN particles (as observed in Figure 58).

However the presence of P and F in PPZ, which is not present in GuDN, and provides good resolution (no peaks overlap) with the background of C, N and O allowed the use of EDX in extracting significant information. When examining formulations 8, 9 and 10 a qualitative increase in P and F is readily observable in line with the proportionate increase in PPZ in each composition (Figure 60).

^{xxxiii} See Appendix 8.9 for introductory theory on the EDX technique.



**Figure 60: EDX graphic showing relative abundance of C, N, O F and P in PPZ formulations
(composition 8 = magenta, composition 9 = green and composition 10 =red)**

Although this graphical representation does not offer a direct appraisal of the homogeneity of the compositions tested it does give some insight into the value of EDX in evaluating solvent evaporation as a method of formulation. It is possible by using more advanced EDX systems to quantify the elements present but this was not possible in this work.

5.3 Squib Preparation

5.3.1 Pressure Calculation and Risk Assessment

Prior to testing the novel formulations it was necessary to assess the risk posed by firing the squibs in the laboratory. This assessment involved the calculation of the theoretical maximum pressure generated by each formulation and assuring that the equipment in use would be capable of these pressures.

As the pressure bomb and squibs had been previously risk assessed by Leaffield Engineering it was possible to acquire the relevant information from experienced engineers. Mr Gordon Dyte, the engineer responsible for the previous squib reports cited here, suggested that a pressure of 300 MPa could be sustained using the experimental apparatus. The locking ring, as shown in Figure 61, which holds the header assembly in contact with the explosive, was not designed to withstand a pressure greater than 428 MPa as calculated by the Leaffield stress report on the squib.¹¹⁷

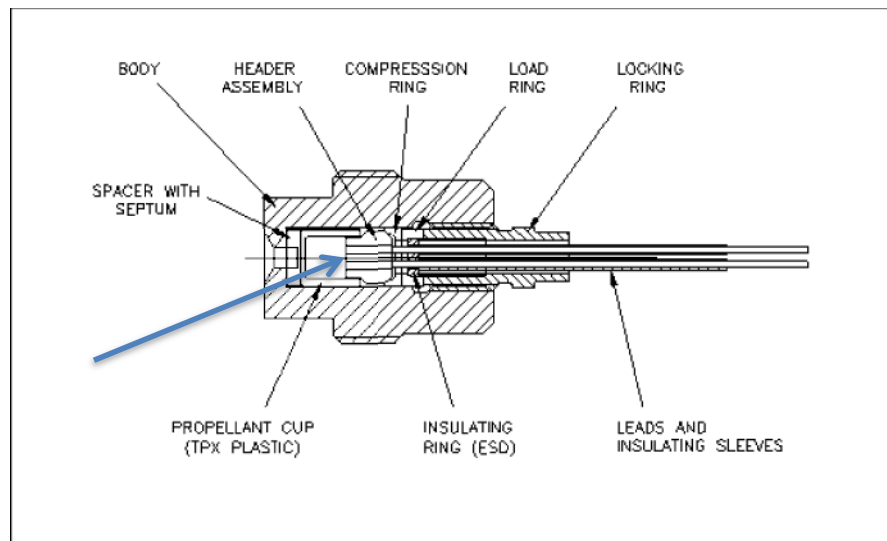


Figure 61: Project squib with blue arrow highlighting the point of contact between bridgewire and explosive composition

With the value of 300 MPa defined as the pressure output limit that each squib formulation should not exceed, it was possible to calculate safe quantities of composition to be tested using the ICT code.¹¹⁸

The ICT code is a thermodynamic software package that is used to calculate the energetic output of explosive formulations. It does this by first calculating the enthalpy of explosion for the energetic compositions, then iterating the explosion temperature from the heat released and the heat capacities of the decomposition products. By using the calculated temperature of explosion, the decomposition product ratio and the volume of the combustion chamber, the code can then apply an equation of state to provide a value for the pressure output. By default the code uses the ideal gas law for moderate temperatures and low pressures and switches to the Vlril equation of state at temperatures over 1000 K.

By design the software assumes the explosive formulation has a mass of 100 g and so it was necessary to scale up the internal volume of the pressure bomb to attain a representative pressure. The scaling ratios are presented below in Table 15.

ICT Mass (g)	ICT Volume (cm ³)	Actual Mass (mg)	Actual Volume (cm ³)	Ratio
100	500	50	0.25	0.0005
100	250	100	0.25	0.001

Table 15: Ratio of actual mass and volume to ICT calculation mass and volume

By using these ratios it was possible to define the theoretical maximum pressures that could be expected when using either 100mg or 50mg of a novel squib formulation.

Formulation	GuDN Proportion (%)	Performance Modifier	Performance Modifier Proportion (%)	TMD (g/ml)	Pressure Generated by 50 mg (MPa)	Pressure Generated by 100 mg (MPa)
1	100	N/A	N/A	1.75	240	610
2	90	NG-N1	10	1.755	251	638
3	80	NG-N1	20	1.76	262	663
4	70	NG-N1	30	1.764	272	686
5	90	Hy5At	10	1.727	248	636
6	80	Hy5At	20	1.705	256	662
7	70	Hy5At	30	1.684	264	687
8	90	PPZ	10	1.717	228	581
9	80	PPZ	20	1.686	216	551
10	70	PPZ	30	1.655	203	519

Table 16: The pressure generated by 50mg and 100mg of the proposed novel squib formulations (TMD = calculated theoretical maximum density)

Table 16 shows that the ignition of 100 mg of formulation within the closed volume of the pressure bomb could theoretically exceed the safety pressure limit of 300 MPa. Therefore it was decided that 50 mg of each formulation should be used. It was thought that this quantity of each composition would provide sufficient insight into the ability for an insensitive formulation to take the place of a primary explosive in a squib. By choosing to use a reduced sample size it was also possible to reduce the synthetic effort required to produce the materials for testing.

5.3.2 Replicate Firing Experiments

In the previous research into replacing the energetic material in use, Leaffield Engineering used 29 replica squibs to ascertain a desired level of confidence in the results. While this level of confidence was considered useful and indeed essential when optimising an application-ready device, 29 replicates would have substantially increased the duration of synthesis and formulation of the novel compositions. Hence the decision was made to limit the number of replicates to 10 as the focus of the

project was to prove the suitability of the novel low sensitivity squib formulations rather than deliver an optimised and application-ready composition.

5.3.3 Density of the Formulations and the Internal Volume of the Squib

With the knowledge that each formulation would require 10 replicate squibs containing 50mg of energetic composition it was necessary to adapt the internal volume for each device. As the compositions were fine powders, and so had the potential to clog the apparatus, their density could not be measured accurately using gas pycnometry and instead their calculated theoretical maximum densities (TMD) were used. These were calculated using the ICT code for convenience and are merely a summation of the formulation component's TMDs. The values were used to calculate the volume occupied by 50 mg of each composition at 90 % TMD and accordingly determined the internal dimensions of the squib (Table 17 and pull-out diagrams on Pg 127).

Formulation	TMD (g/ml)	90% TMD (g/ml)	Mass (mg)	Volume Occupied (mm ³)	Propellant Cup Width (mm)	Formulation Charge Length (mm)	Propellant Cup Internal Length (mm)	Aluminium Spacer Length (mm)
1	1.750	1.575	50	31.7	3.8	2.8	5.3	2.5
2	1.755	1.580	50	31.7	3.8	2.8	5.3	2.5
3	1.760	1.584	50	31.6	3.8	2.8	5.3	2.5
4	1.764	1.588	50	31.5	3.8	2.8	5.3	2.5
5	1.727	1.554	50	32.2	3.8	2.8	5.3	2.5
6	1.705	1.535	50	32.6	3.8	2.9	5.3	2.4
7	1.684	1.516	50	33.0	3.8	2.9	5.3	2.4
8	1.717	1.545	50	32.4	3.8	2.9	5.3	2.4
9	1.686	1.517	50	33.0	3.8	2.9	5.3	2.4
10	1.655	1.490	50	33.6	3.8	3.0	5.3	2.3

Table 17: The dimensions of the novel squib formulation charges (refer to pull-out diagrams on Pg 127)

5.3.4 Pressing the Squib Pellets

Upon the successful preparation of the propellant cups and aluminium spacers it was necessary to fill the squibs with the novel formulations. As one of the main aims of the

project was to relate the performance of the novel squib compositions to the past research in the area, the Leaffield Engineering protocol for filling and pressing energetic compositions into the devices was consulted. This would allow a degree of consistency between current and past research and allow for some critical comparison of the results.

The pressing method was designed to achieve a consistently intimate contact between the header assembly and the explosive formulation. This was accomplished previously by pressing the explosive into the squib in several pre-determined increments before pressing the bridgewire directly into the formulation. For simplicity it was decided that the pressing of the novel squib formulations reported herein would be achieved in two steps. An initial fill of 50 % of the composition, 25 mg, was placed inside the squib and pressed with a flat ended tool to a load of 1.2 kN. The remaining 25 mg was then added onto the surface of the pressed pellet and the header assembly directly pressed into the formulation using a load of 2 kN.

Initially this procedure was investigated using a lever-operated hand press, manufactured by Specac, similar to the type used to prepare KBr discs for infrared spectroscopy experiments. The hand press was equipped with a 10 kN load cell and a blast shield to mitigate the risk of fragmentation in the unlikely event of an accidental ignition (Figure 62).

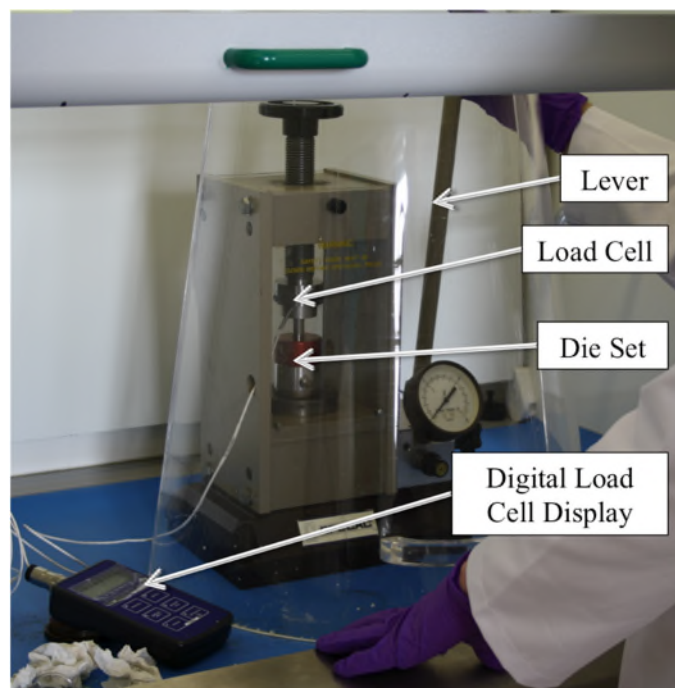


Figure 62: Specac hand press equipped for squib preparation^{xxxiv}

Unfortunately, although the hand press provided a convenient solution to the preparation of the squibs, the results achieved upon testing with an inert powder (talcum) were not reproducible. It was thought that the lever operation of the hand press was not capable of delivering the required accuracy and “fine control” to allow for the level of consistency required. This can be observed in the low R^2 value ($R^2 = 0.64702$), which describes the “spread” or regression in the data points, observed in the density vs load curve shown below (Figure 63). While the effect of load upon density is less significant for the squib device (as the formulation is confined at a given density by the dimensions of the internal volume) an accurate pressing method that can provide a consistent load value was preferred.

^{xxxiv} Photograph courtesy of Dr Matthew Andrews.

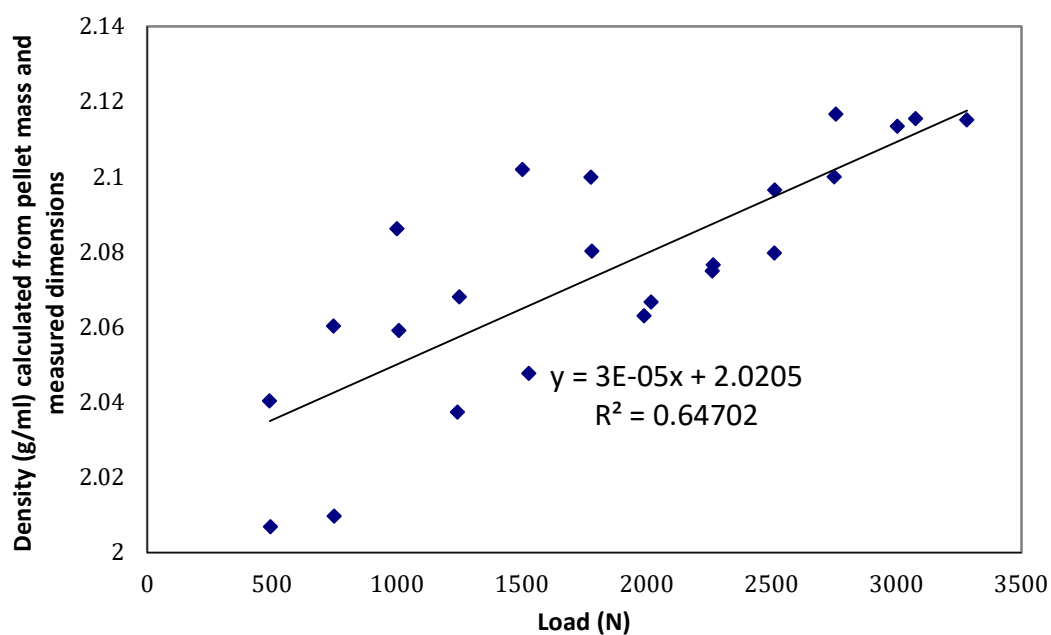


Figure 63: Density vs load curve for talcum pellets prepared using the Specac hand press

The Instron automated hydraulic press was investigated as an alternative means of sample pressing (Figure 64). This device allowed control of both the rate of compression and the maximum load applied. By maintaining a consistent rate and a maximum applied load it was possible to effectively eliminate density variations. In further work it would be preferable if a means of density analysis were used to investigate the pellet pressed within the squib body. This means of analysis would also allow insight into the contact between the bridgewire and explosive charge.



Figure 64: Instron 4206 universal testing machine

5.3.4.1 Experimental procedure for the squib pressing

The squib filling and pressing was achieved in two stages. Initially 25 mg of the composition was placed inside the pre-weighed squib using a funnel and brushed into the propellant cup. This portion of composition was then compressed with a steel dowel using the Instron hydraulic press. The load applied was 1.2 kN and the ram speed was maintained at 0.25 mm s^{-1} . The second 25 mg portion of the composition was added onto the compressed pellet within the propellant cup and consolidated into the cup using a brush. The squib was reweighed to confirm the addition of precisely 50 mg of composition. The header assembly complete with compression and load ring was pushed into contact with the composition using the Instron hydraulic press and bespoke mandrel (Figure 65). The load applied was 2 kN and the ram speed was 0.25 mm s^{-1} . The ESD disc was then fitted and the locking ring fixed in place with a torque of 3 N m.

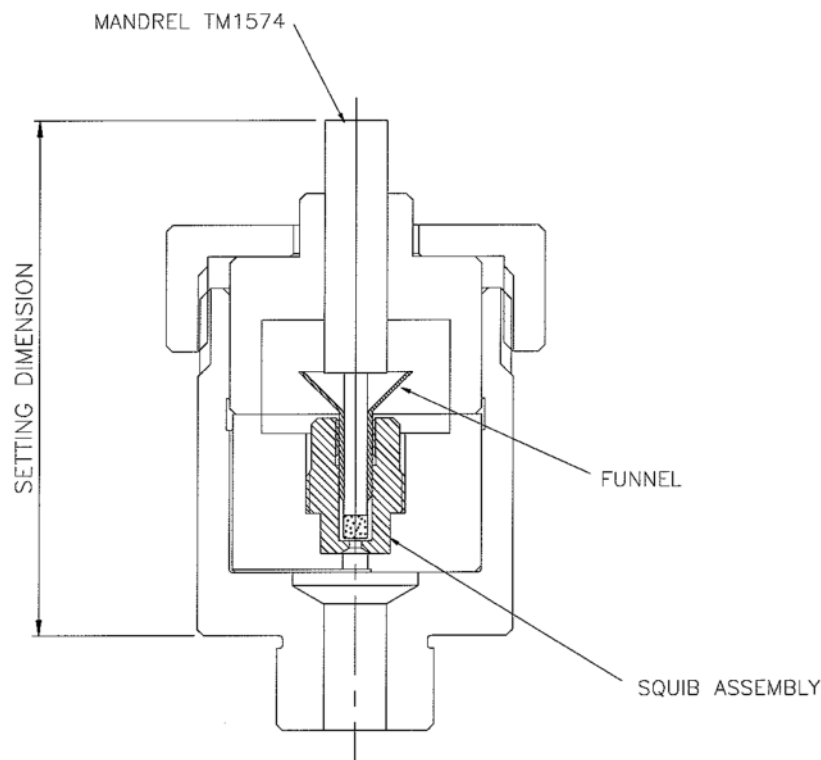


Figure 65: Squib press assembly, funnel and mandrel

5.3.5 Intimacy of Explosive with Bridgewire

Although it was impossible to directly evaluate the contact of the bridgewire with the explosive, an indirect test had been employed by Leaffield which was loosely based on the electrothermal response test (ETR). The electrothermal response test relies on the measurement of heat dissipated by a bridgewire stimulated by a small current to characterise the intimacy of contact between the hotwire and explosive. The simplified ETR test was conducted using a simple circuit that was composed of a sensitive ammeter, voltmeter and a stabilised power supply connected across the terminals of a bridgewire. By measuring the resistance prior to and after the assembly of the squibs it was possible to observe the effect of the energetic composition in contact with the bridgewire on the bridgewire resistance. It was anticipated that, as the squib formulations had been experimentally proved to be ESD insensitive to 0.45 J and therefore must conduct electrical currents, the contact between the bridgewire and the explosive would result in a reduction in the resistance. It was thought that this

would result in a path of lower resistance being provided through the explosive. However the results indicated the opposite, and while the standard deviation observed was too substantial to allow for an evaluation of quality of the intimacy between bridgewire and explosive, the trend was clearly shown that resistance increased when the squib was filled and the bridgewire was placed in contact with the compositions (Figure 66).

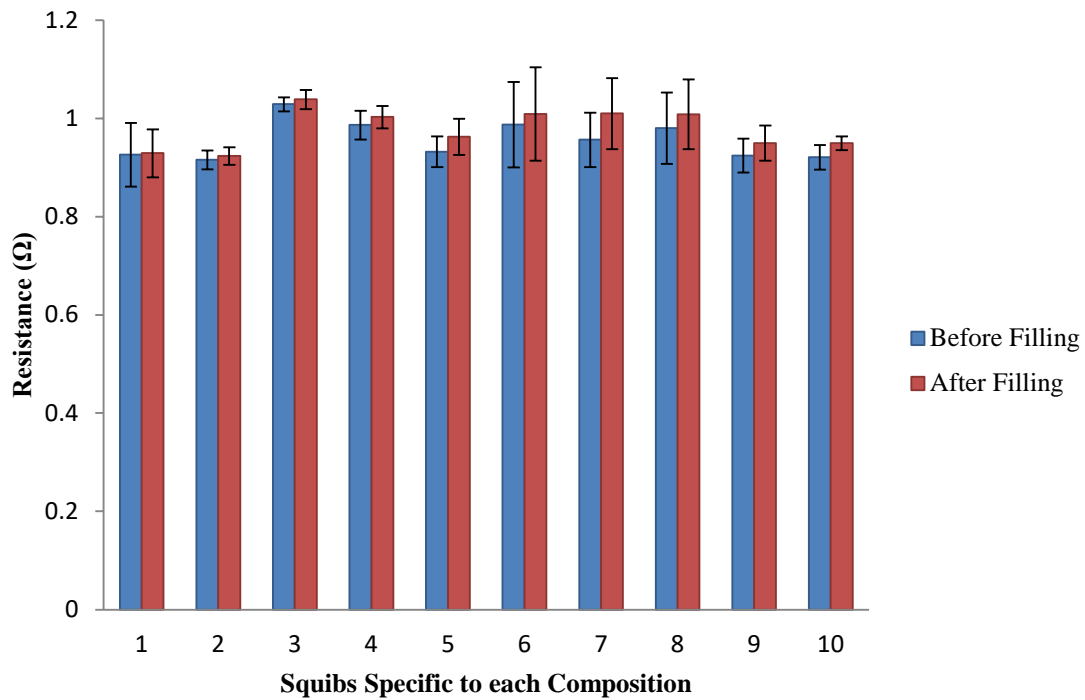


Figure 66: Bridgewire resistances before and after filling with specific compositions at constant temperature (the standard deviation illustrated by the error bars was calculated as outlined in Appendix 8.10)

The variation in the resistance is slight when it is considered that the firing circuit is manufactured with an acceptable tolerance between 0.8 Ω and 1.45 Ω . Nevertheless the variation is still of interest. The observed increase in resistance may be due to the presence of the propellant cup, which is made of insulating material. Equally there may be a chemical interaction between the compositions tested and the bridgewire, which is made from nickel chromium alloy. However without further testing it is not possible to confidently suggest the reason for the observed trend.

5.4 Squib Firing

5.4.1 Experimental Procedure for the Laboratory Firings

The squibs were all fired using an equivalent experimental setup with a 0.25 cm³ pressure bomb fitted with a Kistler 6203 “High-Pressure Quartz Transducer” (Figure 67 and the pull-out diagram on Pg 132). In each case the squib under test was prepared for the firing by coating the end face with a heat resistant jointing fluid and placing a brass O-ring, coated similarly, into the pressure bomb flush with the sealing face. The squib was then threaded into the pressure bomb and, using a wrench and vice, was torqued into position using a force of 6 N m. The squib and pressure bomb were then placed behind a blast shield and the leads connected to a firing box. The piezoelectric gauge was connected to a Kistler 5018 charge amplifier and both this and the firing circuit were coupled to a Nicollet Odyssey storage oscilloscope. The firing box was programmed to produce a 5 A pulse over 50 ms. This was observed on the screen of the oscilloscope as a square wave and was accompanied by a recorded increase in pressure from the piezoelectric gauge on the same display. The fired squib was allowed to cool for approximately 10-15 mins and the firing box disconnected. Any pressure generated in the squib was then released by “cracking” the seal between the squib and pressure bomb using a wrench and vice behind a blast screen. The squib was then removed and the pressure bomb cleaned with acetone and water and allowed to dry prior to the next firing.

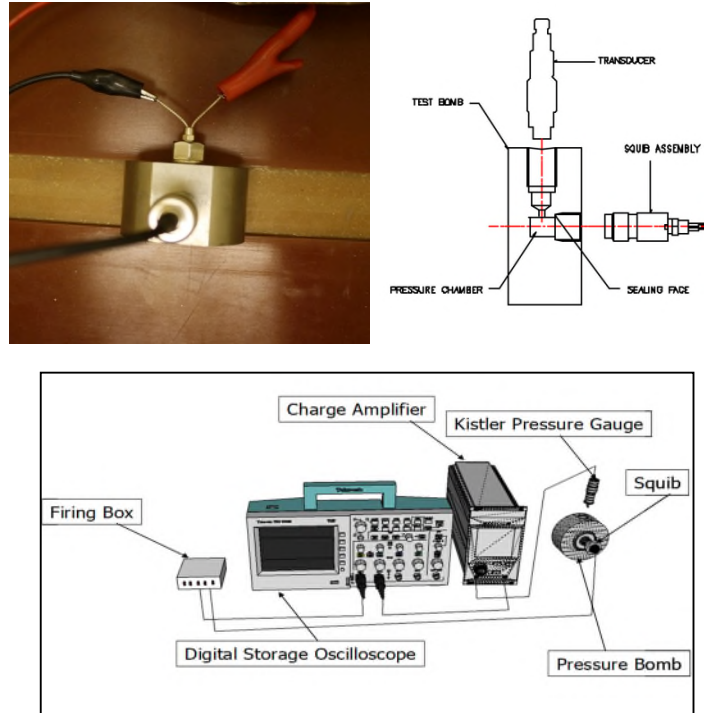


Figure 67: Clockwise from top-left: A photograph of the assembled pressure bomb and squib from above, a diagram of the pressure bomb assembly in profile and the entire experimental apparatus

5.4.2 Composition 1 – GuDN

In prior studies carried out by Leaffield Engineering it was concluded that GuDN could not be reliably ignited within the squib without the use of a primer compound such as lead styphnate or black powder.

Hence the successful ignition of composition 1 in an average of 15.6 ms represents a breakthrough, although it should be noted that, of 19 attempted firings, only 12 were successful and thus the result is not indicative of a successful candidate squib explosive. Regardless, the improved ignitability of GuDN, with reference to the Leaffield testing, may be attributed to the finer particle size that was used in this project and was mentioned previously (see Pg 77). The reduced particle size might have allowed the initial decomposition of the GuDN around the bridgewire to propagate, as the increased surface area would have led to a faster generation of heat and pressure than observed with a coarser sample. In a slower reaction the heat may have been generated at a lower rate than it would dissipate and thus would not have induced further thermal decomposition. This result may be verified by testing a range of GuDN particle sizes within a squib.

The average pressure output observed in the firings of squibs containing composition 1 was substantially lower than expected at an average of 11 MPa. This was thought to be due to incomplete combustion of the GuDN which was clearly observed upon examination of the pressure bomb and fired squib after testing (Figure 68).

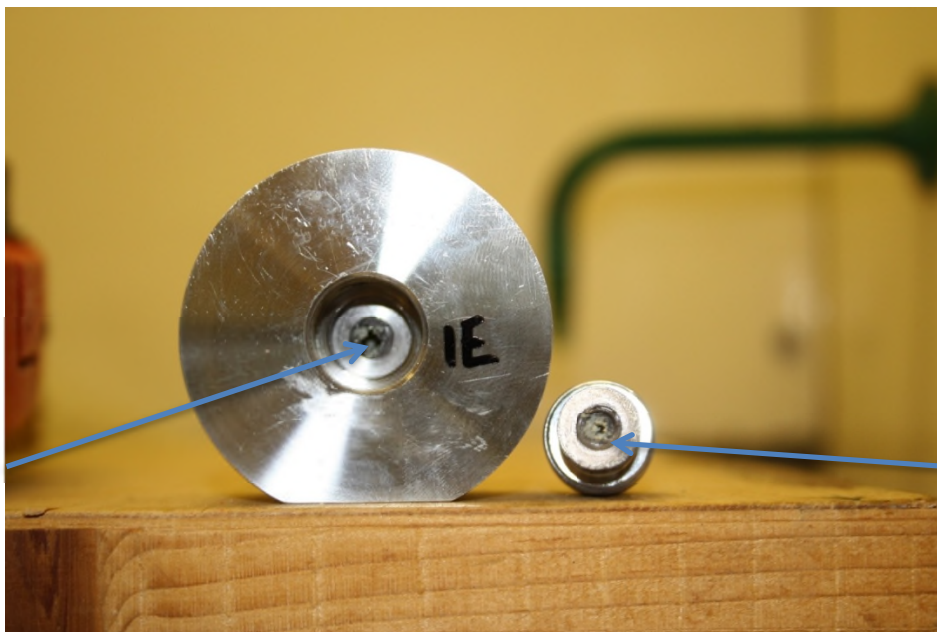


Figure 68: Image seems to show white particulates of GuDN around the septum of the squib and within the pressure bomb (highlighted by arrows).

In all of the composition 1 firing experiments a large quantity of white GuDN particles were visible after the ignition. This suggested that a rapid generation of pressure within the squib had been sufficient to perforate the burst disc and eject unburnt propellant from the squib body. It was hoped, that by introducing the PMs, that decomposition would occur more rapidly and would not similarly halt upon perforation of the squib septum.

5.4.3 Compositions 2, 3 and 4

The Effect of NG-N1 and Oxygen Balance Enhancement on the Ignition of GuDN

Compositions 2, 3 and 4 displayed a marked improvement in performance when compared to composition 1. The ignitability of the compositions was indicated by their repeated ignition from the squib bridgewire. However the reproducibility of the combustion of the formulation and pressure generation was not observed in all of the comparatively oxygen-rich mixtures. While composition 2 was reliably ignited and the mean pressure output was approximately 51 MPa, the standard deviation of that result was 33MPa. Nevertheless by increasing the weight percentage of NG-N1 and

therefore increasing the oxygen balance and exothermicity of the compositions a greater degree of reproducibility was achieved.

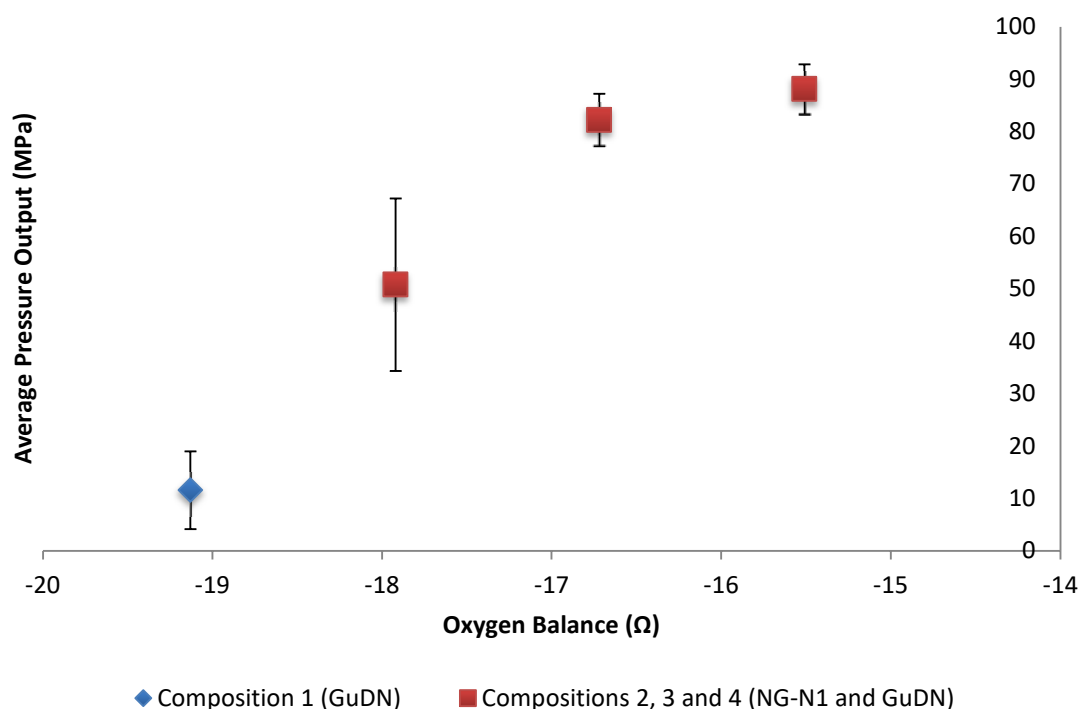


Figure 69: Compositions 1, 2, 3 and 4: oxygen balance vs average pressure output (error bars show standard deviation, Appendix 8.10)

Consequently compositions 3 and 4 displayed a high average pressure output of 82 and 88 MPa respectively with a relatively small standard deviation of approximately 10 MPa in each (see Figure 69). These pressures were achieved with 50 mg of each composition and it is feasible that by increasing the mass of formulation, the pressure output may be increased to the required level of 120 - 150 MPa although this was not attempted during this project.

The improvement with respect to composition 1 was also observed in the mean rise times where compositions 3 and 4 were recorded to reach maximum pressure in 8.3 and 5.9 ms respectively with standard deviations of 3.1 and 1.7 ms each. While 5.9 ms is 12 times slower than the specified 0.5 ms rise time achieved with potassium picrate, the result represents a significant improvement of the average rise time observed for pure GuDN (composition 1), which is 15.6 ms (Figure 70).

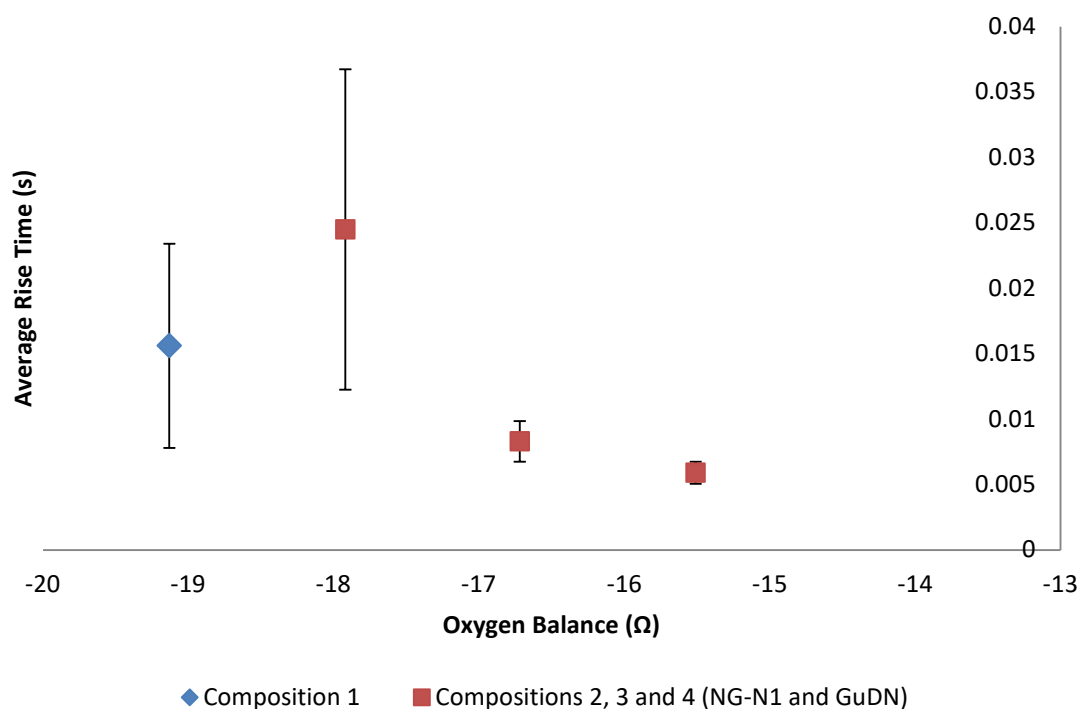


Figure 70: Compositions 1, 2, 3 and 4: oxygen balance vs average rise time (error bars show standard deviation, Appendix 8.10)

The reason why NG-N1 has a positive effect on the ignitability of GuDN is uncertain. However the compound's low melting point and temperature of decomposition are likely to be influential. Firstly the low melting point of NG-N1 (65 °C) may act to increase the low temperature thermal convection in the composition. When heated the NG-N1 turns to liquid and may act as a heat transfer agent. In addition to this, NG-N1 decomposes at approximately 170 °C and so is in effect releasing heat at least 40 °C before GuDN alone would start decomposing. While this temperature of decomposition is substantially lower than outlined in the technical requirements (Table 4 Pg 34) this does suggest that reducing the auto ignition limit (250 °C) might be considered when attempting to thermally ignite a low sensitivity formulation.

The heat of explosion (Q) of NG-N1 may also be significant in improving the performance of the compositions 2, 3 and 4. Upon thermal decomposition in the absence of O₂, NG-N1 releases 6.4 kJ/g, almost twice the heat released by GuDN (Q = - 3.5 kJ/g). Thus NG-N1 contributes a substantial quantity of heat to the decomposition reaction that may aid thermal decomposition of GuDN. Thus NG-N1 may not only

transport heat throughout the sample and decompose more readily but also aid the ignition of GuDN in doing so by effectively magnifying and distributing the heat stimulus provided by the bridgewire.

5.4.4 Compositions 5, 6 and 7

The Effect of Hy5At and Nitrogen Content Enhancement on the Ignition of GuDN

Compositions 5, 6 and 7 failed to show any improvement upon composition 1. As the proportion of Hy5At was increased, the susceptibility of the formulations to ignite and propagate was reduced (Figure 71).

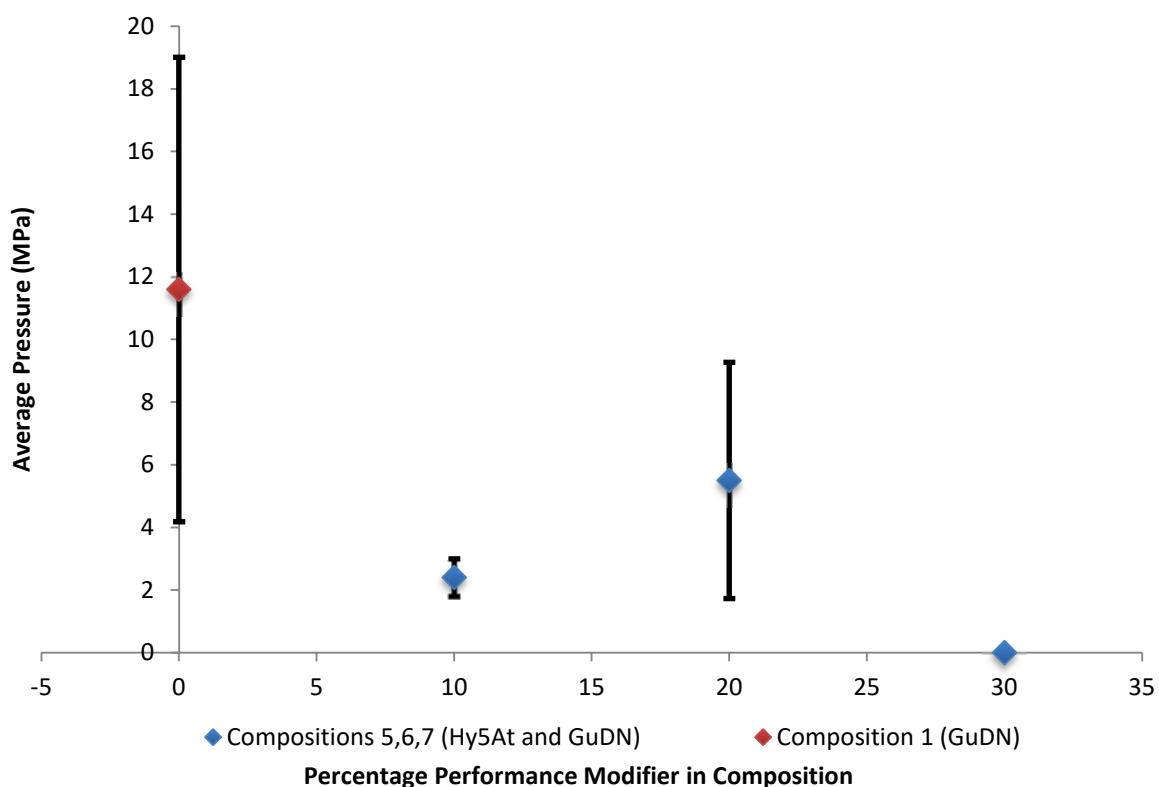


Figure 71: Percentage of Hy5At present in compositions 5, 6 and 7 and its effect on the average pressure output (error bars show standard deviation, Appendix 8.10)

Composition 5 displayed a reduced level of ignitability when compared with composition 1. However composition 6, which contains 20 % by weight of Hy5At, did show some improvement in ignitability but was slower to react to the hotwire stimulus (Figure 72).

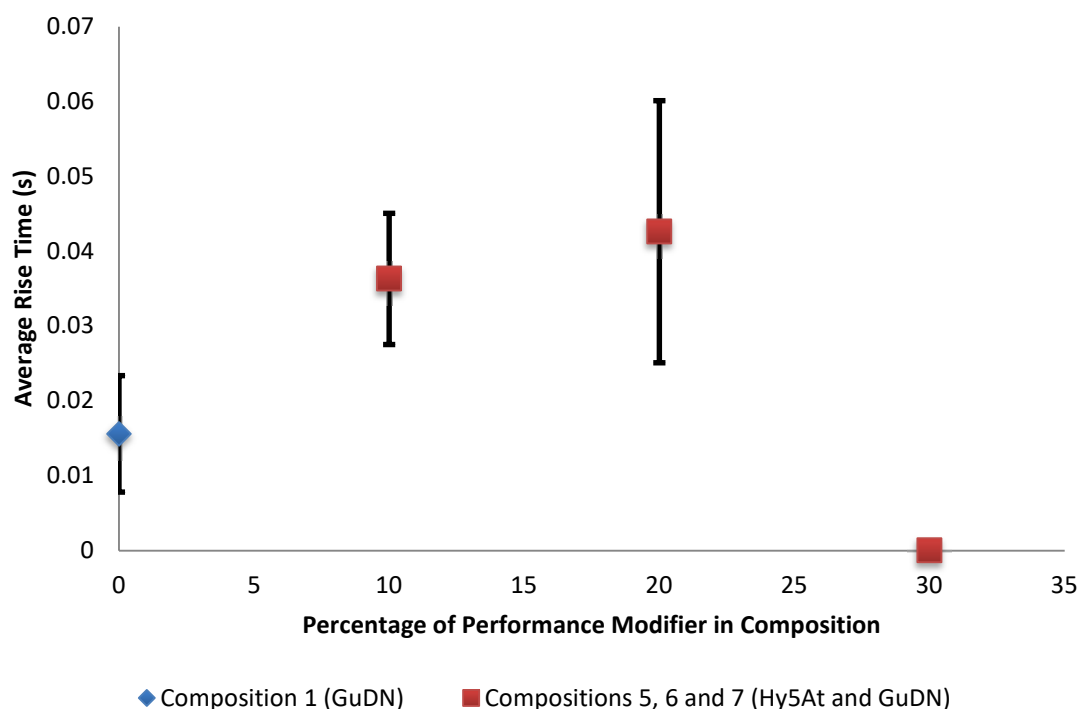


Figure 72: The weight percentage of Hy5At in compositions 5, 6 and 7 and its effect on the average rise time (error bars show standard deviation, Appendix 8.10)

Hy5At is similar in many ways to NG-N1 in that it displays little sensitivity to impact, friction or ESD. When testing both compounds for their impact sensitivity it was observed that both melt when struck. This suggests that heat generated by adiabatic compression of air within the sample is used to change phase rather than effect decomposition. This mechanism is most likely the reason why both compounds display such low sensitivity. In the NG-N1 compositions (2, 3 and 4) it was suggested that the low melting point might increase the thermal conductivity of the formulation as the NG-N1 may act as a heat transfer fluid. Hy5At melts at a higher temperature (118 °C) and decomposes at 186 °C. Therefore, if the heat transfer theory suggested for NG-N1's success was to hold, Hy5At would be expected to also improve the ignitability of GuDN (although to a lesser extent as Hy5At is more thermally stable). The firing results from compositions 5, 6 and 7 obviously contradict this. However there is a vital difference between NG-N1 and Hy5At, which might be key to their effect when mixed with GuDN.

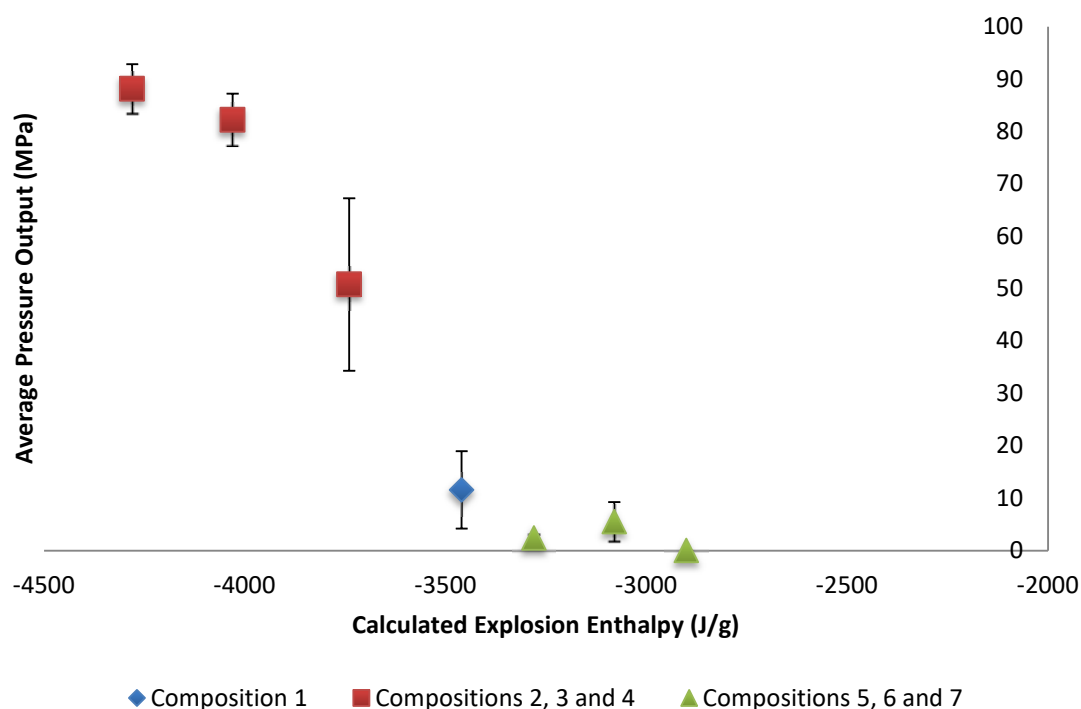


Figure 73: Comparison of the heats of explosion of the compositions including the performance modifiers NG-N1 and Hy5At and the effect on the average pressure output (error bars show standard deviation, Appendix 8.10)^{xxxv}

While NG-N1 possesses an enthalpy of explosion (Q) of - 6.4kJ/g Hy5At releases only 3.2 kJ/g, which is less than the heat released by decomposition of GuDN (Q=-3.5 kJ/g). Thus upon decomposition, Hy5At contributes relatively little to the overall heat released. In this way Hy5At may act as a “heat-sink” absorbing heat energy and decomposing to release a less significant quantity of heat than is required to reliably ignite GuDN. This theory is supported by the failure of any of the squibs filled with composition 7 to register a pressure rise (Figure 73). In the composition 7 squibs the 30% by weight of Hy5At may have absorbed energy from the bridgewire by melting and decomposed to release less heat than is required to thermally ignite GuDN. While this effect is also observed in the 10 % and 20 % Hy5At compositions it is more pronounced at the higher concentration.

^{xxxv} All values of Q quoted were calculated using Hess’s law and assuming decomposition products as predicted by Kistiakowsky Wilson rules.⁴³

5.4.5 Compositions 8, 9 and 10

The Effect of an Energetic Polyphosphazene on the Ignition of GuDN

The firing experiment results for compositions that contain PPZ did not present an improvement compared to composition 1 when considering their potential application as gas-generators in a squib device.

The average rise time observed for compositions 8, 9 and 10 was considerably longer and slower than that of pure GuDN and does not display, as desired, a high level of reproducibility which is reflected in the large standard deviation presented in Figure 74.

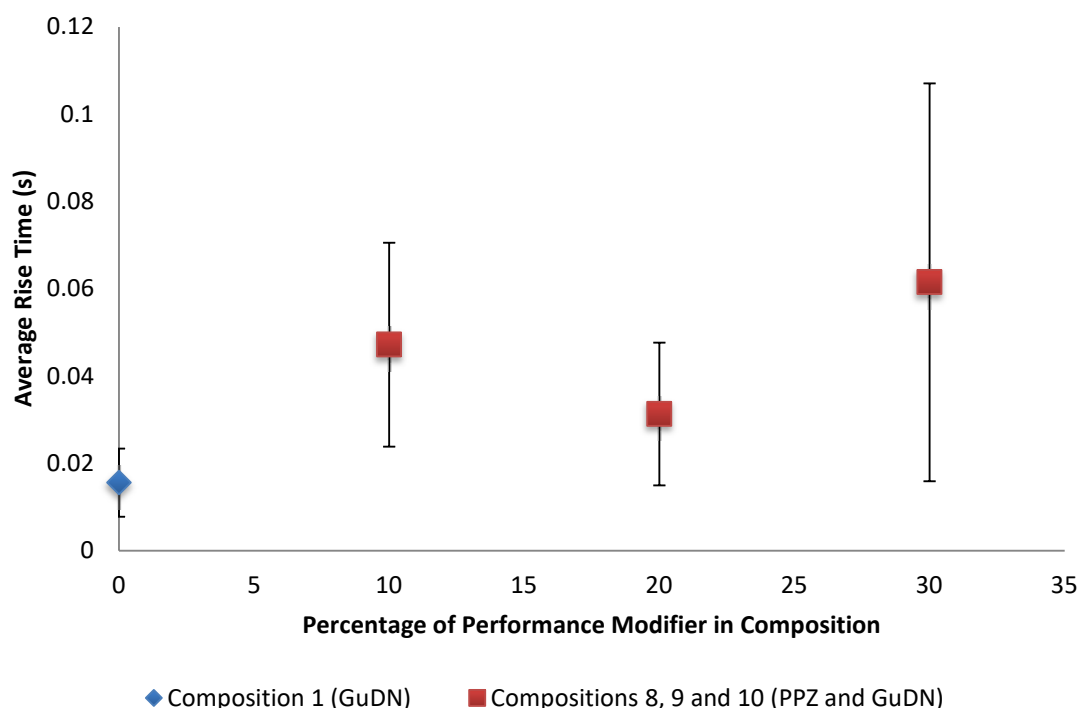


Figure 74: Compositions 8, 9 and 10: average rise time against percentage of PPZ in formulation (error bars show standard deviation, Appendix 8.10)

Conversely the average pressure output for the PPZ compositions does show an improvement upon pure GuDN (Figure 75). However a similar issue is observed with both rise times and pressure output of compositions 8, 9 and 10 in that the reproducibility is not acceptable.

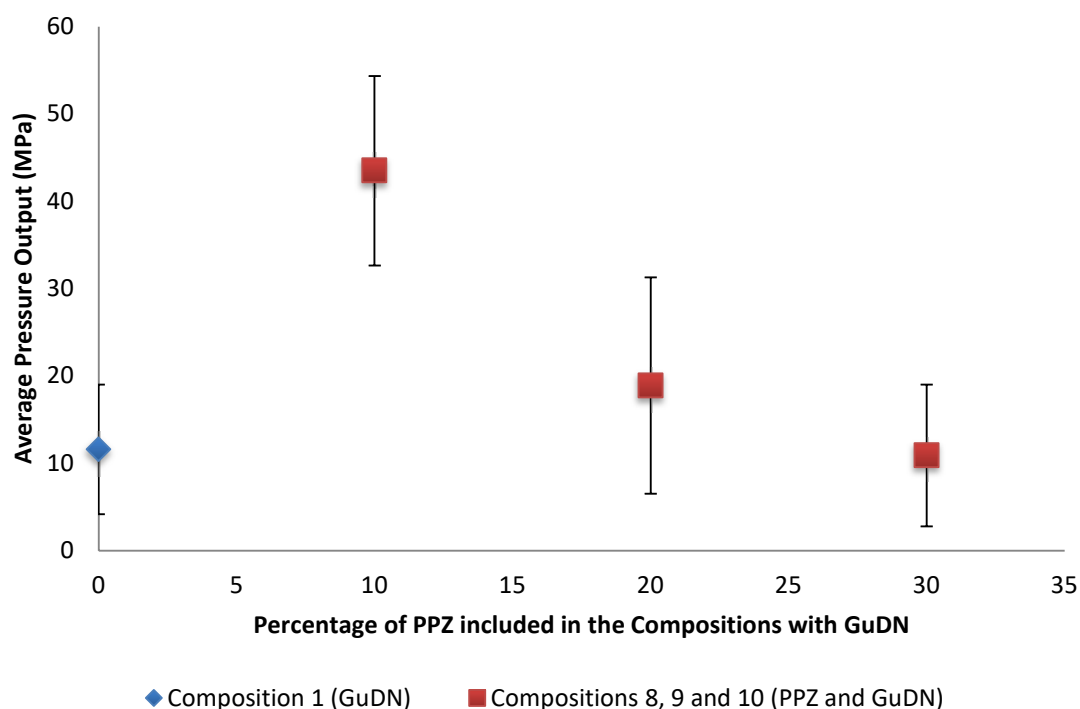


Figure 75: Comparison of the percentages of PPZ included in composition with GuDN and the average pressure output measured (error bars show standard deviation, Appendix 8.10)

The variation in response to the hotwire ignition was evidenced by spurious results observed when firing compositions 9 and 10. Here there were 2 instances where PPZ compositions registered a negligible pressure rise (Firings 9C and 10B – see data included in attached disc) and so were assumed to have misfired. The standard procedure for a misfire was to allow the fired squib to cool for 15 mins before disconnecting it from the pressure bomb. In other misfires the squib would be removed and, in cases where the energetic composition had simply failed to decompose, the aluminium septum would be left intact, as no gas pressure would have been generated to allow for its perforation. In the 2 cases where PPZ compositions yielded a negligible pressure rise the septa were not found intact upon inspection and in both instances decomposed and unburnt particles were visible in the squib and pressure bomb (Figure 76).



Figure 76: Perforated squibs showing signs of decomposition products and light coloured unburnt compositions around the septa (firings 9C and 10B)

As the septa had burst it was possible to assume that a pressure of at least 100 MPa had been generated within the squib volume ($\sim 50 \text{ mm}^3$). As the perforation of the burst disc results in the expansion of the internal volume by 400 % to 250 mm^3 , which would lead to a proportional pressure drop. It was reasoned that in the case of firings 9C and 10B, this reduction in pressure may have extinguished the decomposition reaction. Importantly this pressure reduction is a feature of all of the squib firings but it is only with PPZ, and particularly when it is present in higher concentration (compositions 9 and 10 contain 20 % and 30 % PPZ by weight respectively), that it is observed to limit the ignition and propagation of the compositions.

This slower and less energetic means of decomposition is a feature of polyphosphazene energetic binders, which are capable of fully combusting during a highly energetic decomposition, such as a detonation, but to smoulder and swell to form a foamy char when ignited by lower energy means. Consequently compositions 8, 9 and 10 may require greater impetus to fully ignite and propagate and do not seem fit for use in a hotwire ignited squib as discussed here.

6 Conclusions and Further Work

6.1 Advances

The project has made several advances with respect to the development of a low sensitivity and fast burning gas generating formulation for application in an electro-explosive device (EED) such as a squib.

The project focussed on a specific squib device, which used a primary explosive fill to generating 165 MPa within 0.5 ms when tested in a volume of 0.25 cm³ and ignited by hotwire. By replacing the energetic compound with a novel low sensitivity formulation it was anticipated that a safe alternative could be developed without resulting in a reduction in performance.

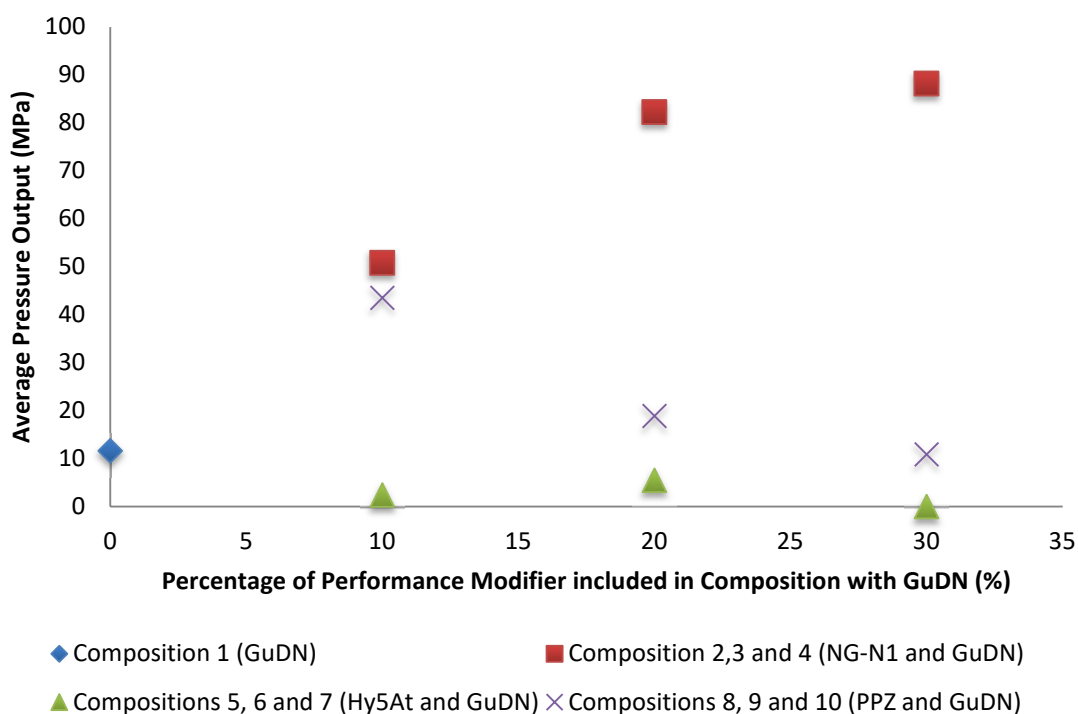


Figure 77: Comparison of the average pressure output from each composition

This target has been partially accomplished in that 50 mg of a novel low sensitivity formulation, namely composition 4, has produced on average 88 MPa. When it is considered that 100 mg of potassium picrate is required to produce 160 MPa, it is clear that the performance of the novel composition is approximately equal in that respect.

However the novel formulations tested have not displayed rise times equivalent with the existing explosive. As of yet the shortest average rise time has been 5.9 ms which is 12 times slower than the rise time of potassium picrate within the generic squib device. However it should be noted that 5.9 ms rise time is comparable with other less exacting devices as seen in airbag igniters, which are required to ignite a gas generating composition on the order of several milliseconds. Therefore It may be possible that composition 4 or a similar formulation could replace the need for a separate igniter and gas generating airbag assembly through its ability to be directly ignited from a hotwire and to effectively evolve hot gas (Figure 77 and Figure 78).

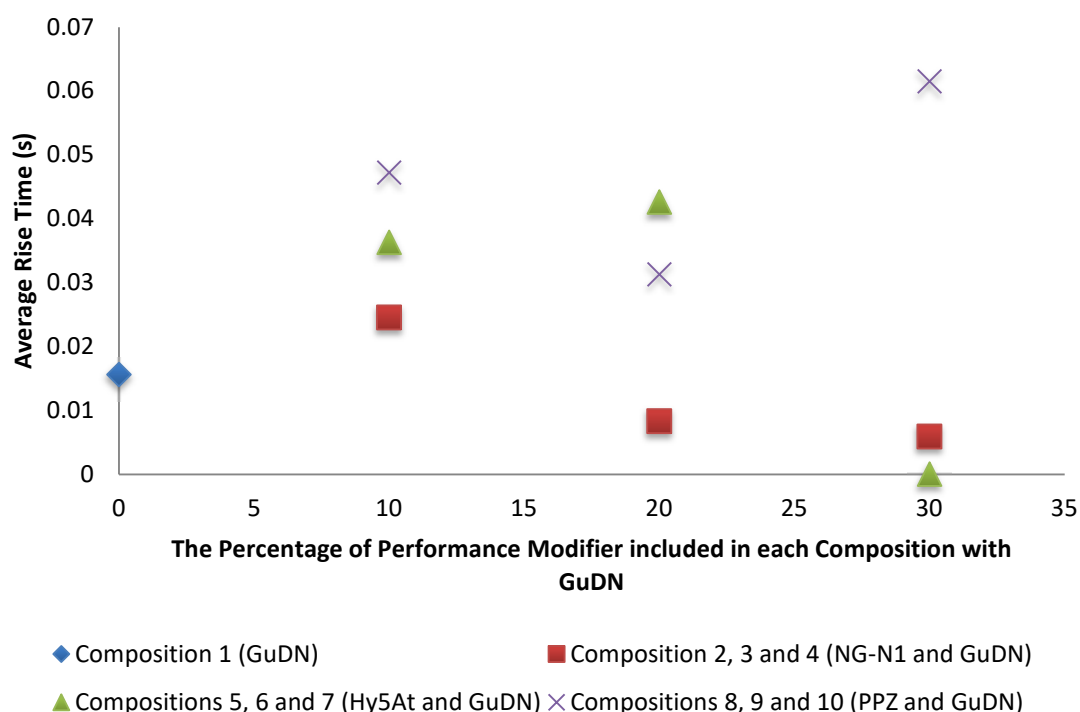


Figure 78: Comparison of the average rise times for each composition

Additionally it has been possible to evaluate the use of low sensitivity PMs in sensitising an insensitive explosive (GuDN) to hotwire ignition. While this strategy requires additional research there is some promise in the results presented here. The strategy itself represents a slight shift in perspective when considering that formulation in explosive science is generally used to mitigate excessive sensitiveness rather than to introduce specific sensitivity.

The means by which an insensitive explosive may be sensitised are still unclear. However from the positive results with composition 3 and 4 it seems likely that a high heat of explosion, which is linked to oxygen balance, is significant in increasing the pressure output and swift propagation of the decomposition reaction.

In the case of high-nitrogen compounds the initial results with Hy5At seem to indicate that these are less effective in increasing ignitability. However it is likely that research into alternative high-nitrogen compounds with greater endothermic heats of formation than Hy5At and therefore higher heats of explosion may revise that assessment due to the huge potential variety of materials.

Furthermore the low melting point of NG-N1 has been suggested to contribute to the ignitability of GuDN by acting as a heat transfer fluid. While this may be the case this theory requires substantial research before it can be confirmed. It is thought that the act of melting to form a liquid within the formulation may allow for the initial thermal conduction to progress into convection using molten NG-N1 as the fluid which heats throughout the sample. This may be verified by measuring the thermal diffusivity of samples of compositions 2, 3 and 4 and comparing them to inert low melting solids in combination with GuDN. The evidence against this theory is that Hy5At also displays a low melting point and that compositions 5, 6 and 7 did not display any improvement in their ignitability. What was observed in the Hy5At compositions was quite the opposite, as the proportion of PM was increased the compositions ceased to respond to the hotwire stimulus, eventually showing a poorer response to ignition than pure GuDN. This suggested that Hy5At might have been preventing ignition in some way. It was thought that this might be via a mechanism analogous to the melting of NG-N1, which was cited as a possible reason for increasing ignitability. The melting of Hy5At may have spread heat effectively throughout the sample but upon the decomposition of Hy5At a relatively small volume of heat was released, not significant enough to ignite GuDN. Thus it was concluded that the NG-N1 proved successful due to a combination of a low melting point and a high heat of explosion.

6.1.1 Energetic Binder – PPZ

Compositions 8, 9 and 10 were successfully ignited in testing however a combination of the large standard deviation in the results and a trend which seemed to show that larger proportions of PPZ lead to a reduction in the speed of ignition and the extent of decomposition would suggest that these formulations are not yet suitable for hotwire ignition as they were generally outperformed by composition 1 (neat GuDN). It may be possible that by applying a higher input energy, these compositions may prove successful as gas-generators however the possible decomposition products such as hydrogen fluoride (HF) and phosphoric acid (H_3PO_4) are highly undesirable and would be difficult to market for applications such as airbag igniters.¹¹⁹ Nevertheless, the less energetic mode of decomposition witnessed in compositions 9 and 10 suggests that there is some promise in these mixtures as IM compliant explosive fills. In the instance of a fire or accidental ignition by any other means a well optimised PPZ:GuDN composition may decompose in the relatively benign manner previously described.

6.2 Limitations of the Research and Further Work

The project provided an insight into alternative formulations for use in squibs. However the research was limited in certain respects and as such there are areas which could be revisited and some which should be looked into which were outside the scope of this project.

The multidisciplinary nature of the research was such that the PMs investigated had to be synthesised. This limited the number of additives made available and ultimately reduced the variation in the formulations tested. As such the conclusions made in regard to oxygen balance, nitrogen content and polymeric additives is limited by the fact that only one example of each was tested. For a greater level of confidence to be granted to the conclusions made herein more control experiments should be carried out e.g. GuDN formulations with non-explosive low melting NG-N1 analogues. Furthermore a wider selection of PMs would allow for more conclusions to be drawn when relating their firing results with physical characteristics such as heat of explosion, oxygen balance, burn rate etc. In addition there would be no requirement for an

insensitive MCE such as GuDN if an insensitive PM compound which exhibited a high oxygen balance or nitrogen content was developed. In this case a high-nitrogen content MCE could be combined with an oxygen rich PM. This combination of materials may then provide a composition with a high enthalpy of explosion, which might ignite more readily than GuDN.

With regards to the quality of the formulations tested it should be noted the quality of the formulations was due to their limited size which was a result of the relatively small quantities of PM available. Therefore to allow the evaluation of the PM at high proportions such as 10, 20 and 30 % it was necessary to reduce the overall mass of the compositions. Thus formulations amounting to no more than a gram in total mass were prepared which satisfied the risk assessment for the preparation of novel compositions. Consequently the homogeneity of the formulations was not equivalent to that achievable for larger scale compositions. In larger formulations it is possible to use mechanical mixing of constituents to improve homogeneity. Instead the comparatively crude method of preparation outlined in section 5.2.1 was used and introduced a degree of inhomogeneity into the formulations. While it was possible to evaluate this inhomogeneity to a limited degree as discussed in section 5.2.2.2, quantitative analysis by CHN or MS would have been preferable. This, however, was not possible due to the absence of CHN or suitable MS apparatus and UN regulations pertaining to the transport of unclassified energetics. UN classification is achieved through hazard characterisation of the explosive formulation; however the required level of characterisation requires several times the mass of each formulation that was prepared for this work. These quantities were not considered safely achievable given the timescale of the project and thus the characterisation of the homogeneity was limited. It may be possible in future research to prepare sufficient formulation for hazard characterisation and UN classification, this will be especially significant once a single composition has been identified and selected for optimisation.

In general the means by which squib formulations react to hotwire stimulus and propagate is determined by analysing the energetic output upon firing. As the squib is simply a small enclosed body much of what is understood of their behaviour has been

inferred by interrogating the output data. As such there is a level of uncertainty when theorising possible means of ignition as suggested for the success of compositions 3 and 4. Thus these theories should be validated by further testing and if possible by experiments either on open bench or in a sealed vessel, as seen in strand burning experiments, where the decomposition products and reaction temperature can be measured through a sapphire window. With this additional data it may be possible to either support or refute the conclusions drawn from the squib firing results reported here.

Finally, any successful formulation produced must then be assessed for its long-term thermal stability as the required lifetime of the product squib is 32 years. Any successful formulation must be shown to be stable and inert in an operational environment for this time period.

6.3 Additional Improvements

This project aimed to improve the safety of a generic squib by solely replacing the energetic material in use. While there has been some success with this strategy it is possible that the generic squib may be improved further by focussing on the construction of the device rather than the chemistry alone.

While hotwire devices are capable of igniting explosives with a relatively small input energy and modest current the output from the bridgewire is similarly small and modest. In general the temperature of a hotwire is approximately 600 °C depending on the material and geometry of the device in use.¹²⁰ Surprisingly this temperature is not capable of directly igniting compounds such as GuDN with an onset temperature of decomposition of 215 °C. However there are devices in the published literature, which use an equivalent or a lower quantity of energy than a traditional bridgewire and are capable of providing a much greater stimulus. The semiconductor bridge (SCB) reported by Baginski et al³⁰ is one such device which is capable of delivering a plasma whose temperature has been shown to be on the order of several thousand degrees Celsius.^{32,33} This stimulus should be capable of igniting the most insensitive of explosives and indeed Professor Baginski confirmed that it was possible to even bring

materials such as PETN to detonation using an SCB.²⁶ Thus it may be possible to ignite a material such as GuDN without the need for PMs or formulation.

7 Experimental

7.1 Nuclear Magnetic Resonance (NMR) Spectrometry

The NMR spectra were recorded at 300 K on a Bruker DPX-250. The chemical shifts are quoted in parts per million (ppm) with reference to tetramethylsilane (TMS) for ^1H and ^{13}C spectra recorded in DMSO- d_6 .

7.2 Differential Scanning Calorimetry (DSC)

The differential scanning calorimetric plots of the synthesised products and squib compositions were recorded on a Mettler TA4000 calorimeter.

7.3 Synthesis of TAGDNAT

7.3.1 Alternative Route to ANTA (Section 5.1.2)¹¹³

To a solution of 3,5-diamino-1,2,4-triazole (1.3 g, 13 mmol) in 30 % hydrogen peroxide (65 ml, 0.8 mol), sodium tungstate (3.5 g, 13 mmol) was added slowly during 1.5 h while the temperature was maintained at 15-20 °C by the use of external cooling. The mixture was stirred at room temperature for 4 h. The reaction mixture was then acidified to pH 6 with the minimum volume of 20 % sulphuric acid. The precipitated compound and known side product N,N'-azoxy-3,3'-bis(5-amino-1,2,4-triazole) was filtered, discarded and the filtrate extracted with ethyl acetate (6 x 25 ml). The combined extracts were washed with water and dried over magnesium sulfate monohydrate. The product 3-amino-5-nitro-1,2,4-triazole (ANTA) was recovered by filtration and rotary evaporation. Yield: 60 %

DSC (10 °C min⁻¹): 243 °C (T_{dec}), ^1H NMR (DMSO- d_6): 6.79 (s, 2.00H $-\text{NH}_2$) and 13.13 ppm (br s, 1H $>\text{NH}$) (Appendix 8.6 Figure 90)

7.3.2 DNAT (Section 5.1.3)¹¹⁵

3-amino-5-nitro-1,2,4-triazole (0.56 g, 4.0 mmol) was dissolved in conc. HCl (10 ml) and heated to 45 °C in a 50ml round bottomed flask. An aqueous solution of potassium

permanganate (0.43 g, 3.0 mmol) heated to 50 °C was added dropwise over 10 min and the reaction mixture heated to 50 °C with stirring for 4 h. The resulting solution was then refrigerated at 0 °C for 12 h and the precipitate isolated by cold filtration. The yellow solid was then dissolved in the minimum volume of boiling water and insoluble impurities were removed by hot filtration. The product was re-precipitated by refrigeration at 0 °C for 12 h and the filtered solid triturated with hot ethanol. Yield: 15 %

¹³C NMR (DMSO-d₆): 155.81 and 163.46 ppm (Appendix 8.6, Figure 91)

7.3.3 TAGDNAT (Section 5.1.4)⁵³

5,5'-dinitro-3,3'-azo-1,2,4-triazole (DNAT) (1 g, 4 mmol) in water (20 ml) was treated with a solution of 1 M sodium hydroxide (8 ml, 320 mmol) at 80 °C. To this yellow solution, triaminoguanidinium hydrochloride (1.1 g, 8.0 mmol) was added and after a few minutes a crystalline precipitate began to form. The reaction was allowed to cool to ambient temperature and then to 5 °C with an ice bath. The product was then filtered, washed with ice-cold water and dried in a dessicator within the confines of a fume hood to yield bis(triaminoguanidinium)-3,3'-dinitro-5,5'-azo-1,2,4-triazolate. The dry explosive was handled behind a blast shield and kept in solution when not in use. Crude yield: 15 %, Total crude yield including all synthetic steps: 1 %^{xxxvi}

DSC (10 °C min⁻¹): 191 °C (T_{dec})

7.4 Hy5At (Section 5.1.5)

97 % 5-Aminotetrazole monohydrate (1.3 g, 12 mmol) was dissolved in water (10 ml) and heated with stirring to 50 °C. 80 % Hydrazine monohydrate solution (0.75 ml, 12 mmol) was added drop wise over 10 min and the mixture was stirred at room temperature for 1 h. The product, hydrazinium 5-aminotetrazolate, was isolated by rotary evaporation and recrystallised from hot ethanol. Yield: 59 %

^{xxxvi} TAGDNAT was not isolated as a pure product at a sufficient scale to consider purification. Thus the product remained impure and so a crude yield was recorded.

DSC (10 °C min⁻¹): 123 °C (m.p.), 186 °C (T_{dec}); ¹H NMR (DMSO-d₆): 5.58 ppm (br s); ¹³C NMR (DMSO-d₆): 160.14 ppm (Appendix 8.6, Figure 98 and Figure 99).

7.5 Synthesis of NG-N1 (Section 5.1.6)⁵¹

7.5.1 Synthesis of Ethyl (2,3-dihydroxypropyl)carbamate

3-Aminopropane-1,2-diol (6.3 g, 69 mmol) was dissolved in a mixture of distilled water (50 ml) and ethyl acetate (50 ml). 97 % Ethyl chloroformate (3.9 g, 35 mmol) was added dropwise while the temperature was maintained at ~0 °C. An additional portion of ethyl chloroformate (3.9 g, 35 mmol) was added simultaneously with 2 M sodium hydroxide (35 ml, 69 mmol) which was prepared from solid NaOH pellets. The mixture was stirred for 4 h at room temperature at which point saturated aqueous sodium chloride (100 ml) was added and the product was extracted with ethyl acetate (6 x 100 ml). The combined organic phases were dried over magnesium sulfate monohydrate. The drying agent was filtered off and the solvent removed by rotary evaporation. The crude product was placed in a 150 ml pear-shaped flask and attached to Vigreux distillation apparatus. The filtration yielded a colourless, viscous oil ethyl 2,3-dihydroxypropylcarbamate (main fraction distilled at b.p. 175 °C, 0.5 mmHg).

7.5.2 Synthesis of Ethyl (2,3-dinitrooxypropyl)(n-nitro)carbamate

Ethyl (2,3-dihydroxypropyl)carbamate (1.5 g, 10 mmol) was added dropwise to nitric acid (5.5 ml, 8.4 g, 130 mmol) which was cooled to -5°C in an ice bath. The reaction was stirred vigorously for 1h while the temperature was maintained at 0-5 °C. The reaction mixture was then poured onto ice (50 g) and the aqueous layer discarded once the mixture had melted. The yellow oil was neutralised with saturated aqueous sodium bicarbonate (100 ml) and the product was extracted with diethyl ether (6 x 100 ml). The organic phase was washed with water (100 ml) and dried over magnesium sulfate monohydrate. The product, ethyl 2,3-bis(nitrooxy)propyl(nitro)carbamate, was isolated by rotary evaporation.

7.5.3 Aminolysis of Ethyl (2,3-dinitrooxypropyl)(n-nitro)carbamate to synthesise NG-N1

Ethyl (2,3-dinitrooxypropyl)(n-nitro)carbamate (1.6 g, 5.4 mmol) was dissolved in diethyl ether (30 ml) and cooled in an ice bath to 0 °C. Gaseous ammonia was bubbled through the solution for 10 min. The reaction mixture was extracted with water (2 x 50 ml) and the aqueous phase acidified to pH 3 using conc. HCl using methyl orange. The organic products were extracted with DCM (3 x 40 ml) and dried over magnesium sulfate monohydrate. The solvent was removed by rotary evaporation and the product, n-nitro-2,3-dinitrooxypropan-1-amine, recrystallised from hot chloroform. Combined Yield: 30 %

DSC (10 °C min⁻¹): 65 °C (m.p.), 176°C (T_{dec}); ¹H NMR (DMSO-d₆): 3.71 – 3.74 (dd, 1H, CH), 3.77 – 3.80 (dd, 1H, CH), 4.75 – 4.80 (dd, 1H, CH), 4.92 – 4.98 (dd, 1H, CH), 5.57 – 5.63 (m, 1H, CH) and 12.36 ppm (s, 1H, NH); ¹³C NMR (DMSO-d₆): 43.33, 70.09 and 76.45 ppm (Appendix 8.6 and Figure 96 and Figure 97).

7.6 Small Scale Characterisation and Chemical Compatibility (Section 5.2.2.1)

7.6.1 Direct Impact: Steel Hammer on Steel Anvil

A small sample of the composition (~5 mg) was placed on the flat side of a cylindrical steel anvil and struck 10 times with force by the flat side of a steel hammer. Between each blow the sample was evaluated for signs of decomposition (Figure 83).

7.6.2 Glancing Blow: Steel Hammer on Steel Anvil

A small sample of the composition (~5 mg) was placed on the flat side of a cylindrical steel anvil and struck with a glancing blow by the curved edge of a steel hammer. Between each blow the sample was evaluated for signs of decomposition (Figure 84).

7.6.3 Small Scale and Large Scale Electrostatic Discharge

A sample of the composition was placed into the aperture of the nylon spark test strip and sealed with copper tape. The sample was positioned under the terminals of the ESD testing apparatus and a spark of 0.45 J was discharged through the composition.

The copper tape was inspected for bulging or perforation and the sample for discolouration, charring or obvious signs of decomposition (Figure 86 and Figure 87).

7.7 Bridgewire Resistance (Section 5.3.5)

A circuit consisting of an ammeter and voltmeter in series with a stabilised dc power supply was constructed with a spring loaded connector terminal included. The test bridgewire was connected to the terminals and completed the circuit. By using a low voltage (approx. 25 mV) and low current (25 mA) it was possible to test the bridgewires when combined with the compositions in the squib body. These were connected to the circuit behind a safety screen and in a fumehood to protect from the unlikely event of an ignition.

8 Appendix

8.1 Generic Squib

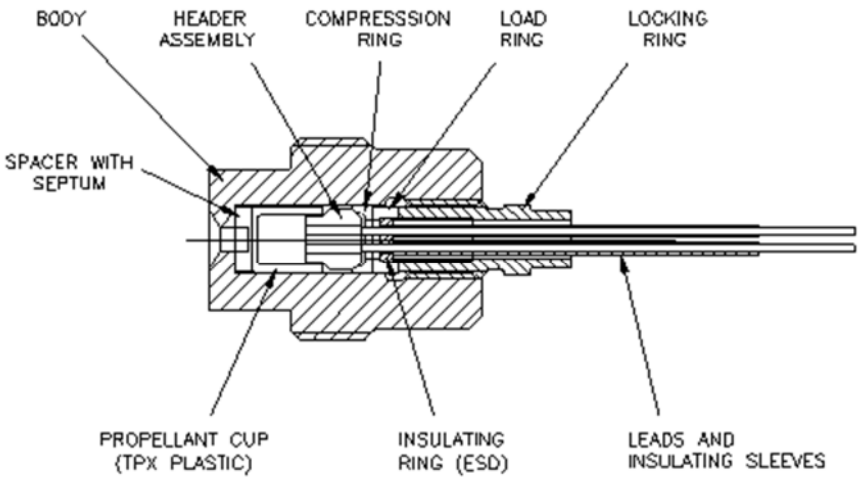


Figure 79: Diagram of the project squib

8.2 Compositions

Composition Number	Percentage GuDN (%)	Performance Modifier	Performance Modifier (%)	Oxygen Balance (%)	Nitrogen Content (%)
1	100	N/A	N/A	-19.13	46.86
2	90	NG-N1	10	-17.92	44.65
3	80	NG-N1	20	-16.72	42.44
4	70	NG-N1	30	-15.51	40.23
5	90	Hy5At	10	-24.34	50.49
6	80	Hy5At	20	-29.55	54.11
7	70	Hy5At	30	-34.76	57.73
8	90	PPZ	10	-24.35	43.44
9	80	PPZ	20	-29.58	40.02
10	70	PPZ	30	34.81	36.60

Figure 80: Composition constituents

8.3 Small Scale Characterisation Equipment



Figure 81: Steel hammer



Figure 82: Steel anvil



Figure 83: Example of direct blow steel hammer on steel anvil



Figure 84: Example of glancing blow steel hammer on steel anvil

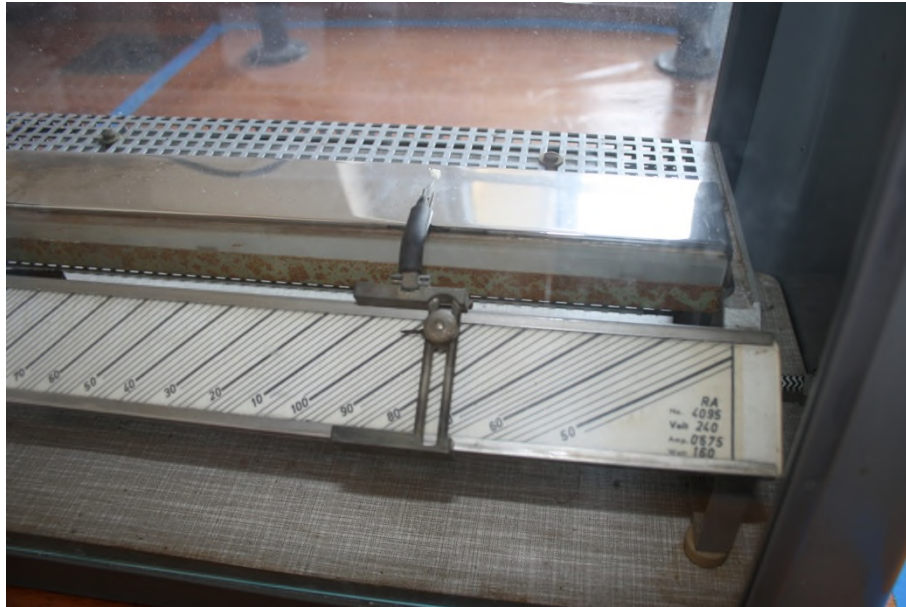


Figure 85: The Kofler hotplate for isothermal storage @100 °C for 1 h

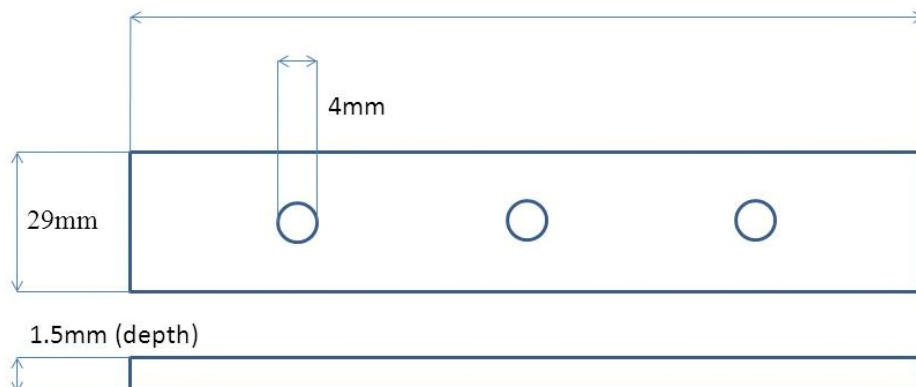


Figure 86: Small-scale spark test strip

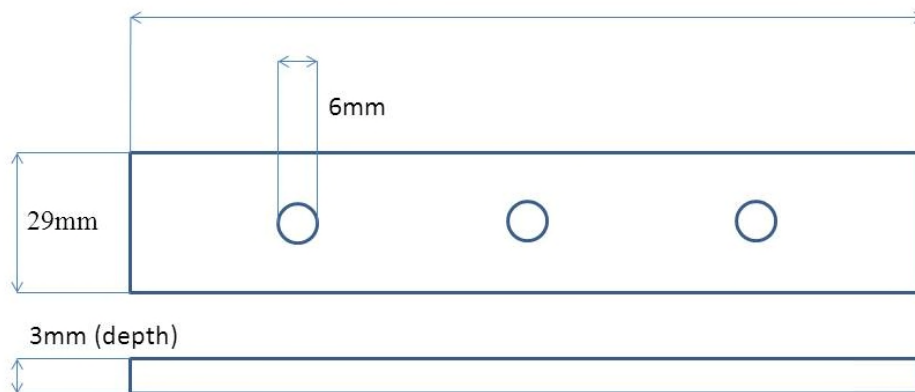


Figure 87: Large-scale spark test strip

8.4 Squib Testing Setup

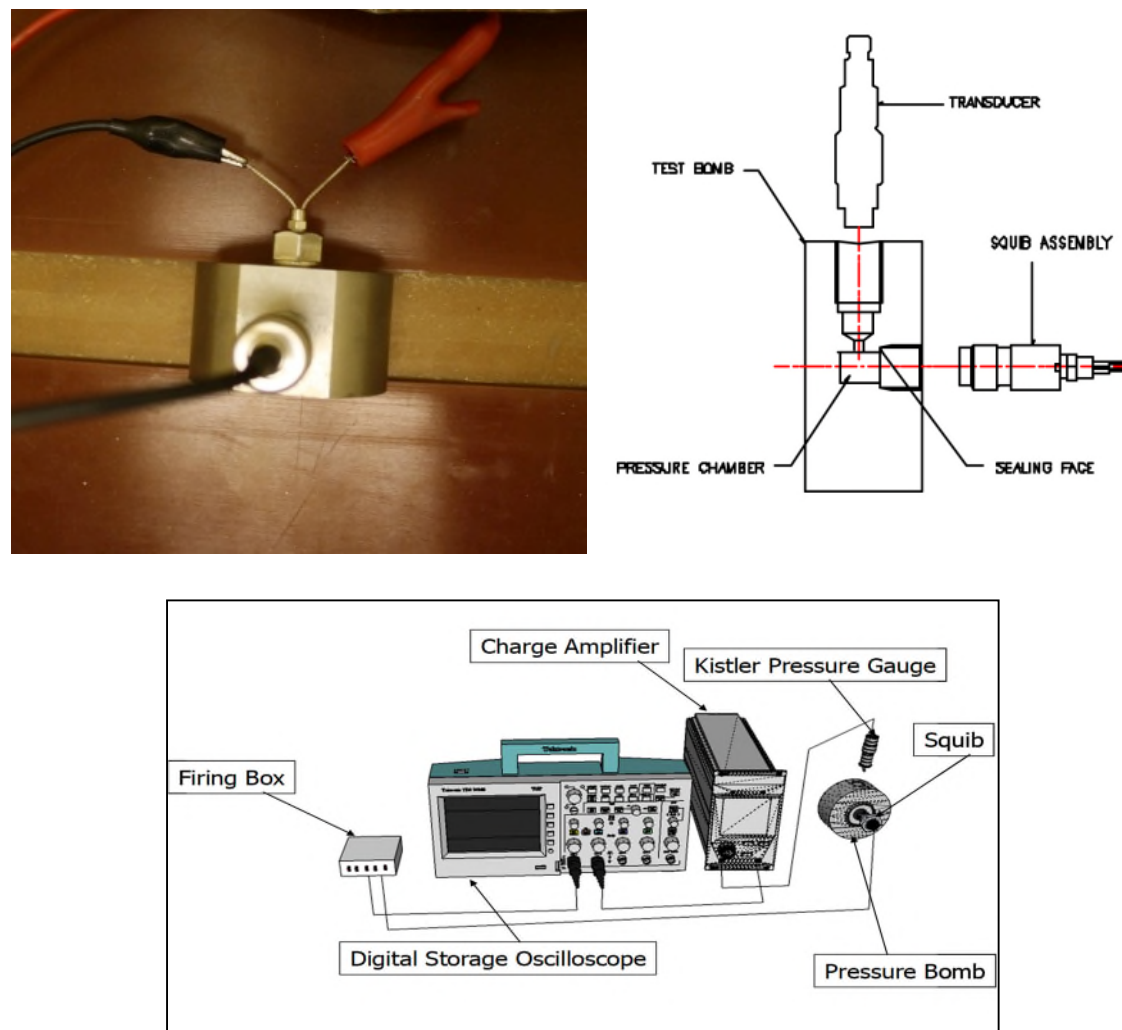


Figure 88: Clockwise from top-left: A photograph of the assembled pressure bomb and squib, a diagram of the pressure bomb assembly and the entire experimental apparatus

8.5 Performance Modifiers

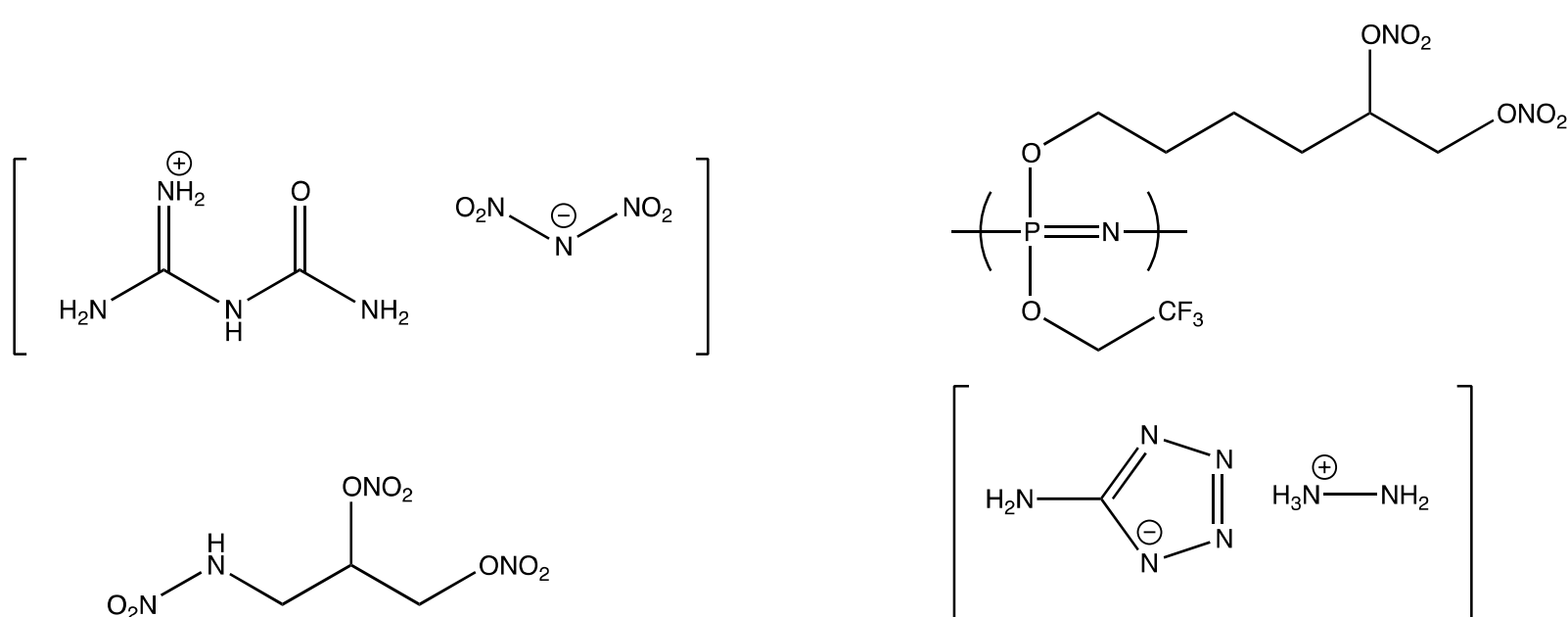


Figure 89: The energetic materials (clockwise from top left) GuDN, PPZ, NG-N1 and Hy5At

8.6 Enthalpy and Activation Energy

When measuring the enthalpy of decomposition it is common to utilise bomb calorimetry to measure the internal energy change and convert to the enthalpy. In a case where the products and reactants are solids and liquids the conversion is slight due to the relatively small molar volumes of the components present however in a combustion reaction, where the majority of the products are gases the conversion is more marked and is calculated as shown below.

$$\Delta H = \Delta U + \Delta nRT$$

Equation 11: Enthalpy [where ΔH = enthalpy change (kJ), ΔU = internal energy change (kJ), Δn = change in the number of moles of gas, R = the ideal gas constant and T = the temperature]¹²¹

When quantifying the activation energy of a decomposition reaction it is common to apply the Arrhenius equation to experimental data. In general a plot of the natural log of the rate vs. the inverse of the temperature yields values for both the pre-exponential factor and E_A (Equation 12).^{122,121}

$$k = Ae^{\left(\frac{-E_A}{RT}\right)}$$

Equation 12: Arrhenius equation [where k = rate of the decomposition reaction, A = the pre-exponential factor, E_A = activation energy, R = the ideal gas constant and T = the temperature]¹²¹

8.7 Nuclear Magnetic Resonance (NMR) Spectroscopy

8.7.1 Fundamental NMR Theory

NMR is one of the most significant characterisation methods available to organic chemists. The technique operates through the interaction of atomic nuclei with an applied magnetic field. Upon application of this magnetic field the nuclei tend to align themselves either with or against the field and as such are split by an energy difference (ΔE) where the higher energy nuclei are positioned against the field. It is possible to excite the nuclei from alignment with the field to alignment against the field by application of an electromagnetic frequency defined by Planck's expression.

$$E = h\lambda$$

Equation 13: Planck's relationship [where E = The energy gap between the with and against states, h = Planck's constant ($6.626 \times 10^{-34} \text{ m}^2 \text{ kg s}^{-1}$) and λ = the frequency (Hz)]

As the nuclei "relax" from being positioned against the field to with the field they emit a photon whose frequency is equivalent to the energy required to induce the initial excitation. In proton (^1H) NMR this figure is typically around 100 MHz (in the radio frequency) depending on the field strength of the magnet used (100 MHz is the frequency when a 2.35 tesla magnet is used).

When protons are bound in a molecule they experience the electronegativity of the atoms that they are bonded to. This leads to the "de-shielding effect" where electron density is attracted away from the ^1H nuclei. This de-shielding results in a very slightly higher energy gap between the two states of alignment that is unique to the chemical environment experienced by the nuclei. By quantifying this energy difference which is measured in Hz, or more formally ppm, it is possible to predict the chemical environment and location of a nuclei in a molecule. NMR is used with a large variety of nuclei but most commonly with ^1H and ^{13}C and as such is valued highly by organic chemists.^{xxxvii}

^{xxxvii} For more information on NMR there are a large number of texts available, in particular "NMR in Chemistry: A Multinuclear Introduction" by William Kemp provides a detailed introductory explanation of the technique.^{123–125}

8.7.2 NMR Spectra

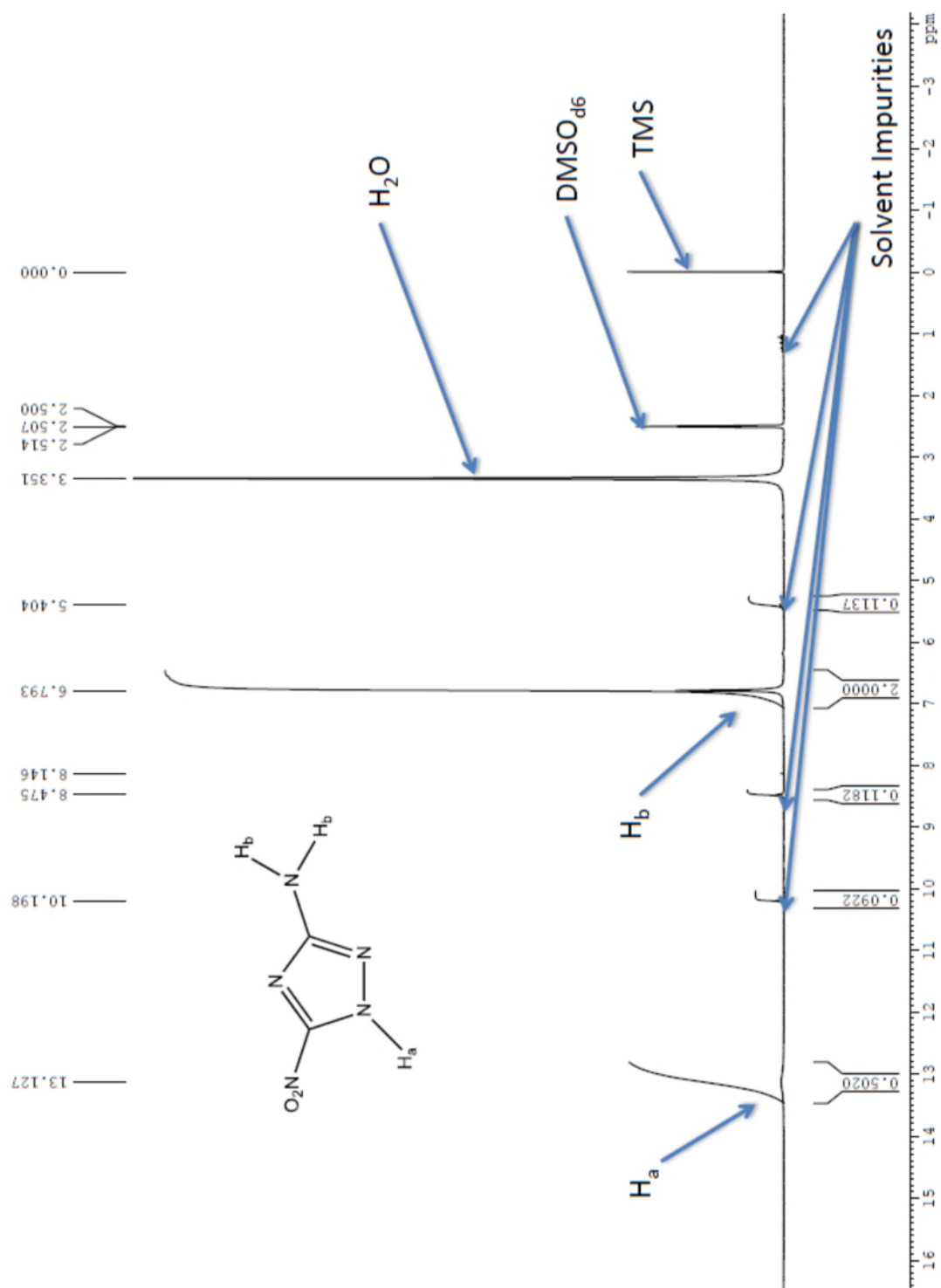


Figure 90: ^1H spectra of ANTA in DMSO-d_6

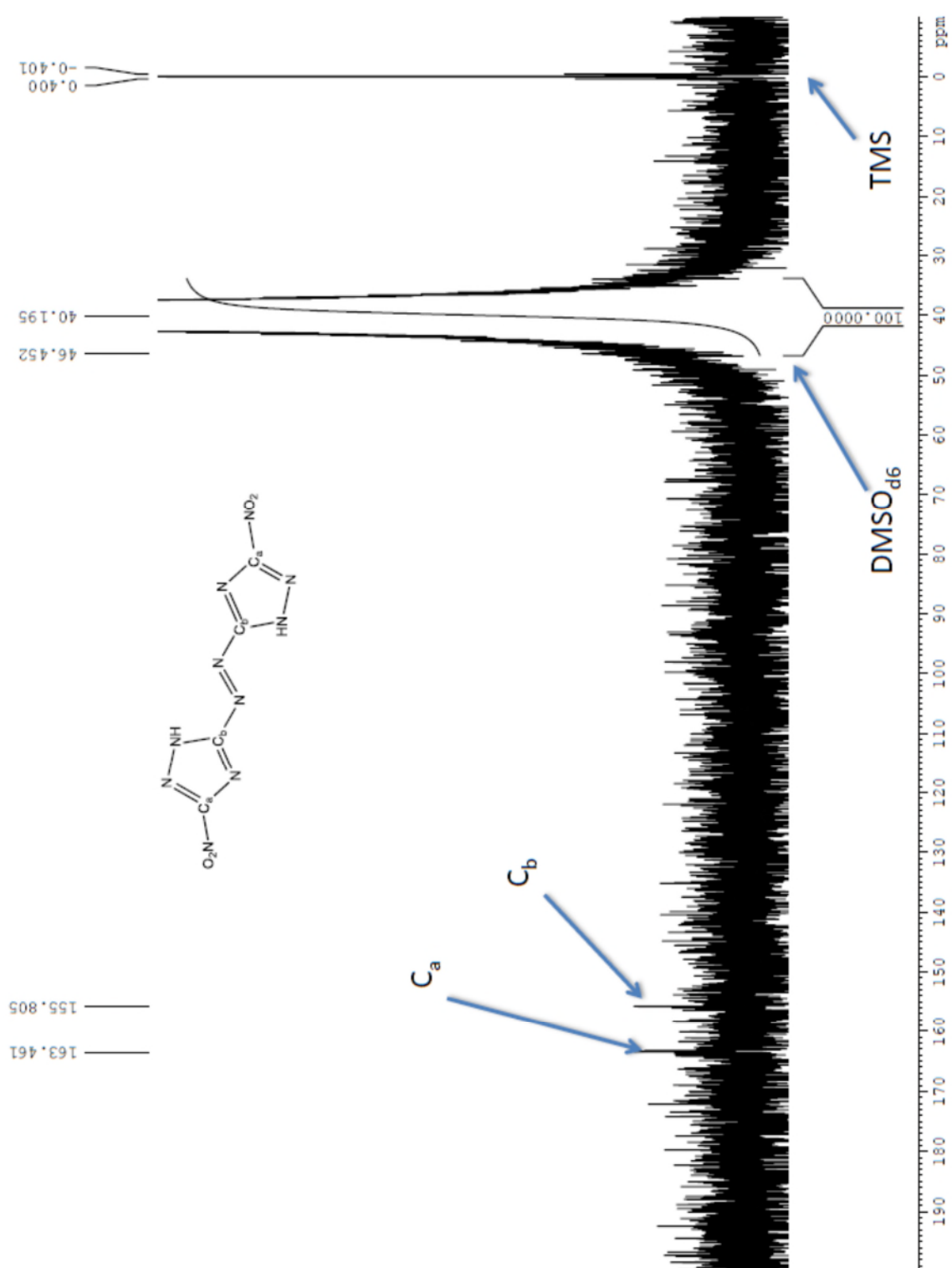
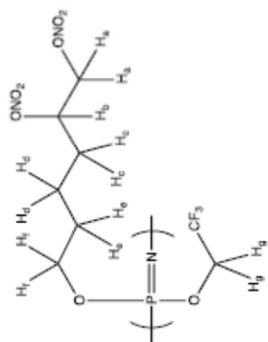


Figure 91: ^{13}C spectra showing weak signals of DNAT in DMSO-d_6



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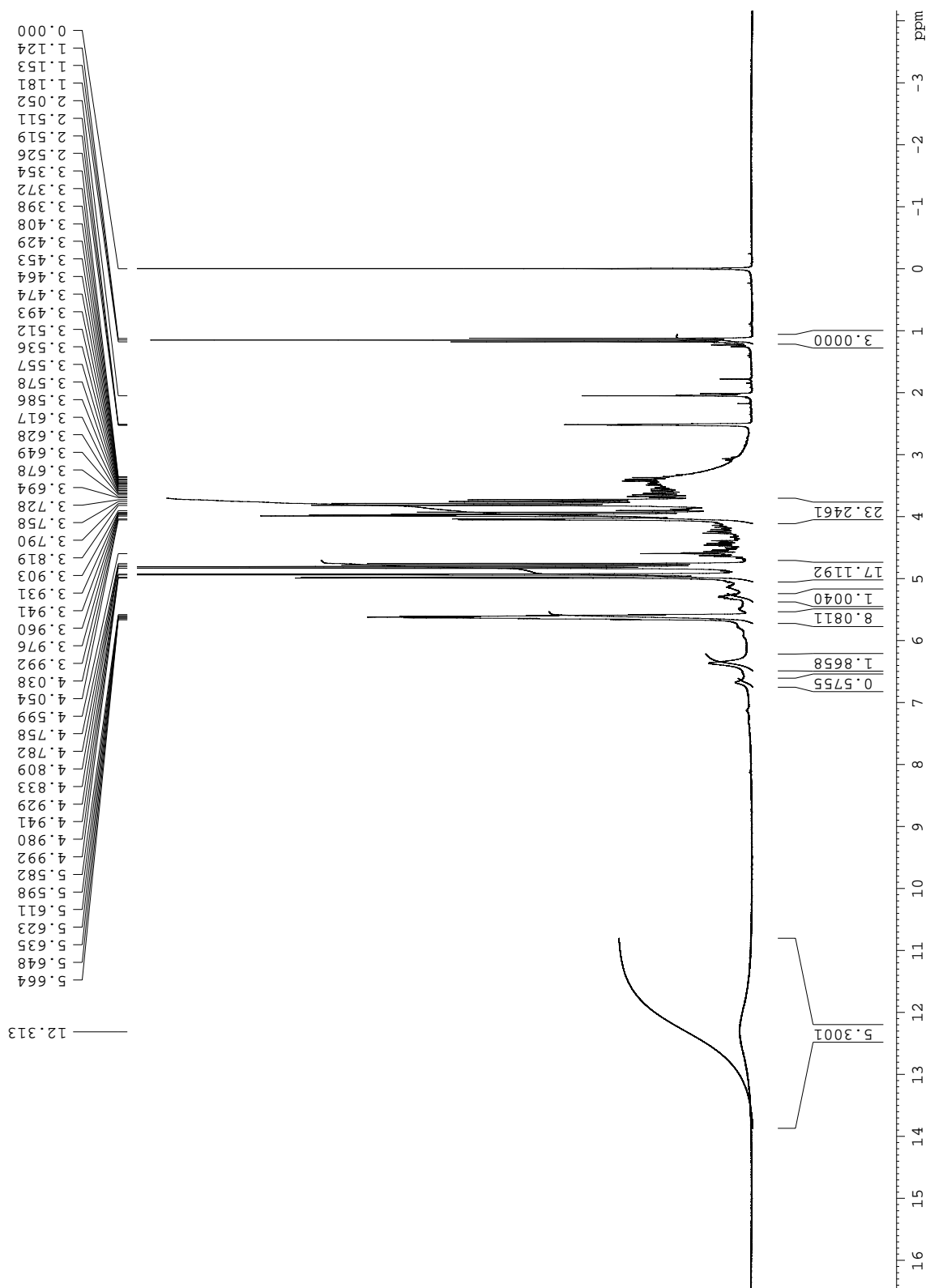


Figure 93: ^1H of NG-N1 (contaminated with ethyl carbamate) in DMSO-d_6 (see Figure 94, Figure 95 and Figure 96 for individual spectra of NG-N1 and ethyl carbamate)

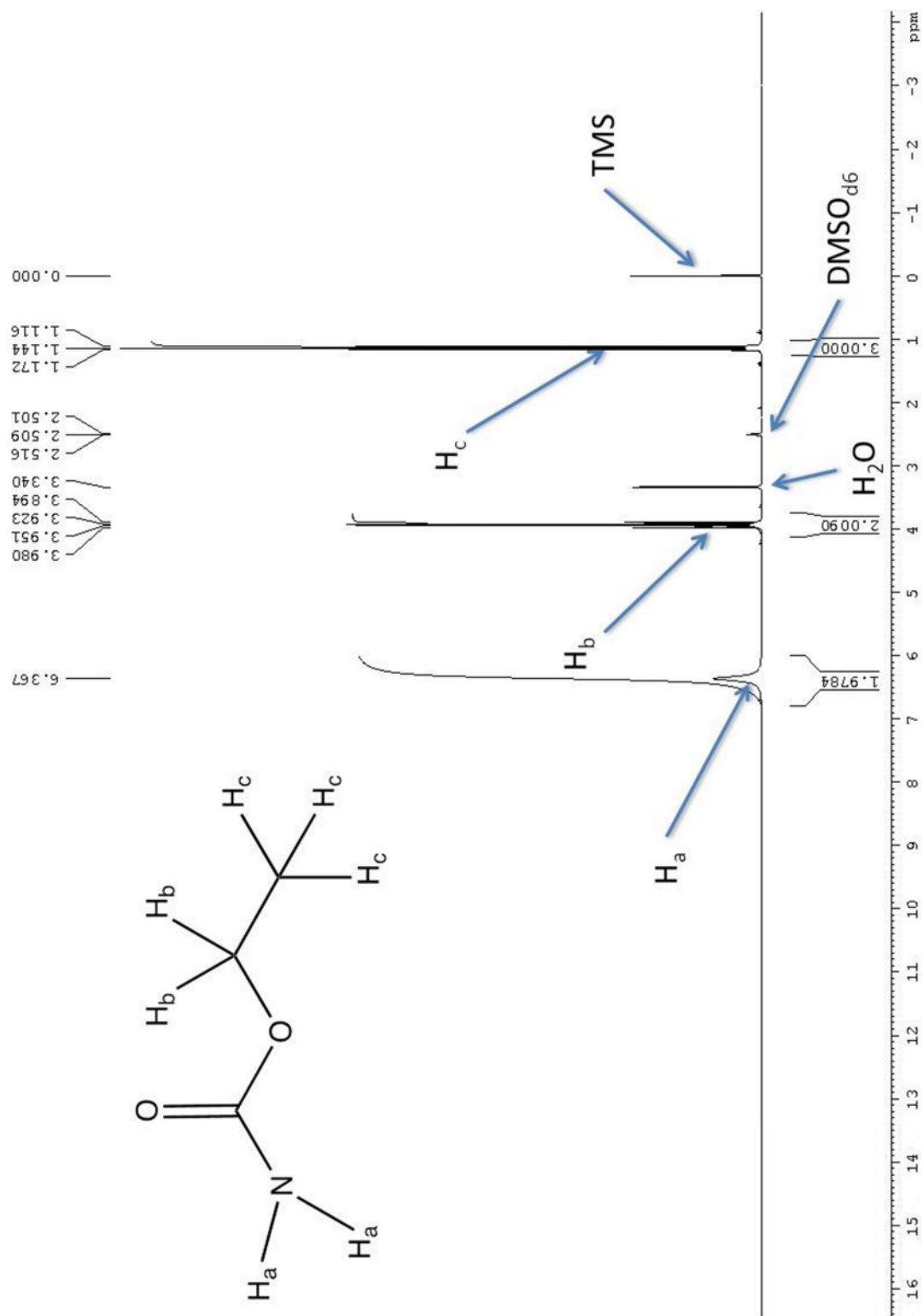


Figure 94: ¹H spectra of ethyl carbamate (collected from the neck of the rotary evaporator) in DMSO-*d*₆

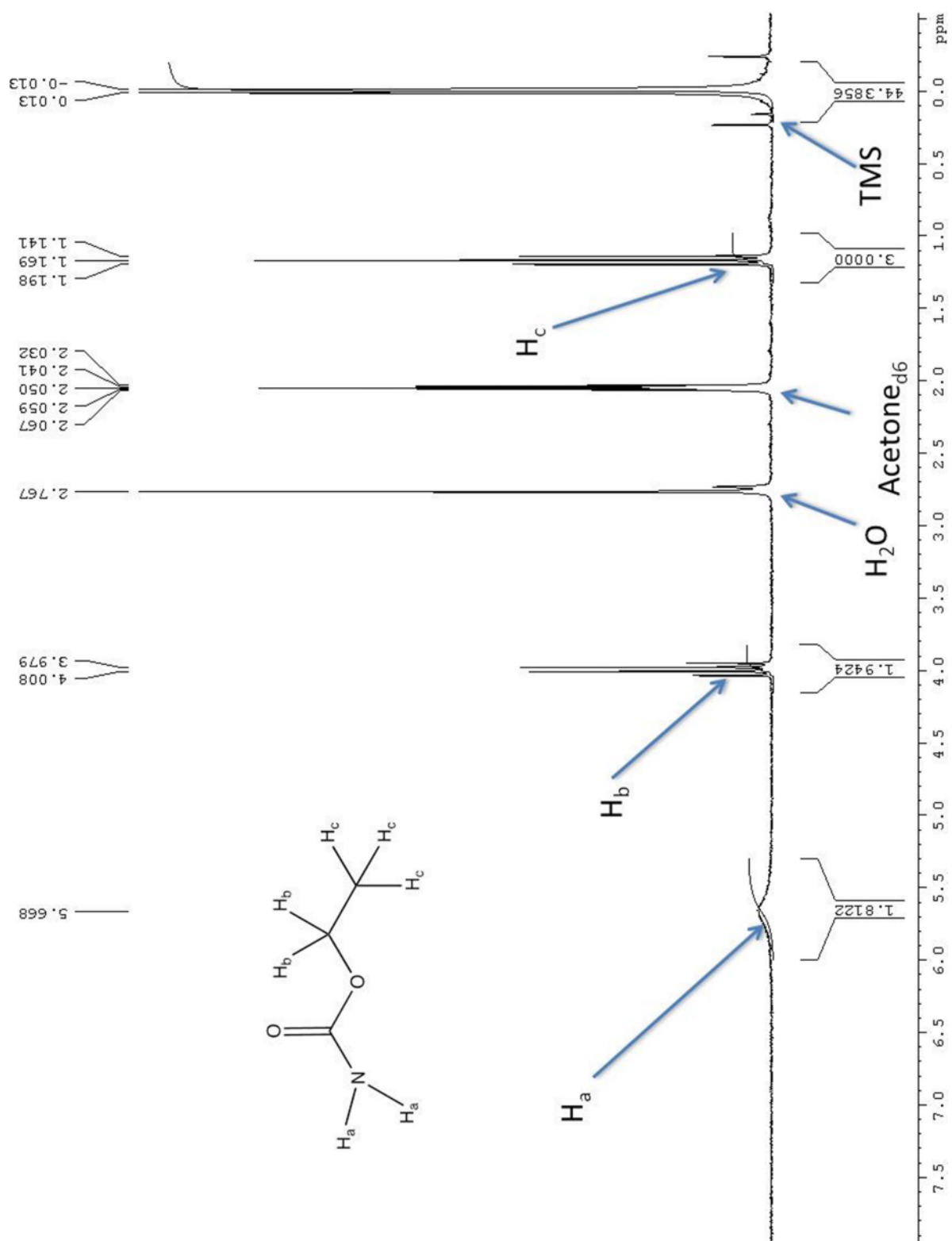


Figure 95: ¹H spectra of ethyl carbamate (synthesised) in Acetone-d₆

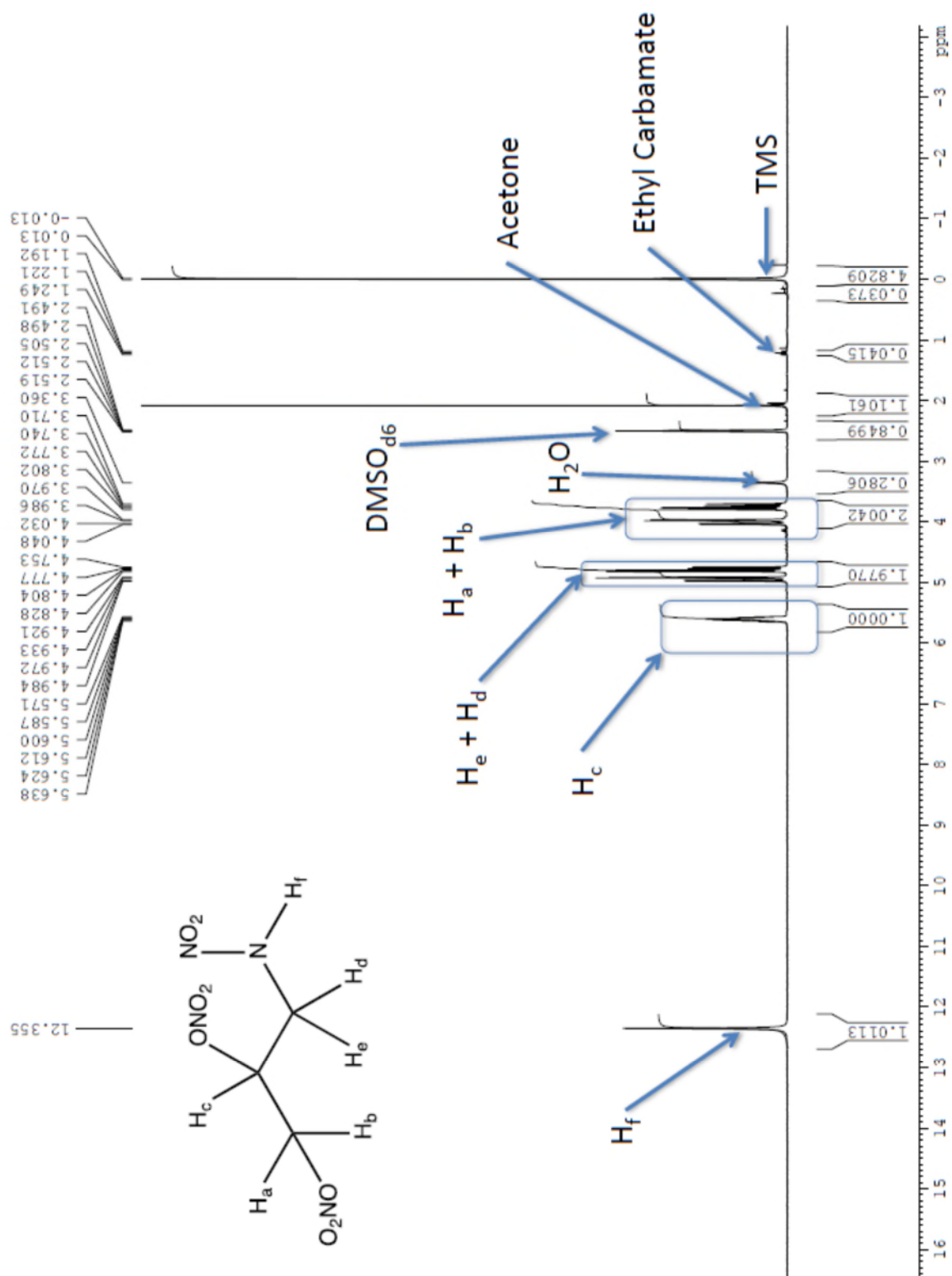


Figure 96: ¹H spectra of NG-N1 in DMSO-d₆

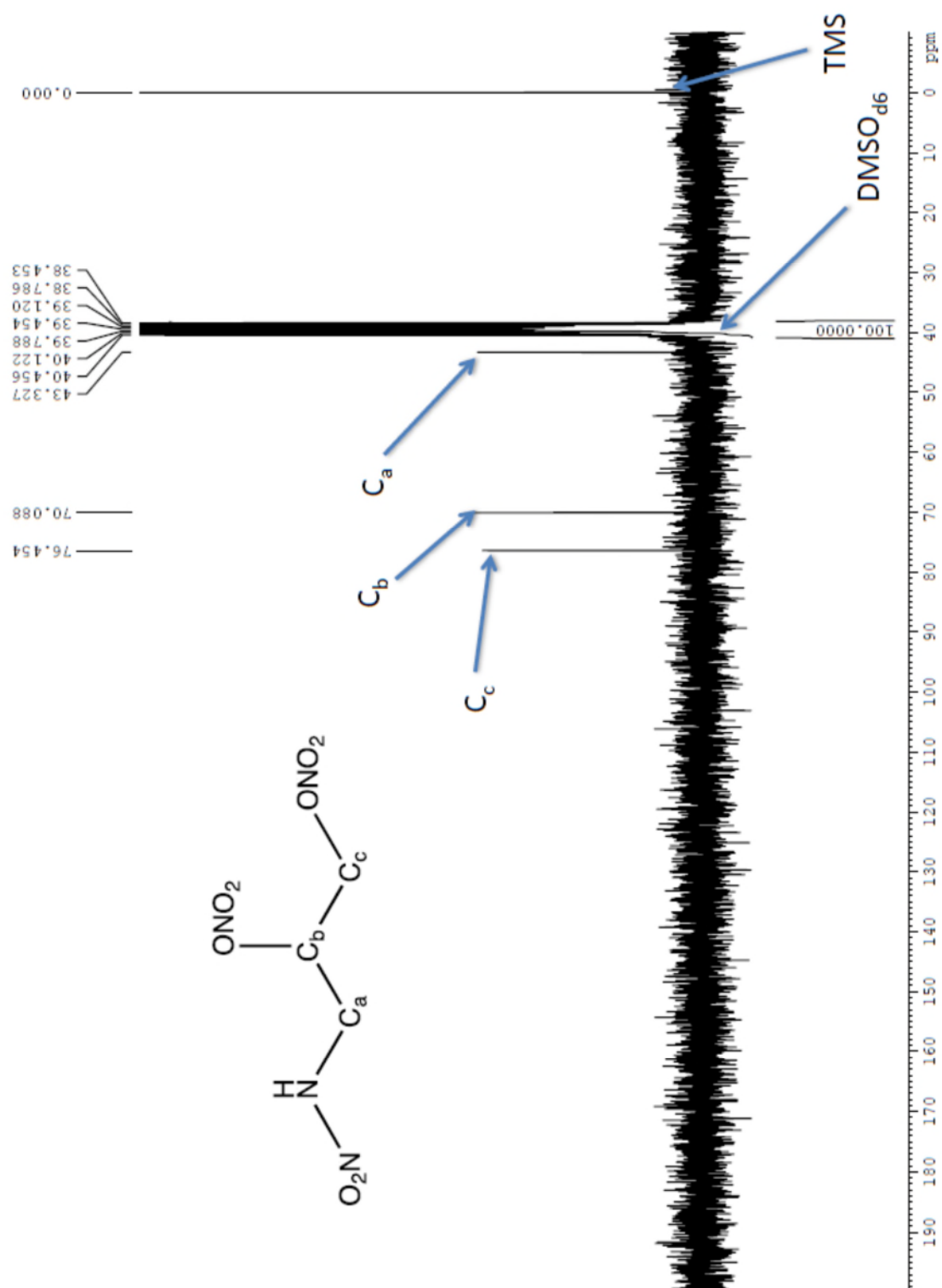


Figure 97: ^{13}C spectra of NG-N1 in DMSO-d_6

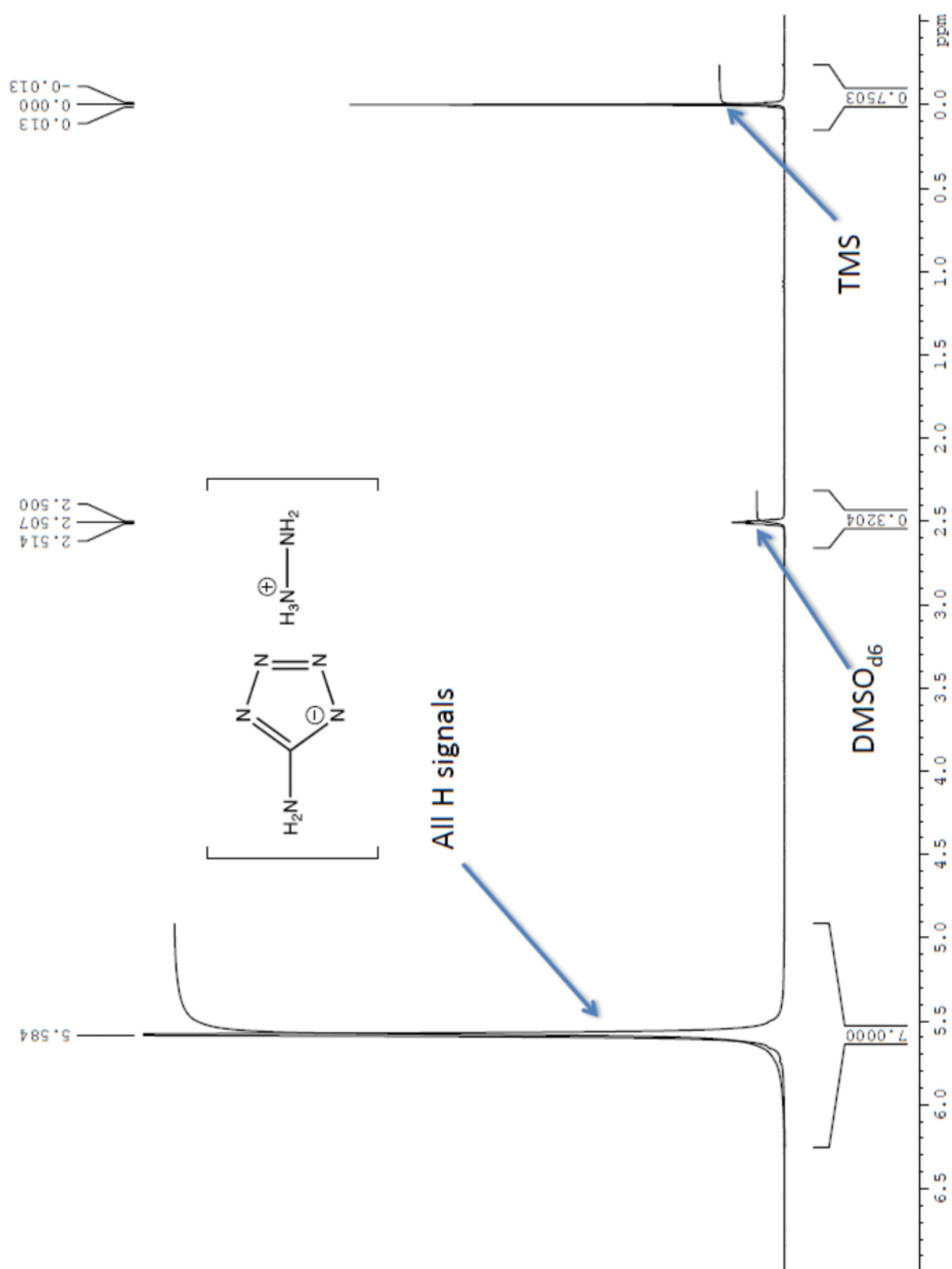


Figure 98: ^1H spectra of Hy5At in DMSO- d_6

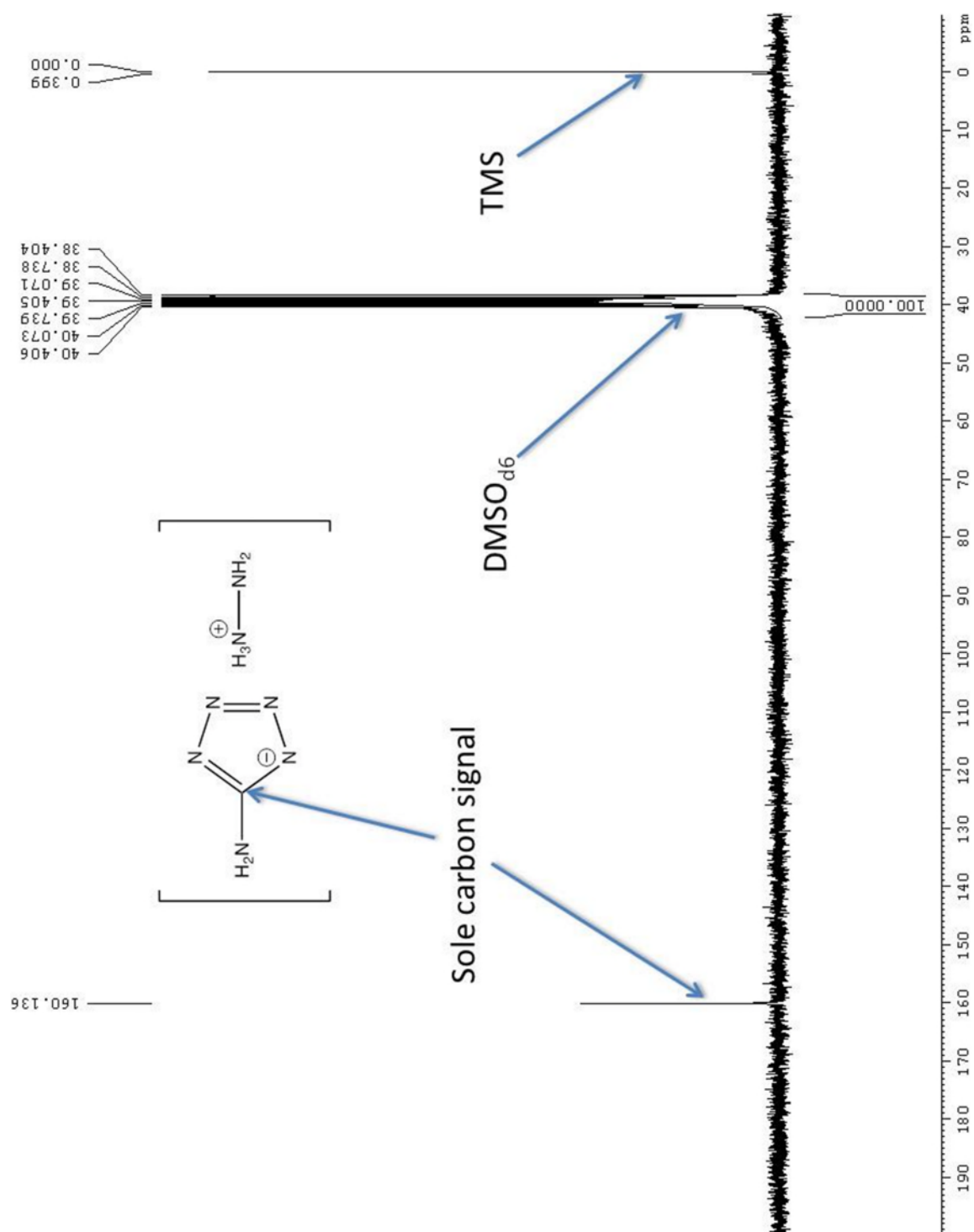


Figure 99: ¹³C spectra of Hy5At in DMSO-d₆

8.8 Differential Scanning Calorimetry (DSC)

8.8.1 Fundamental DSC Theory

In the simplest terms, differential scanning calorimetry (DSC) is a measure of the uptake and release of heat by a sample. DSC apparatus are grouped in two main families, heat flux and power compensated, all DSCs measurements reported here were recorded using a heat flux calorimeter.

The heat flux calorimeter consists of a sample and reference located in an oven and heated identically over a given time. During the temperature program, the heat flux (energy required) to heat the reference and the sample to the same temperature is recorded and the difference measured. Any excess heat observed is recorded as an exothermic event such as an energetic decomposition and any deficit in energy is recorded as an endothermic event as would be observed upon the solid sample melting. By measuring the sample mass prior to the experiment it is possible to gain energy values for the thermal decomposition per unit mass of the sample tested.¹²⁶

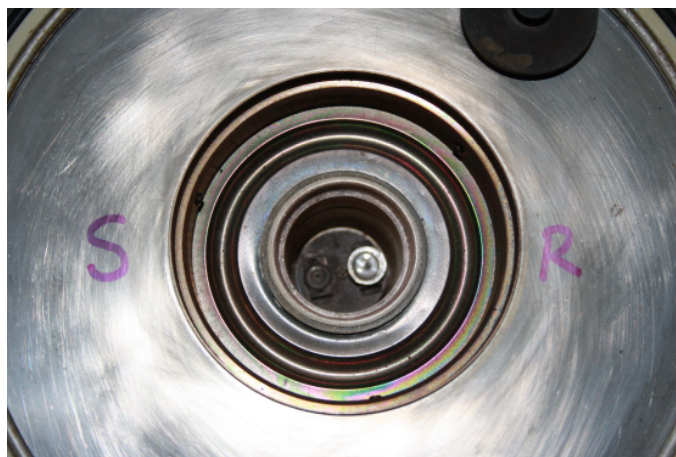


Figure 101: Image of the differential scanning calorimeter furnace (DSC) showing the sample holder (on left) and reference sample (on right)¹²⁶

8.8.2 Use of DSC Thermograms

In this work the measurement of melting and decomposition temperatures was necessary for the assessment of the purity and stability of the materials studied. Additionally repeated measurements of these values from each composition were used to provide an indication of the homogeneity of the mixtures. The DSC thermograms recorded during this work have been included in section 8.8.3 and an annotated thermogram is included for clarity in Figure 102.

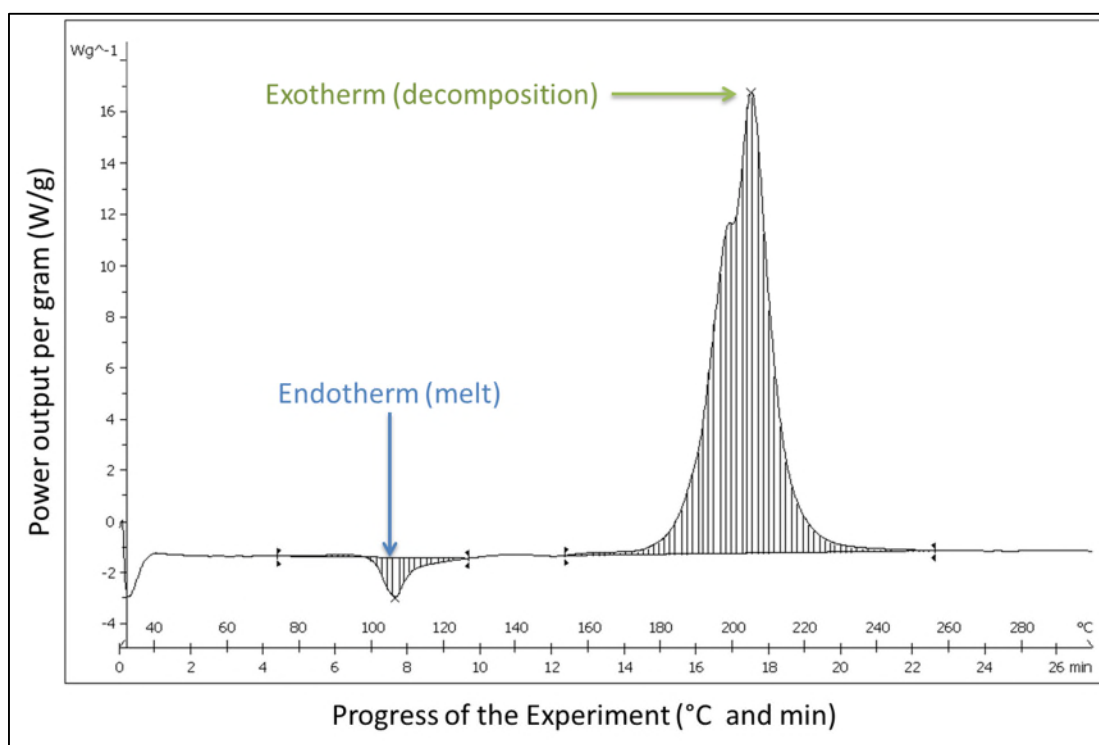


Figure 102: Idealised DSC Thermogram

8.8.3 DSC Thermograms

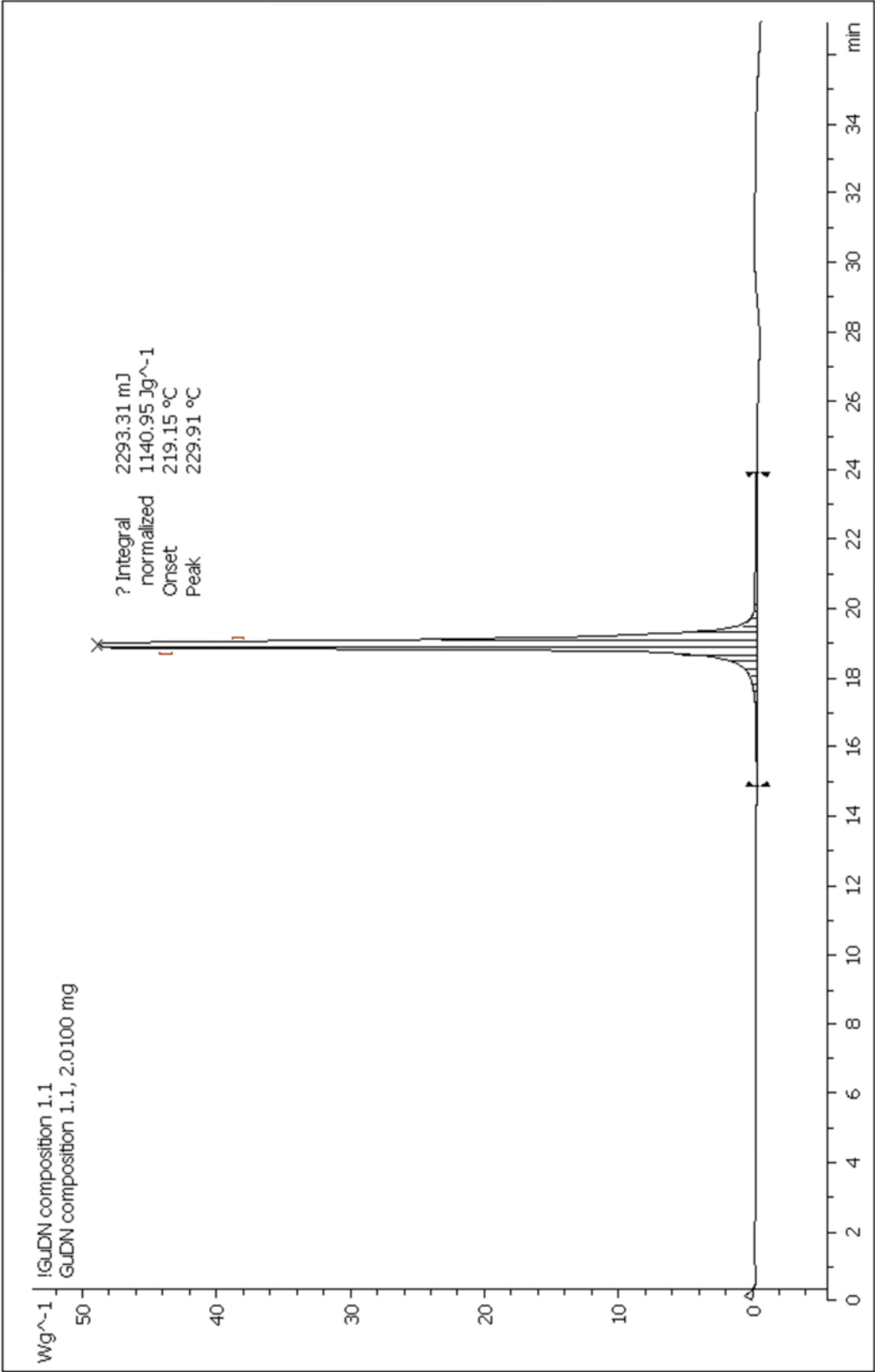


Figure 103: DSC measurement 1 of composition 1 (GuDN)

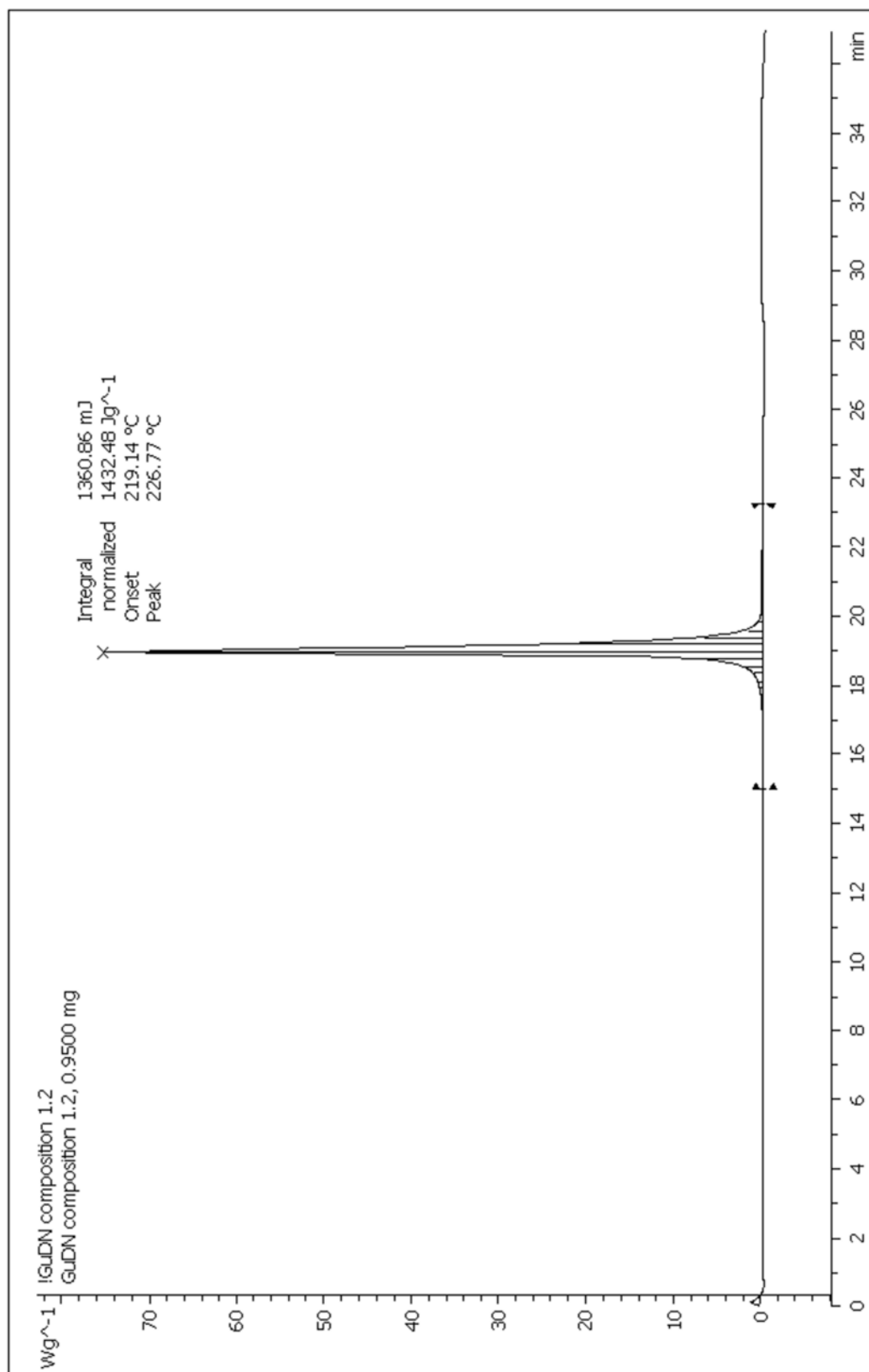


Figure 104: DSC measurement 2 of composition 1 (GuDN)

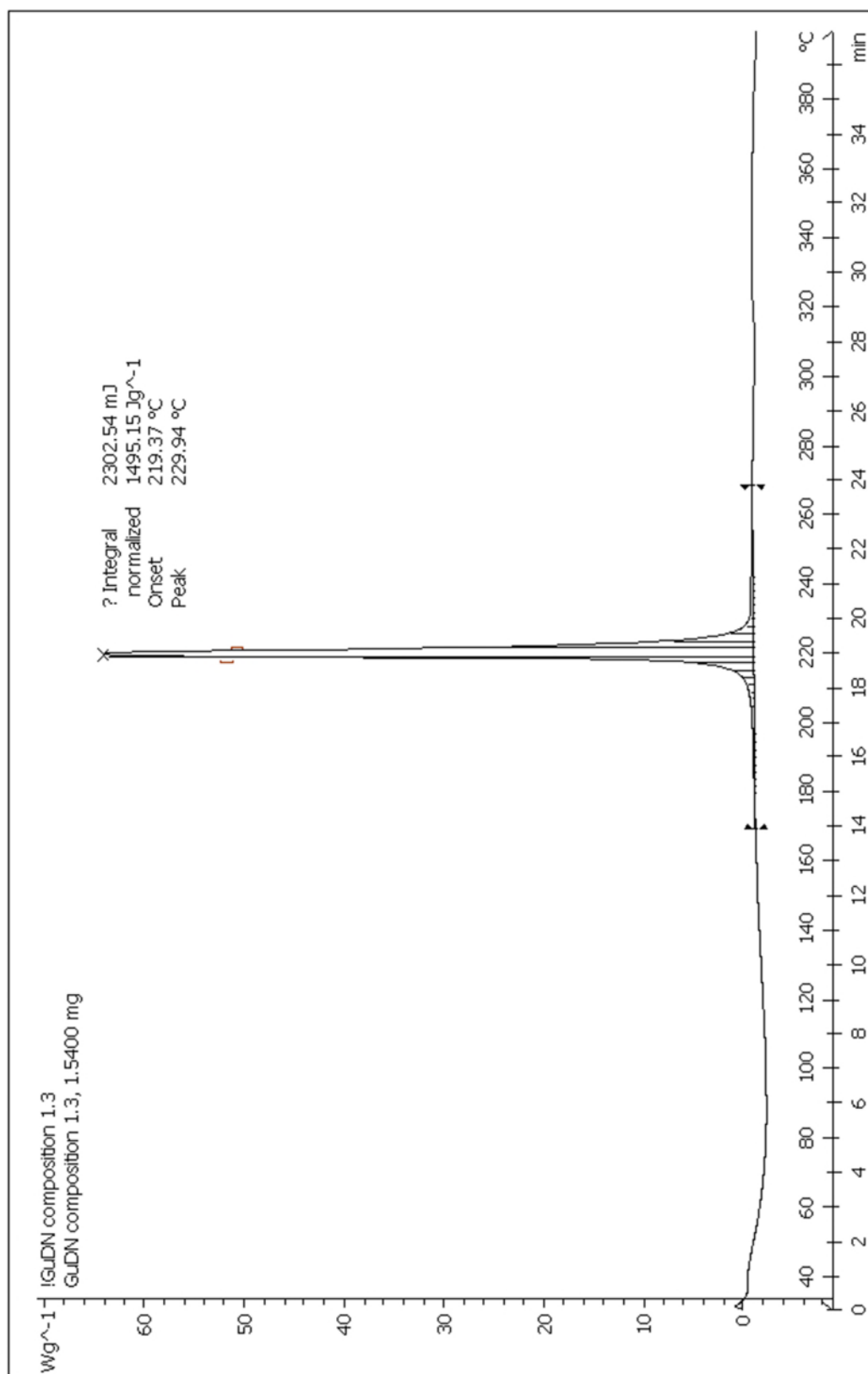


Figure 105: DSC measurement 3 of composition 1 (GuDN)

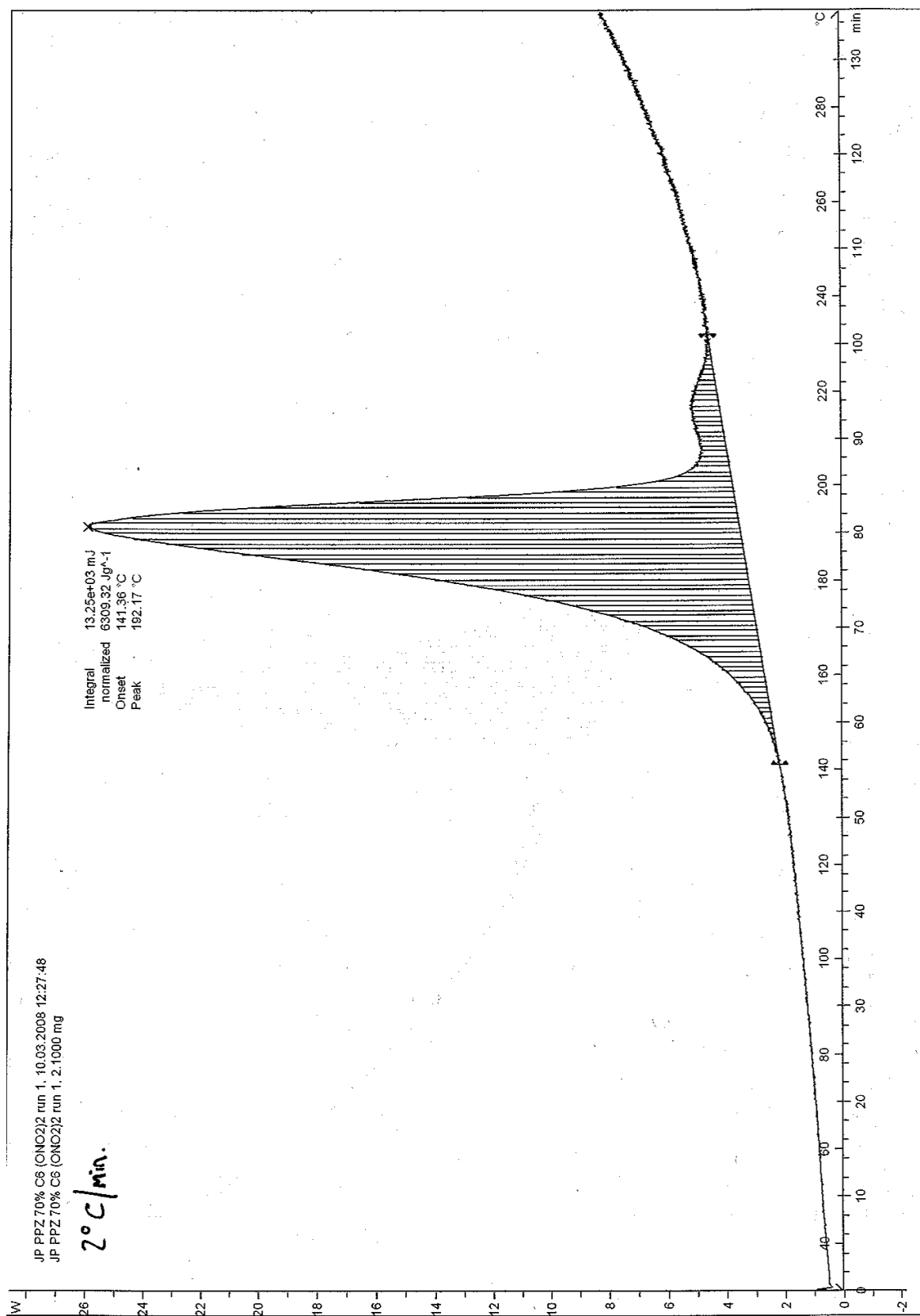


Figure 106: DSC measurement of PPZ (courtesy of Dr J Padfield)

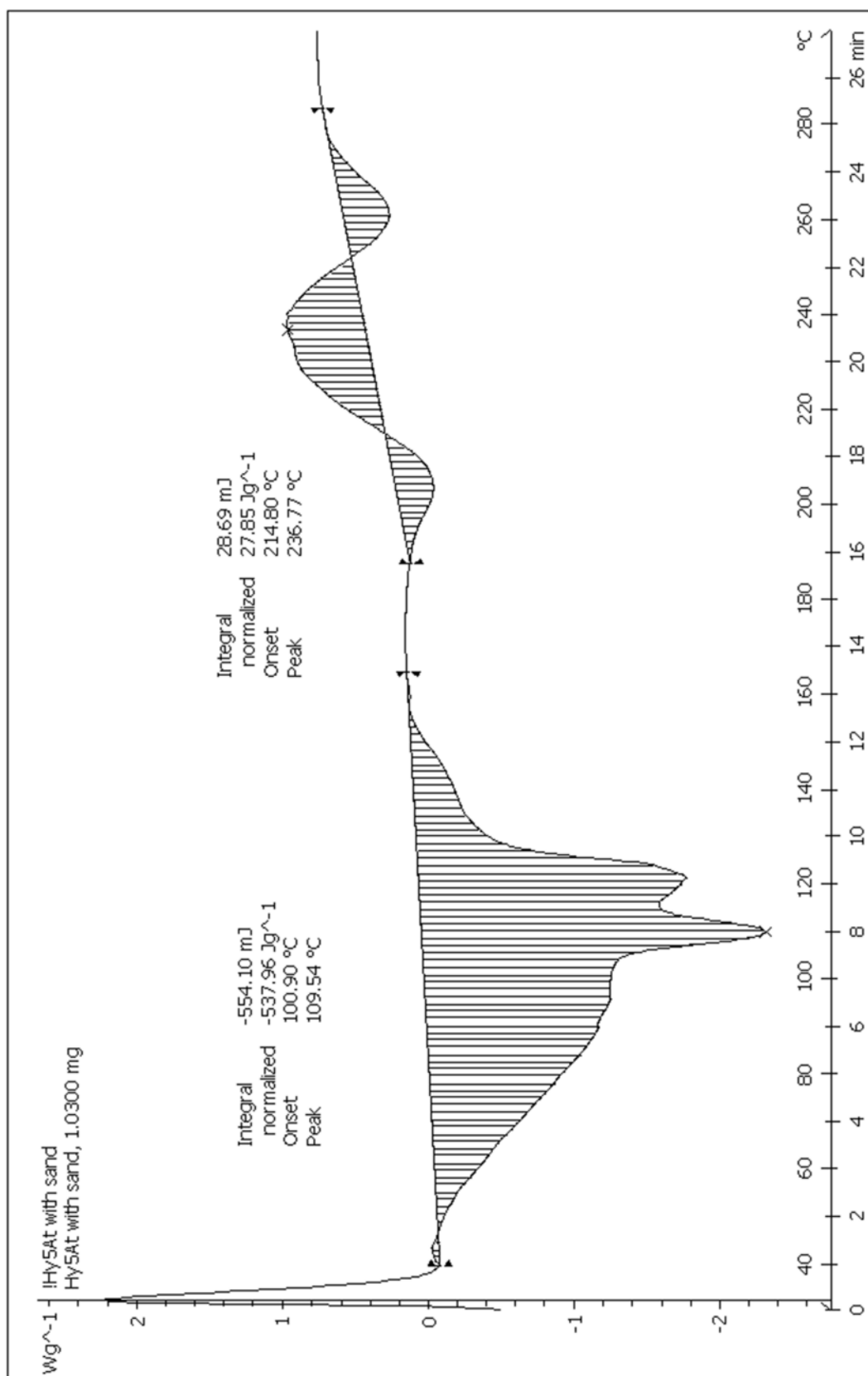


Figure 107: DSC measurement of Hy5At (with sand in DSC pan to reduce sample loss to evaporation)

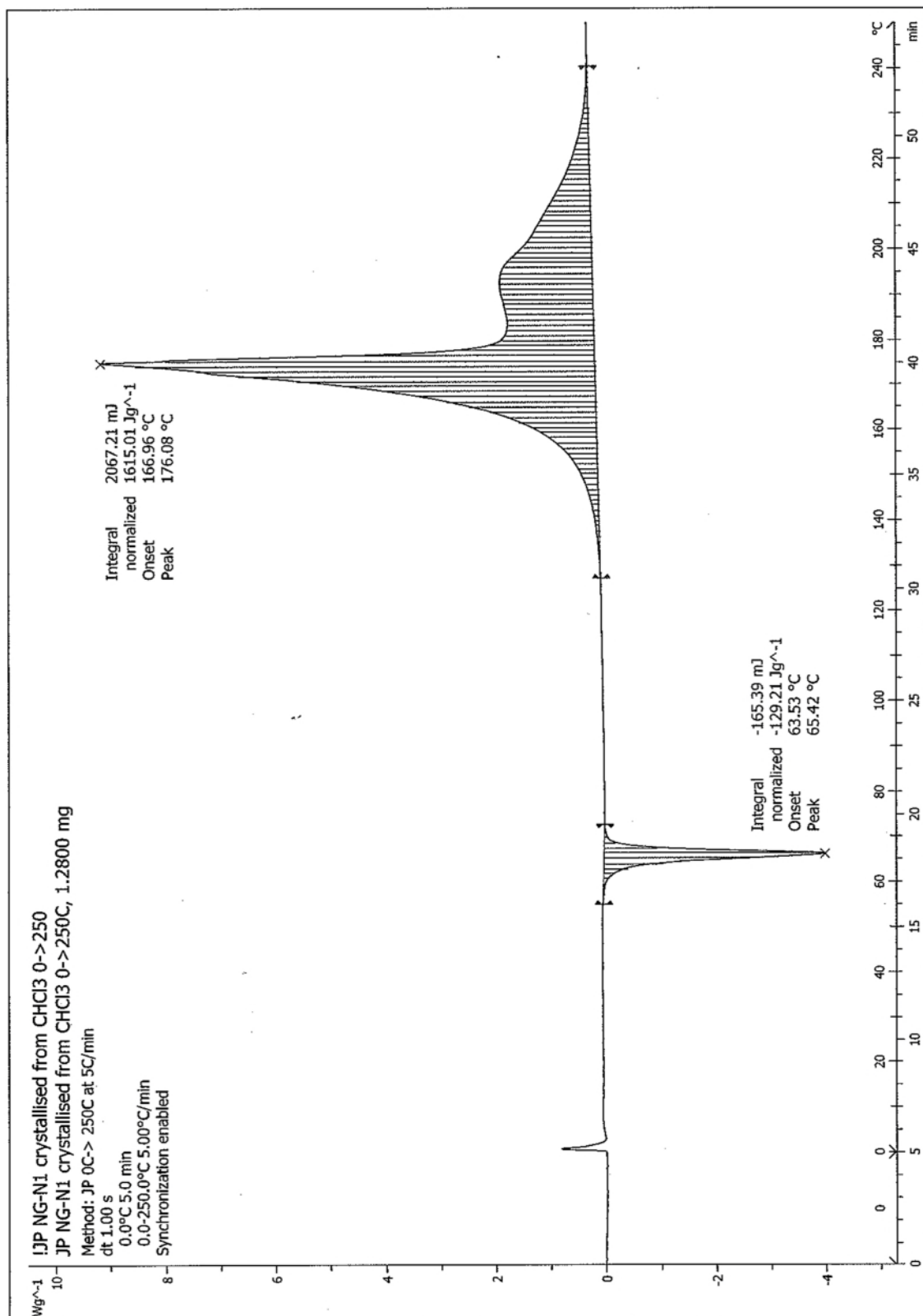


Figure 108: DSC measurement of NG-N1 (with artefact at 0 mins)

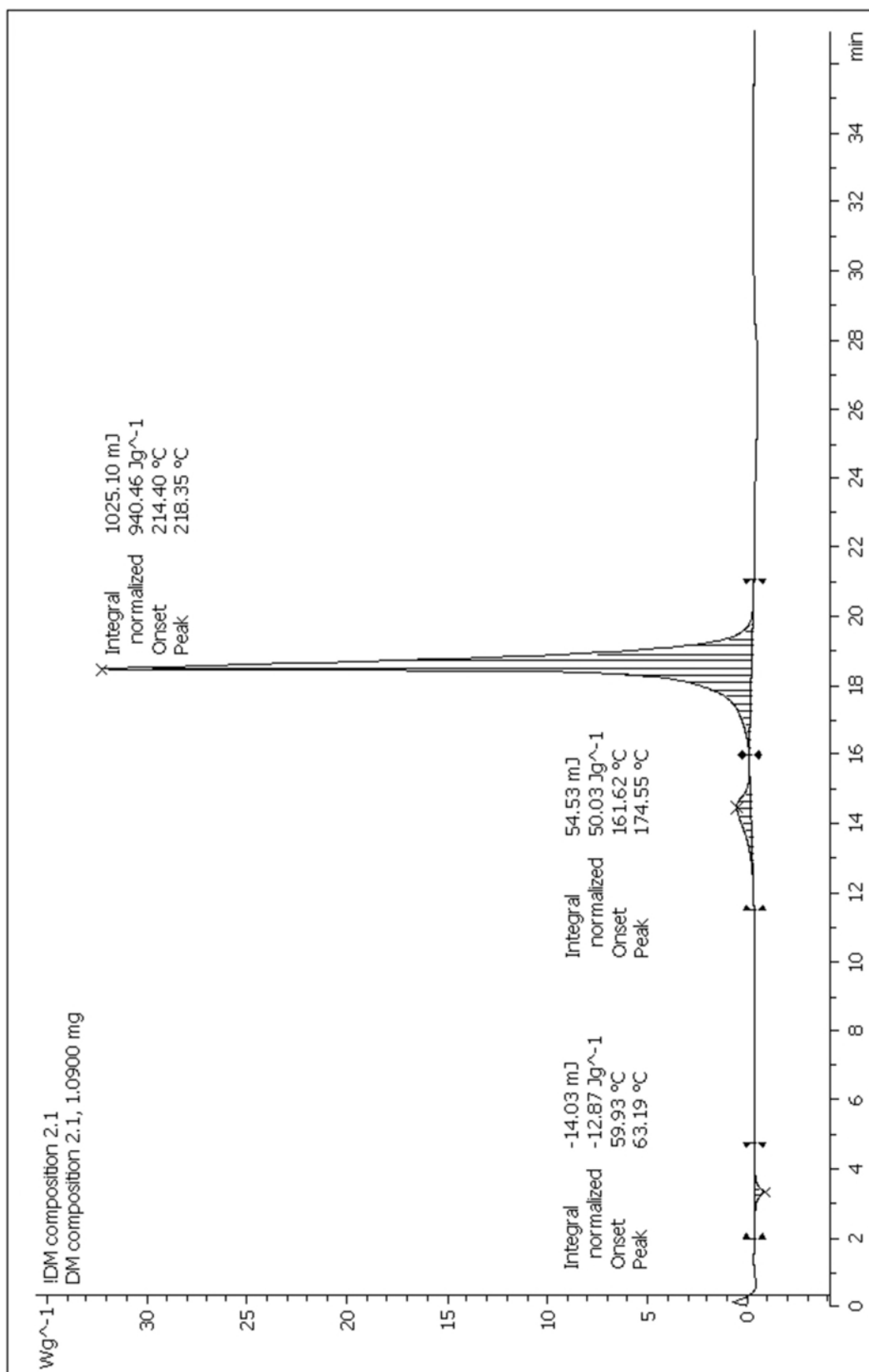


Figure 109: DSC measurement 1 of composition 2 (GuDN:NG-N1 9:1)

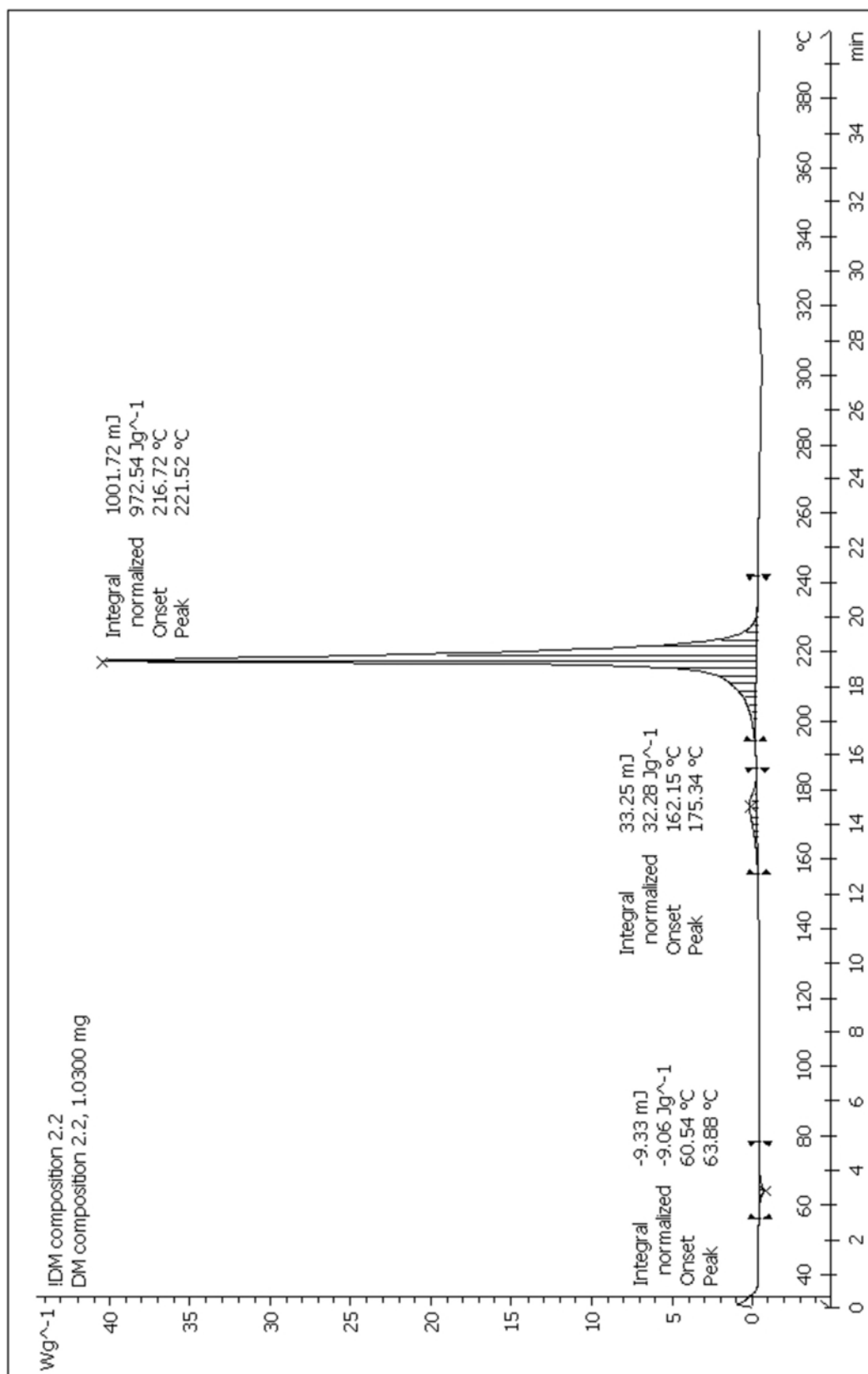


Figure 110: DSC measurement 2 of composition 2 (GuDN:NG-N1 9:1)

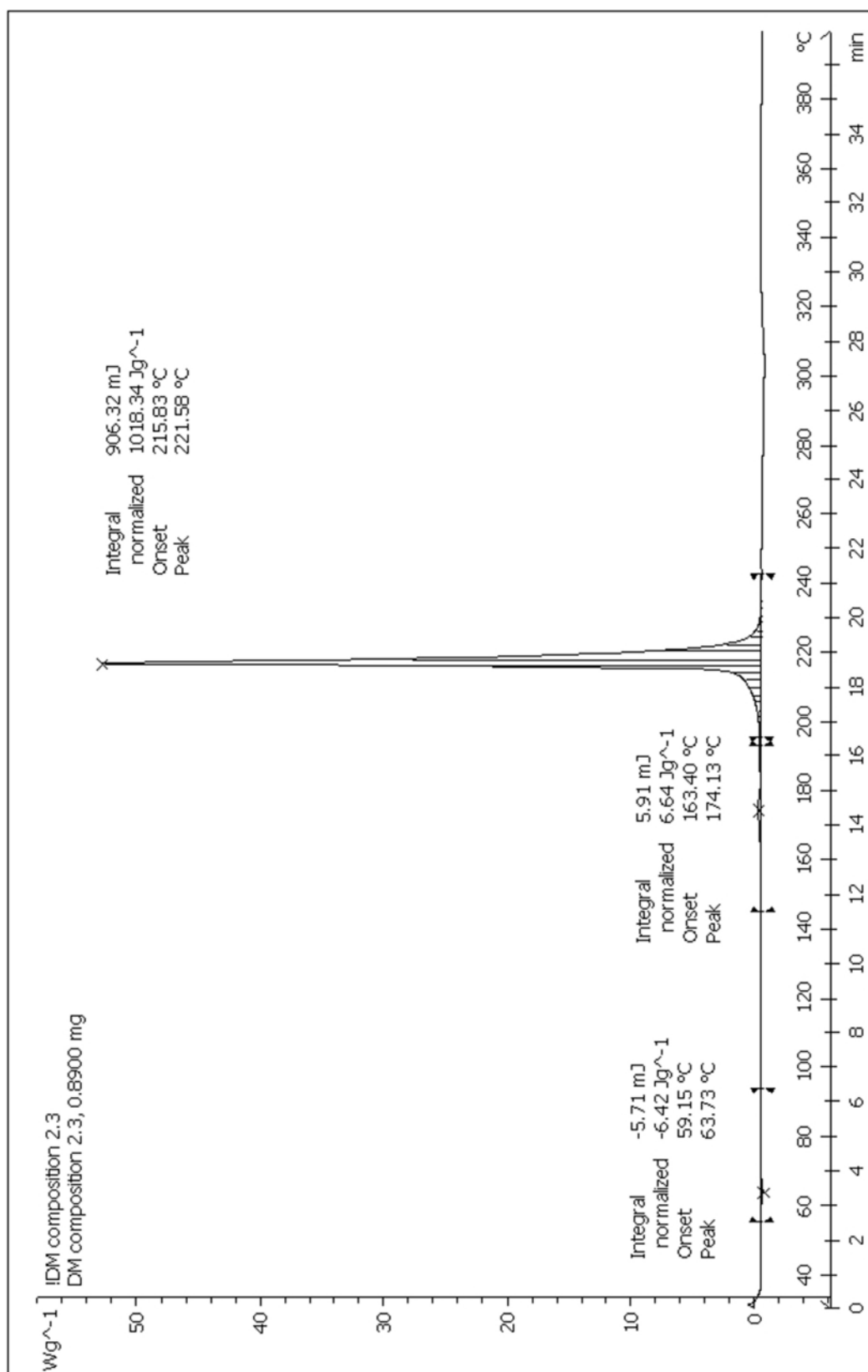


Figure 111: DSC measurement 3 of composition 2 (GuDN:NG-N1 9:1)

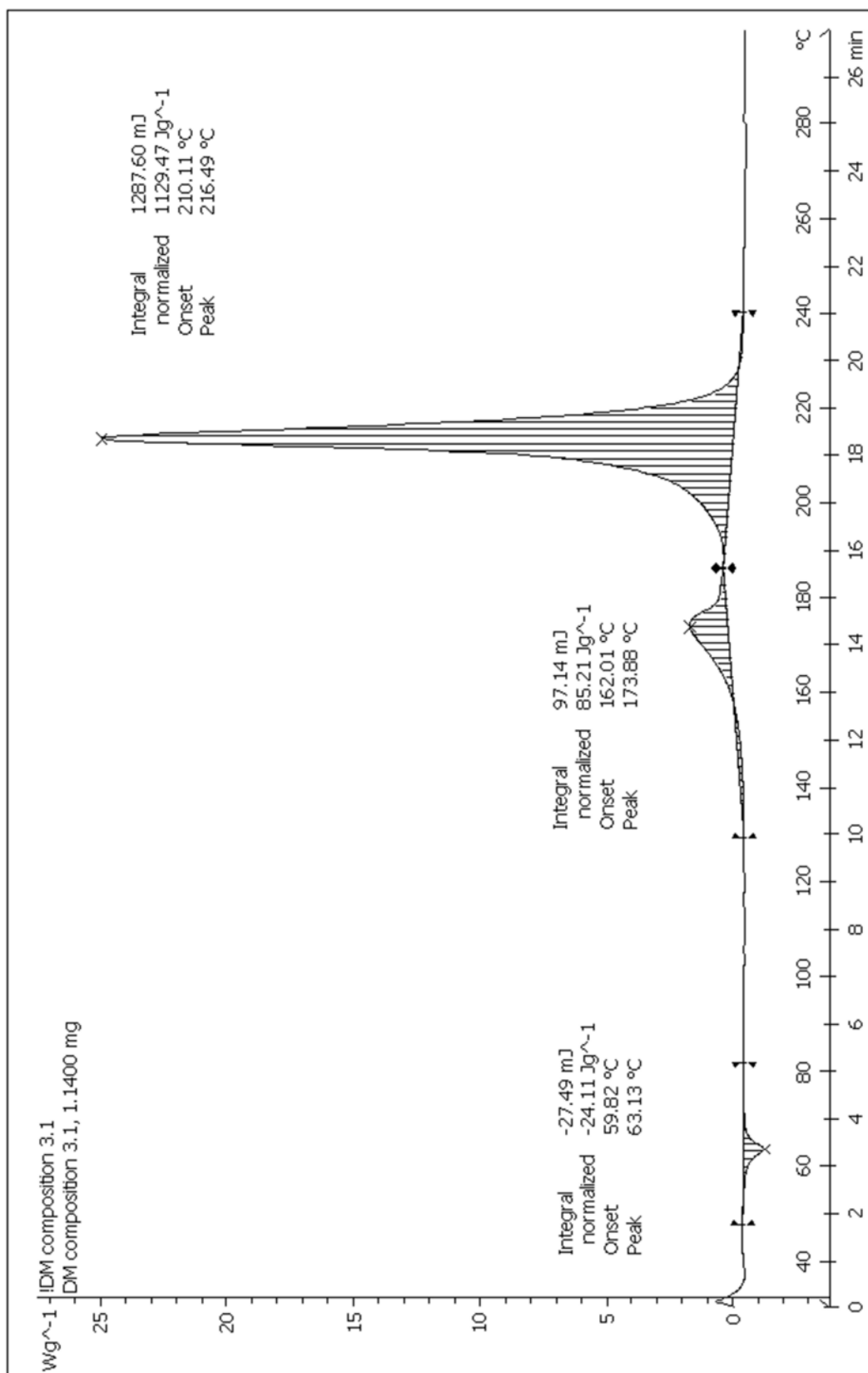


Figure 112: DSC measurement 1 of composition 3 (GuDN:NG-N1 8:2)

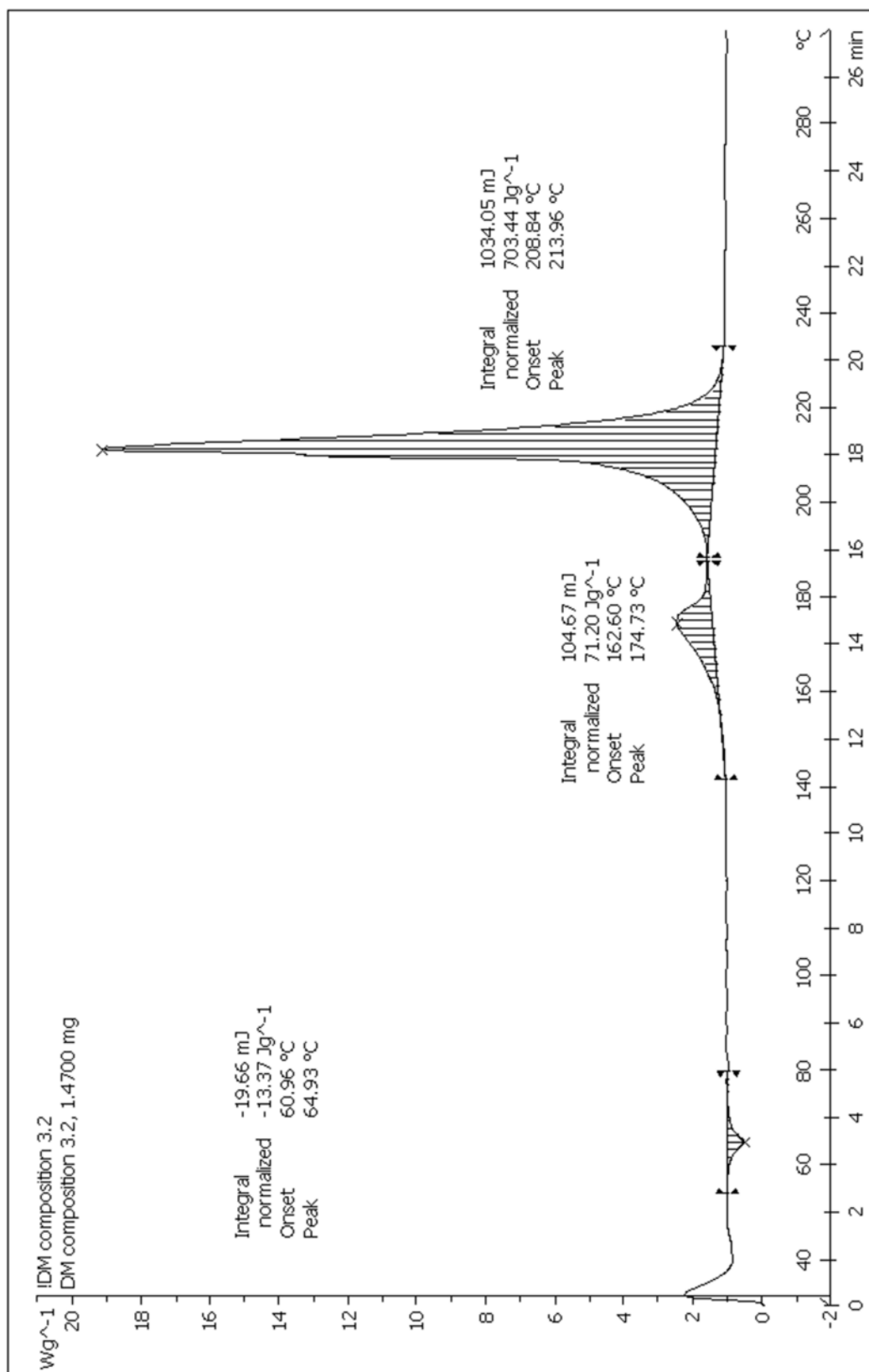


Figure 113: DSC measurement 2 of composition 3 (GuDN:NG-N1 8:2)

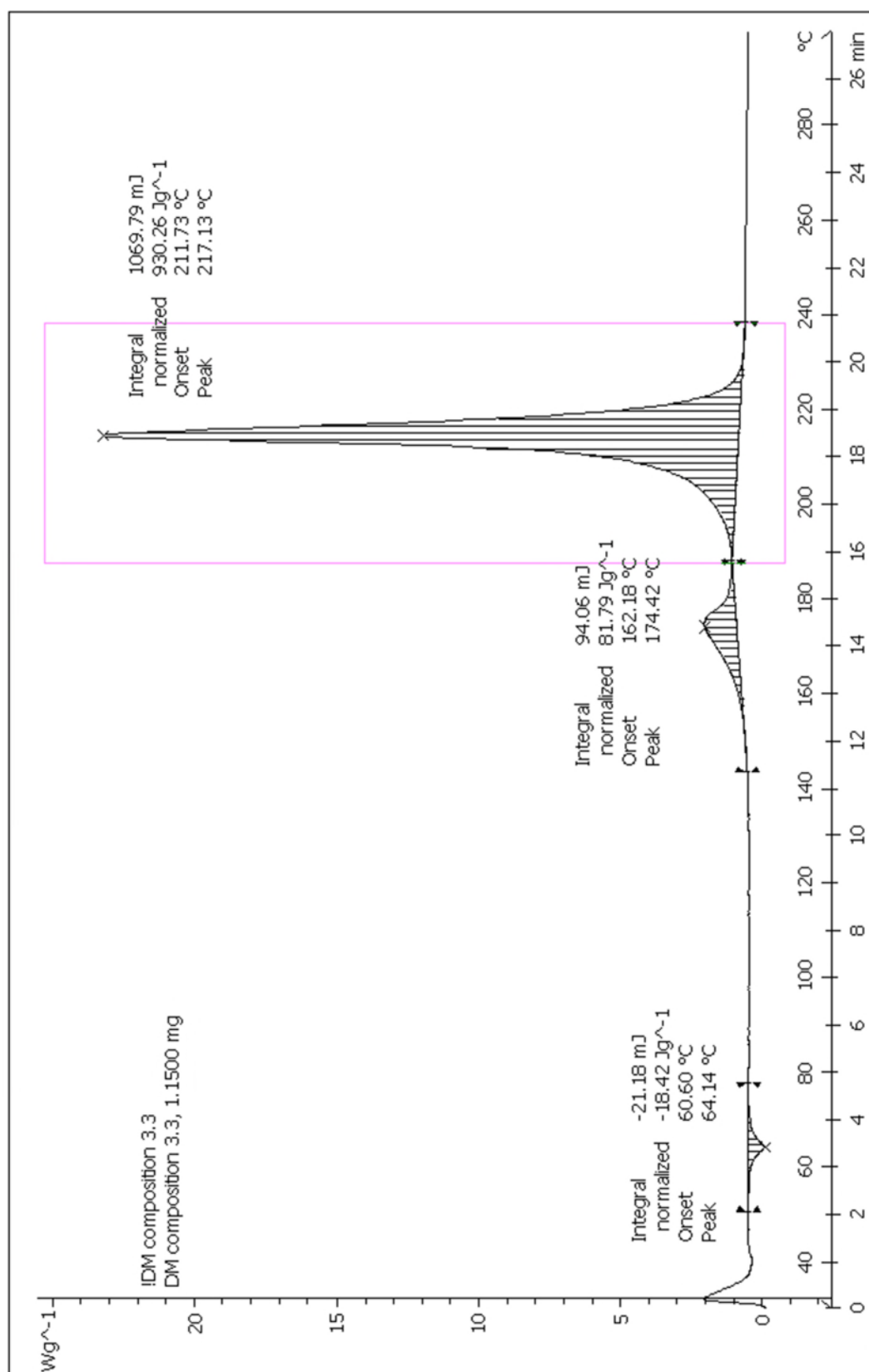


Figure 114: DSC measurement 3 of composition 3 (GuDN:NG-N1 8:2)

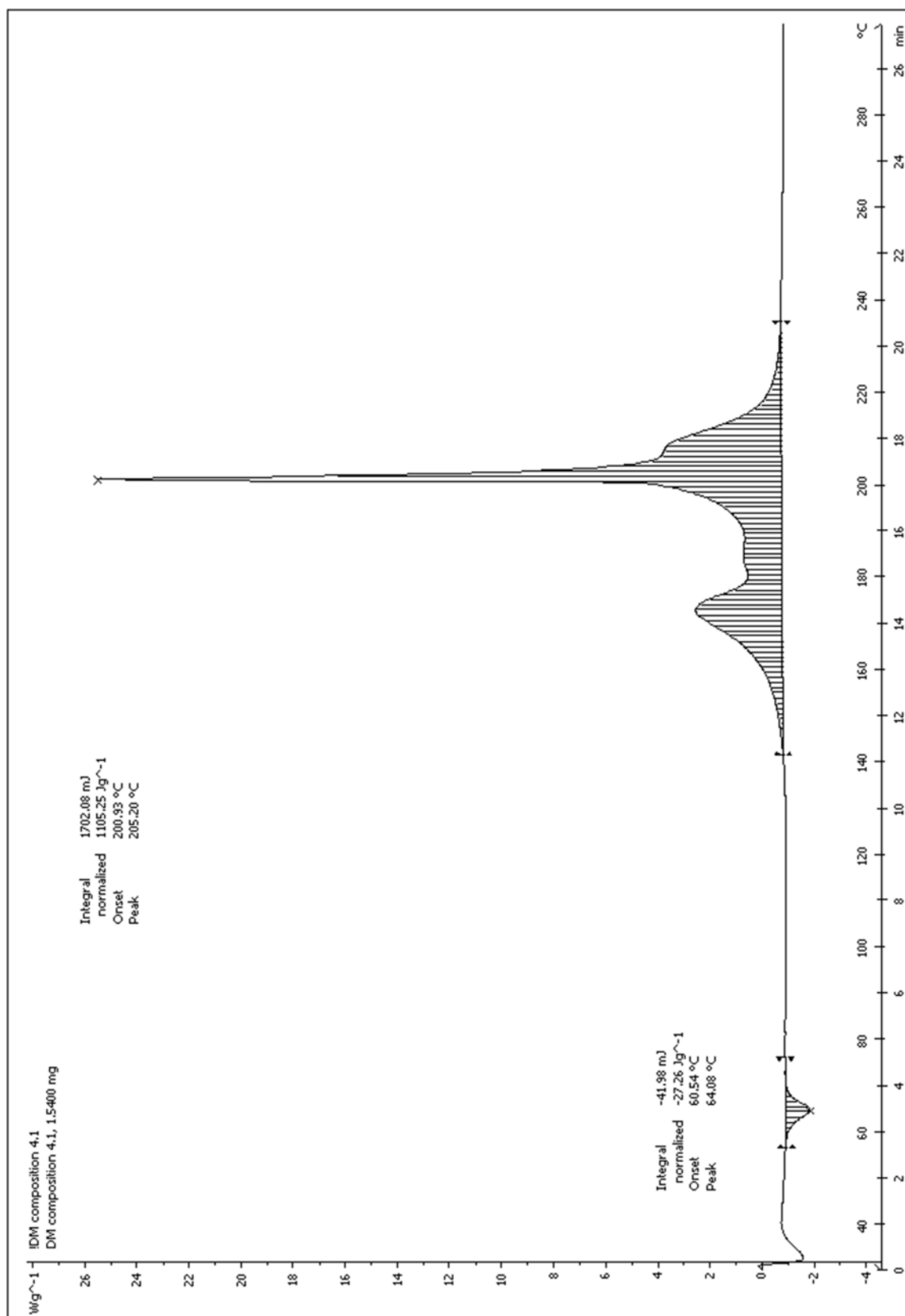


Figure 115: DSC measurement 1 of composition 4 (GuDN:NG-N1 7:3)

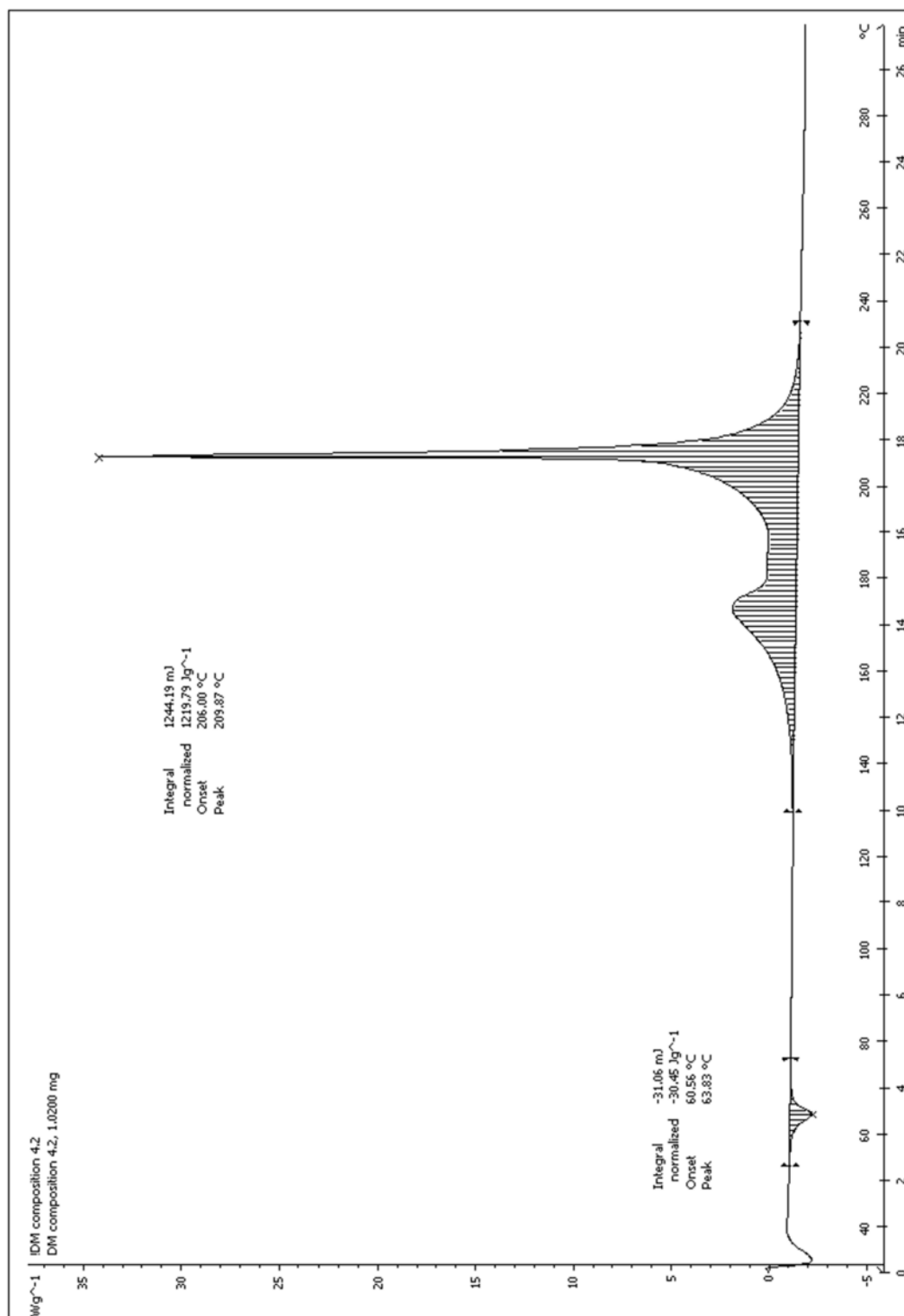


Figure 116: DSC measurement 2 of composition 4 (GuDN:NG-N1 7:3)

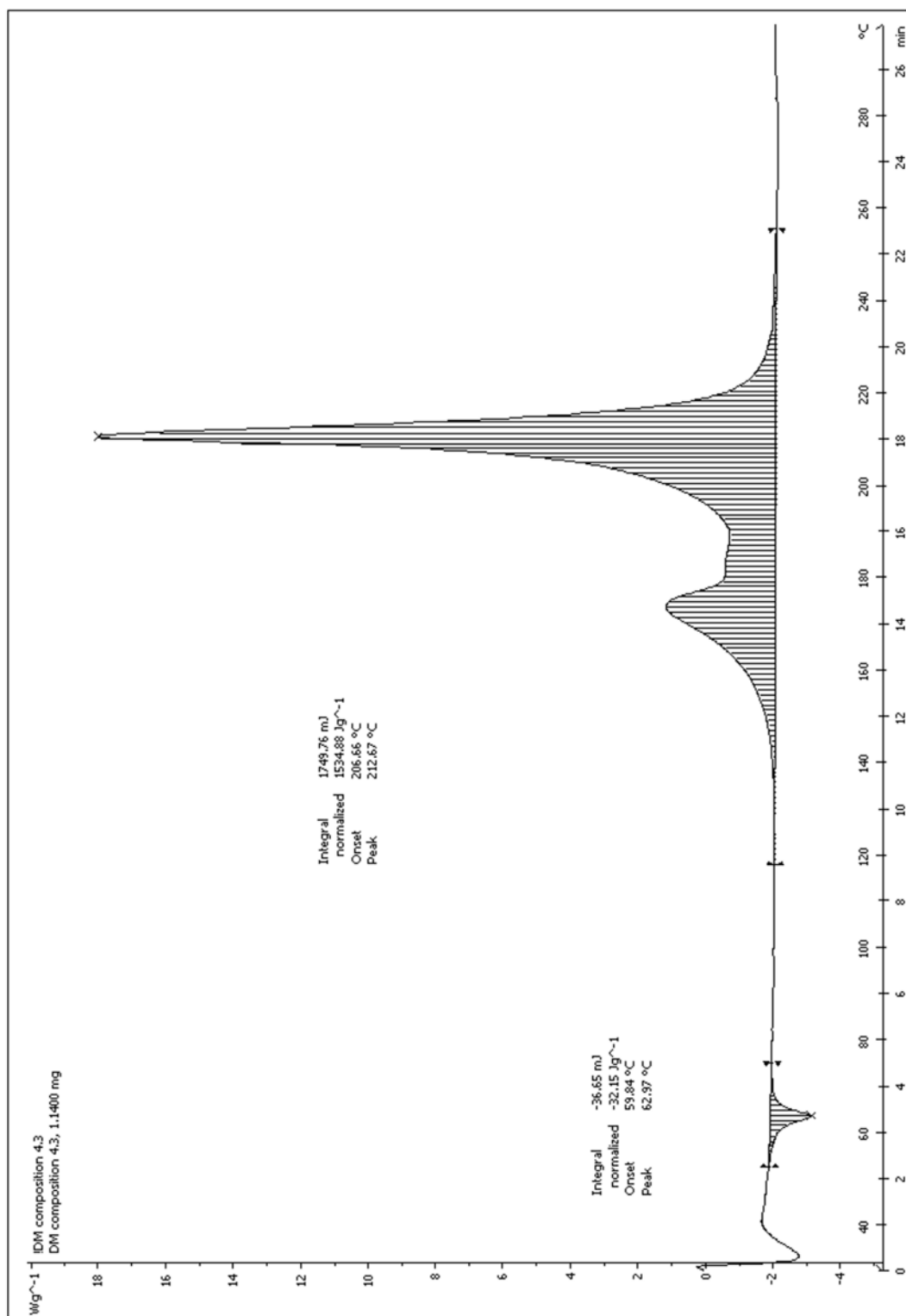


Figure 117: DSC measurement 3 of composition 4 (GuDN:NG-N1 7:3)

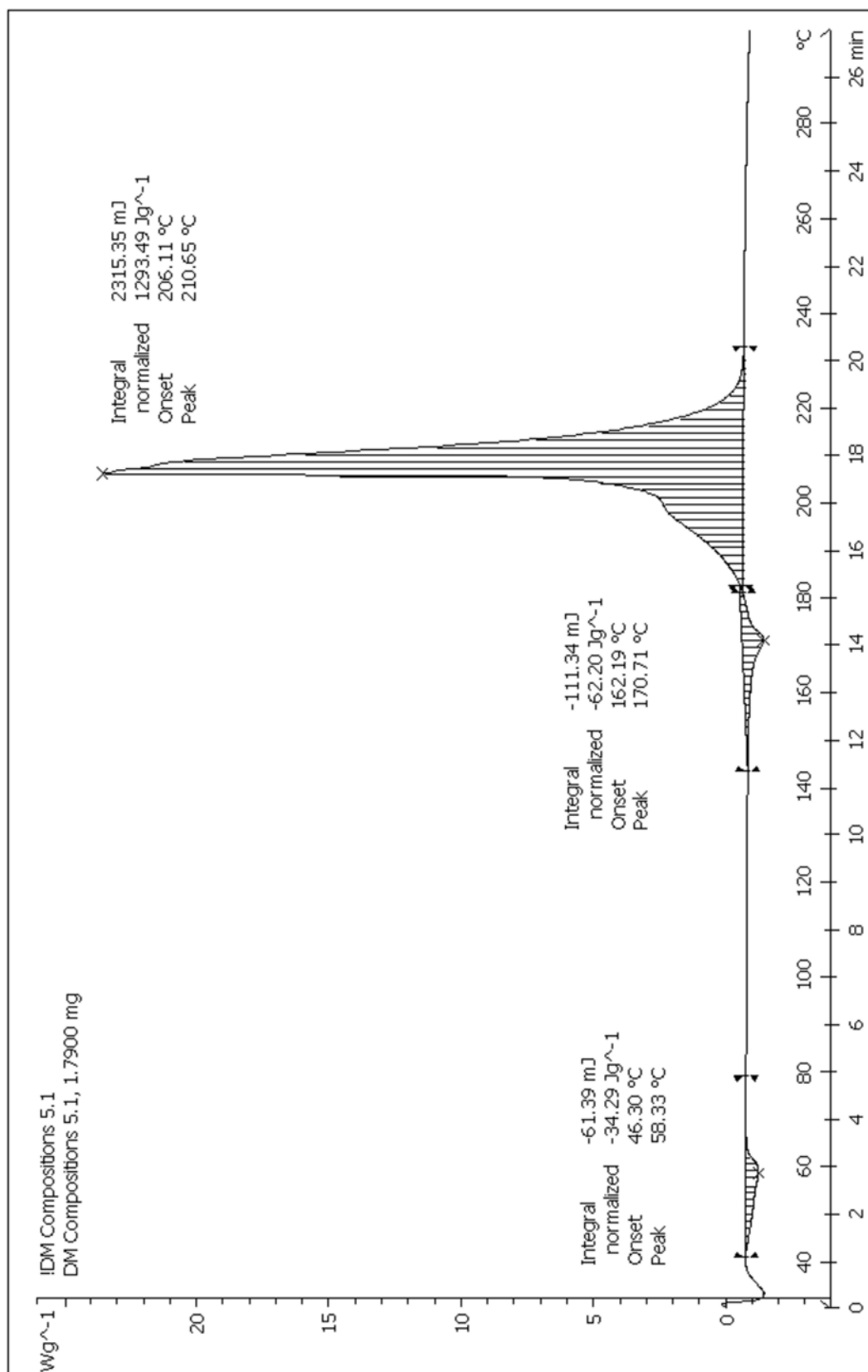


Figure 118: DSC measurement 1 of composition 5 (GuDN:Hy5At 9:1)

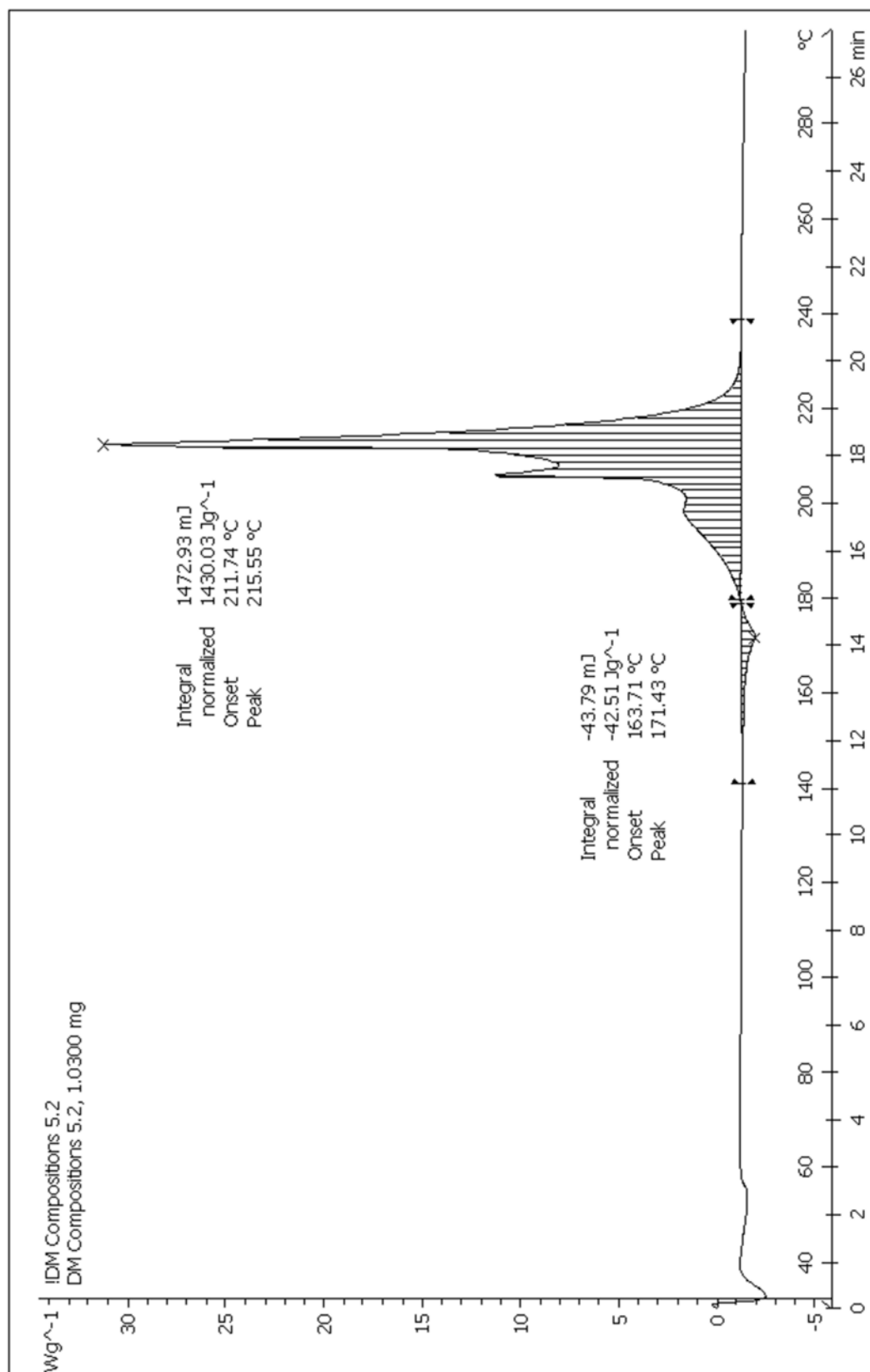


Figure 119: DSC measurement 2 of composition 5 (GuDN:Hy5At 9:1)

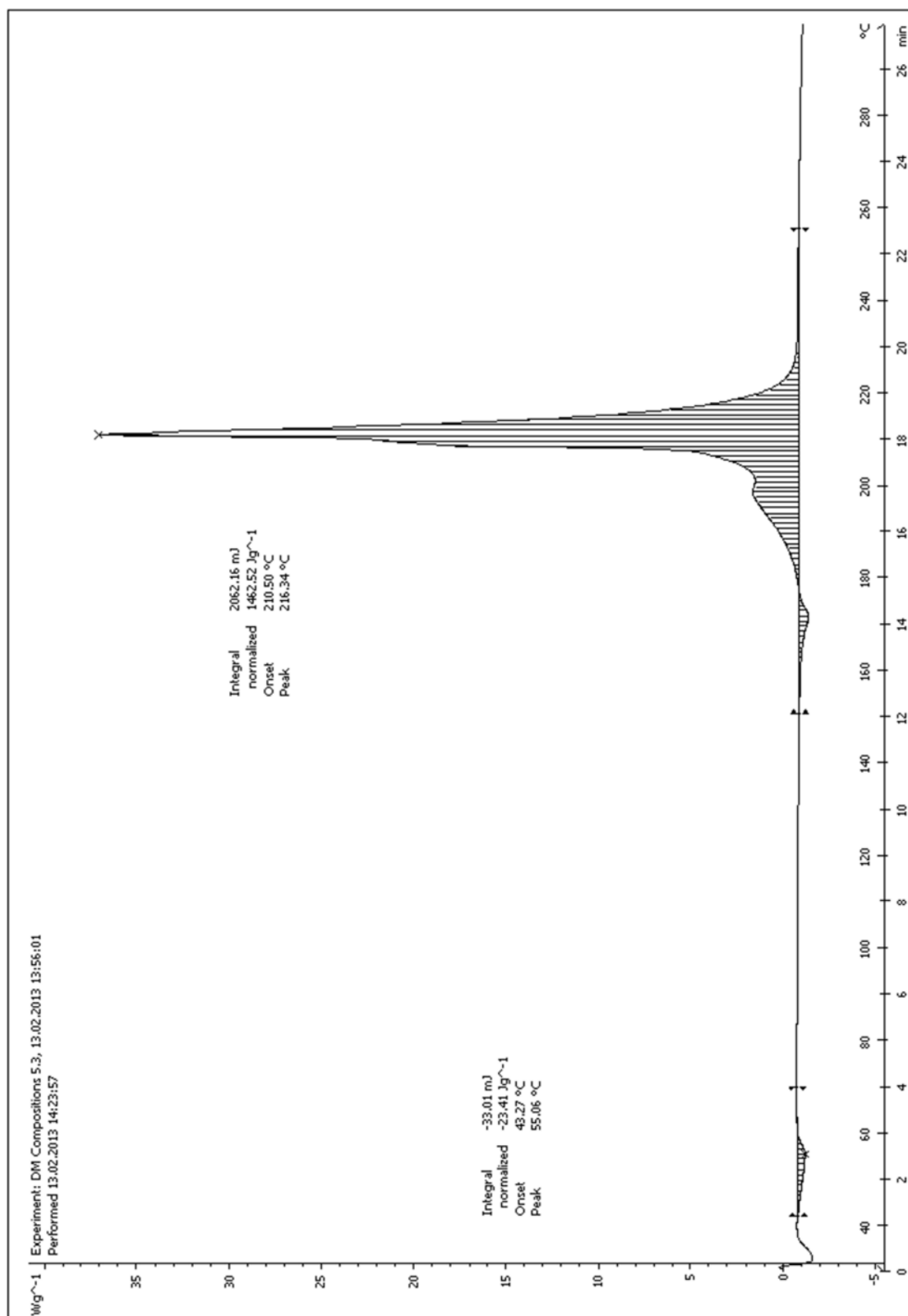


Figure 120: DSC measurement 3 of composition 5 (GuDN:Hy5At 9:1)

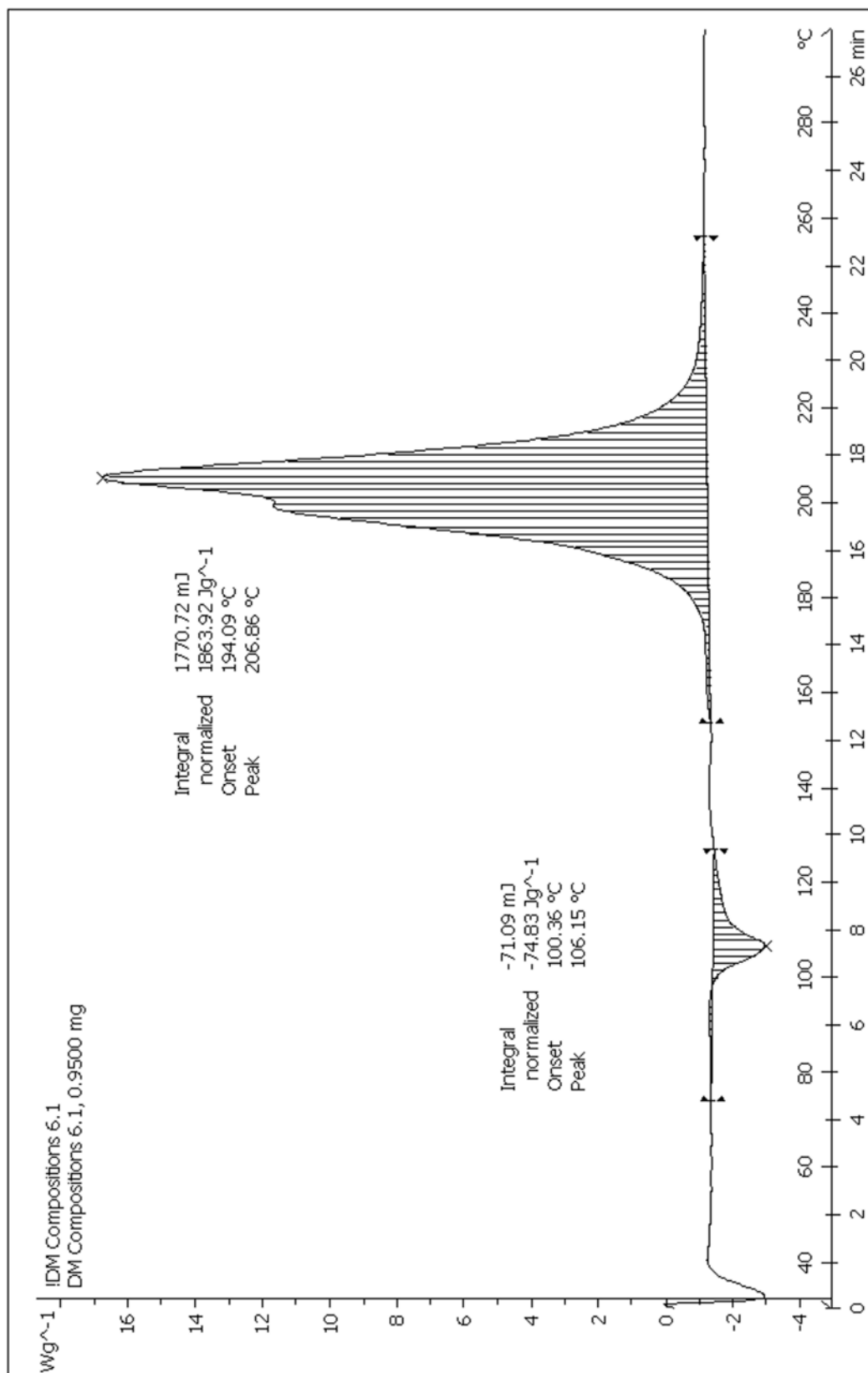


Figure 121: DSC measurement 1 of composition 6 (GuDN:Hy5At 8:2)

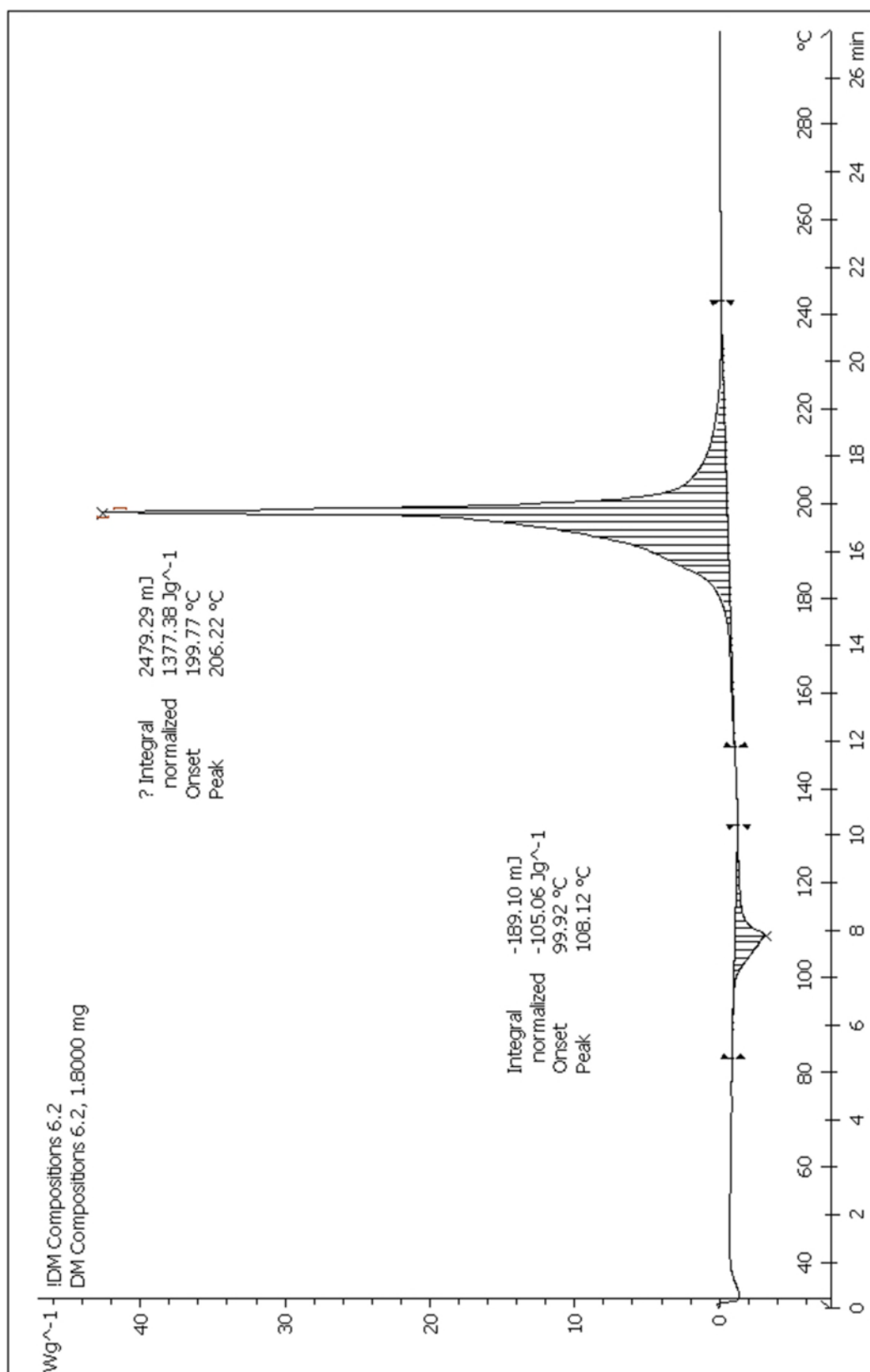


Figure 122: DSC measurement 2 of composition 6 (GuDN:Hy5At 8:2)

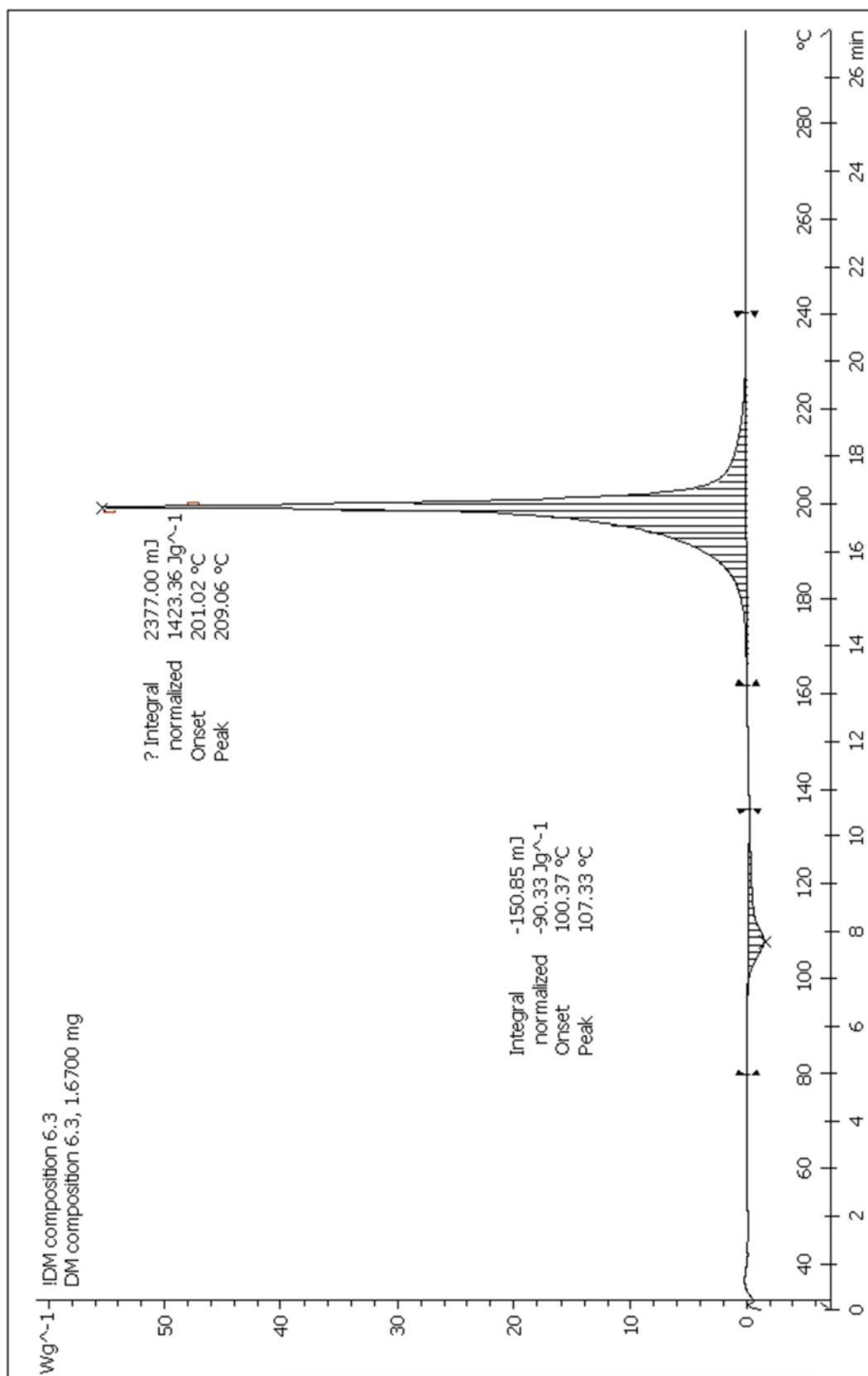


Figure 123: DSC measurement 3 of composition 6 (GuDN:Hy5At 8:2)

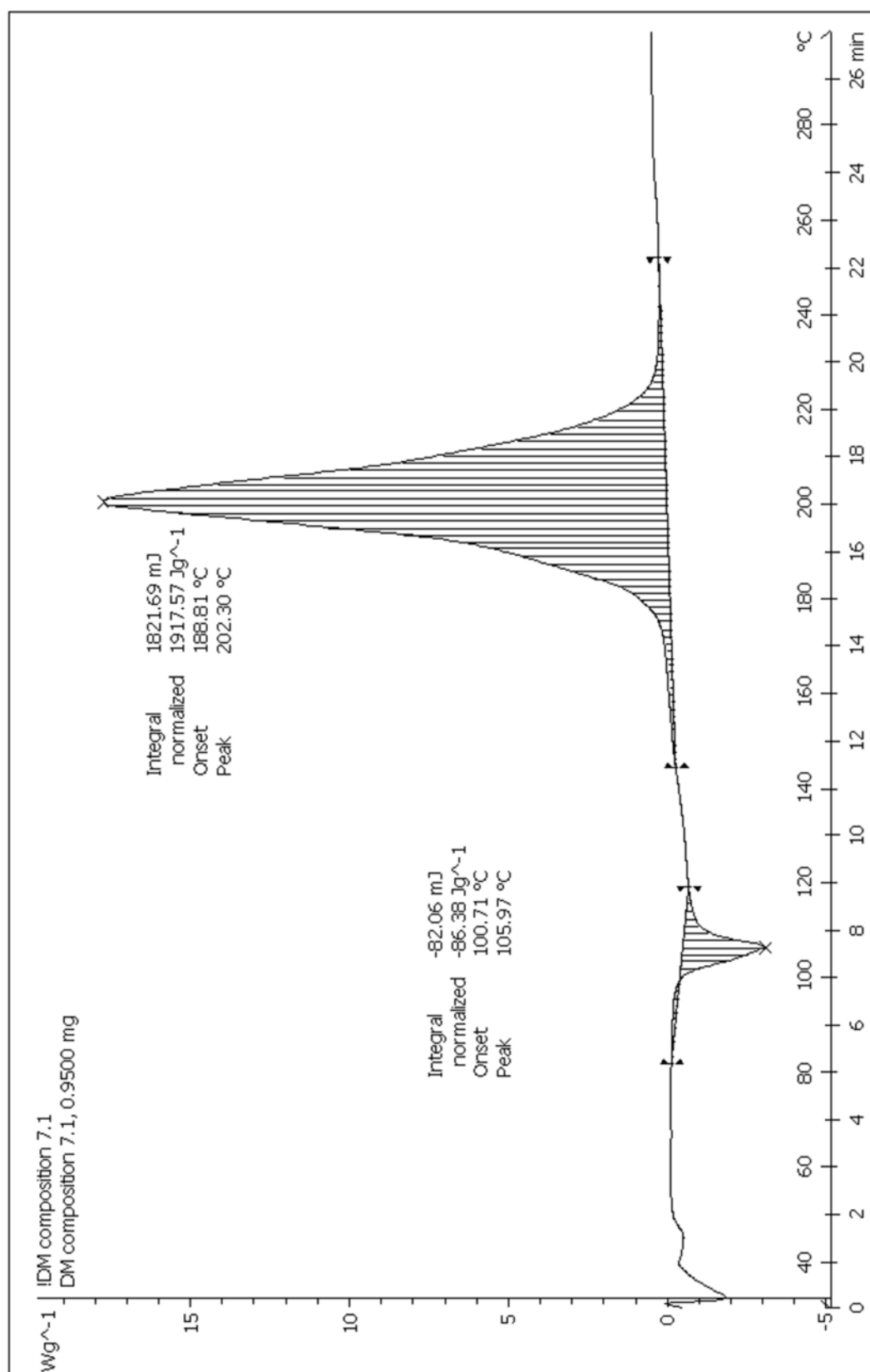


Figure 124: DSC measurement 1 of composition 7 (GuDN:Hy5At 7:3)

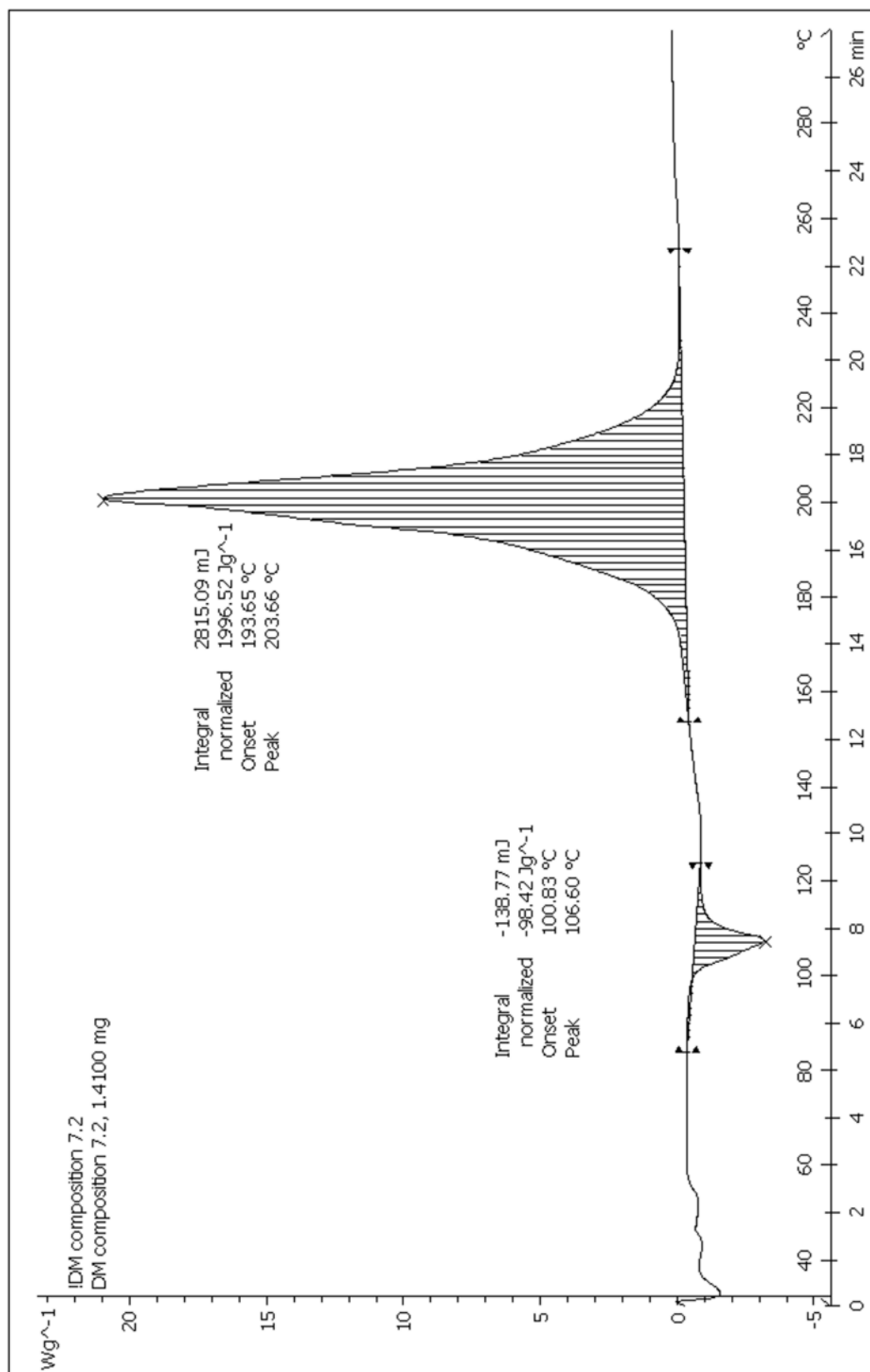


Figure 125: DSC measurement 2 of composition 7 (GuDN:Hy5At 7:3)

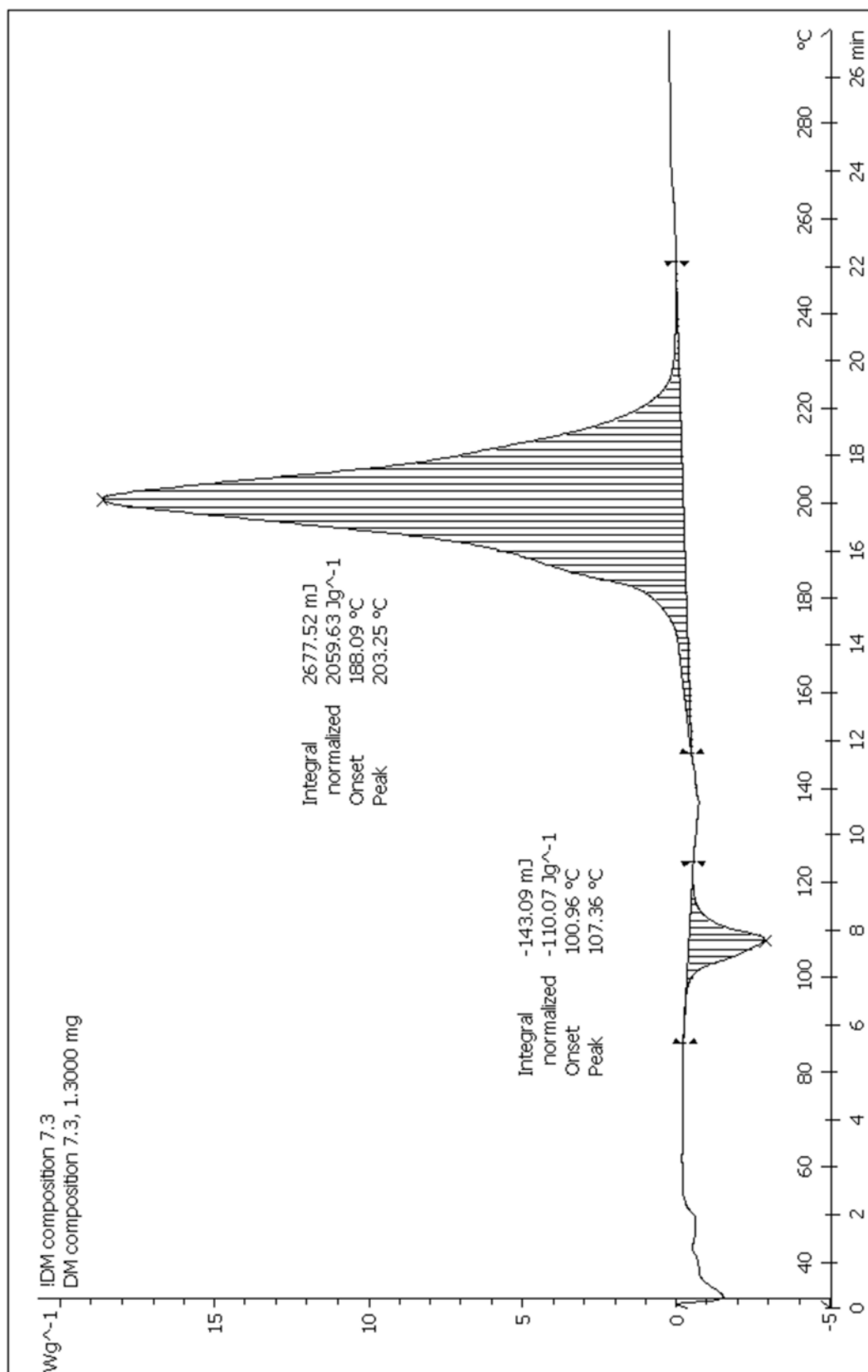


Figure 126: DSC measurement 3 of composition 7 (GuDN:Hy5At 7:3)

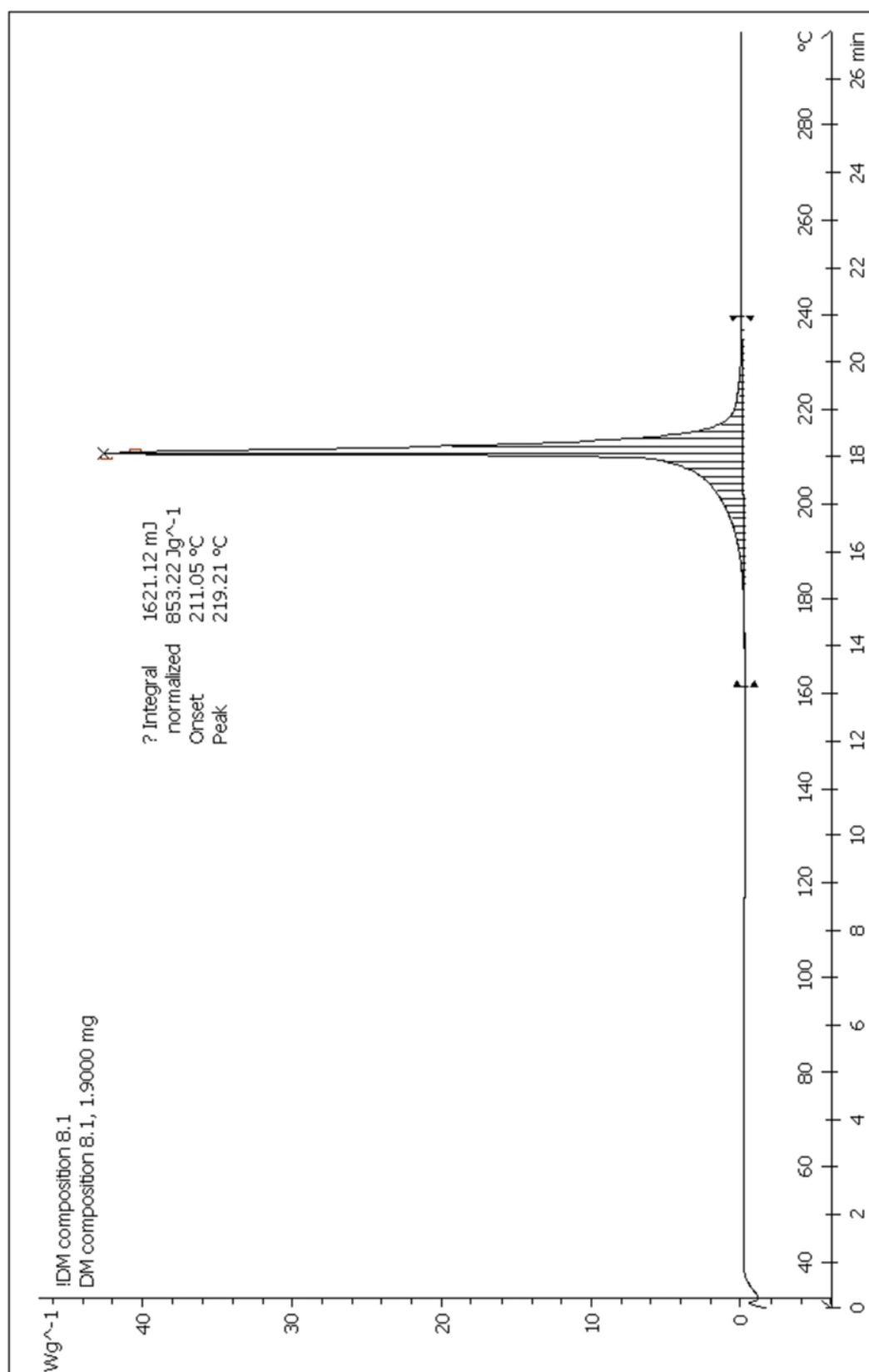


Figure 127: DSC measurement 1 of composition 8 (GuDN:PPZ 9:1)

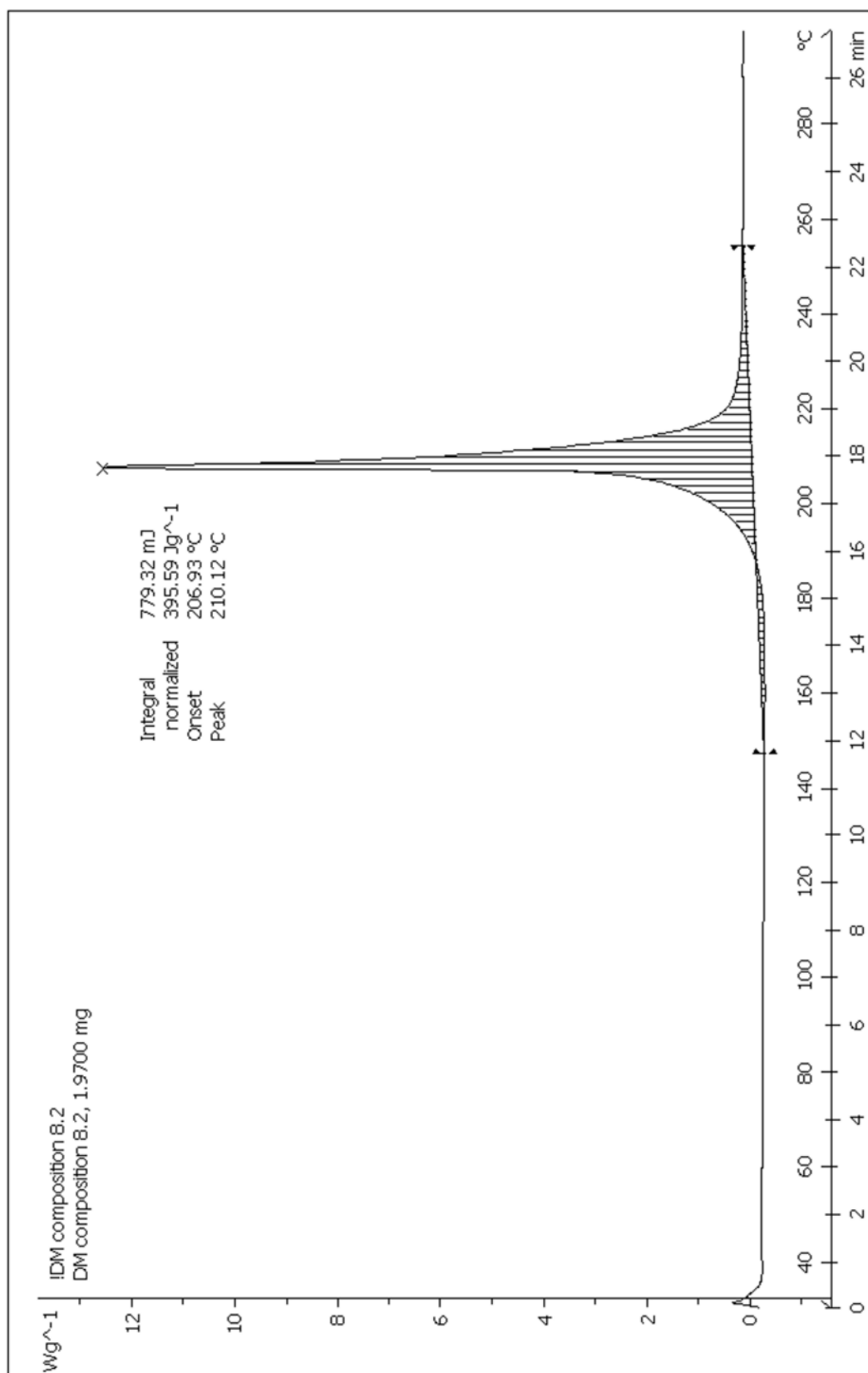


Figure 128: DSC measurement 2 of composition 8 (GuDN:PPZ 9:1)

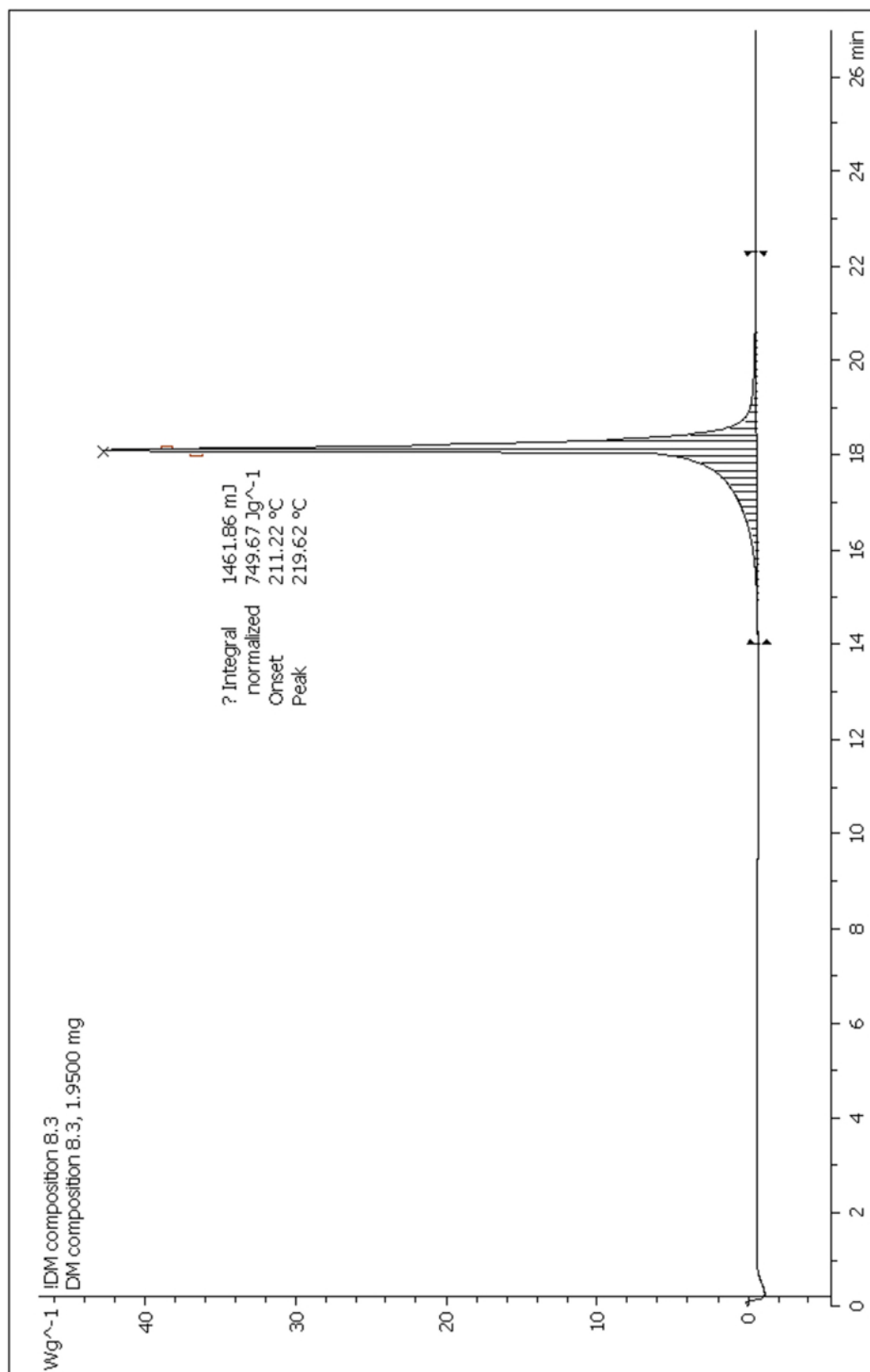


Figure 129: DSC measurement 3 of composition 8 (GuDN:PPZ 9:1)

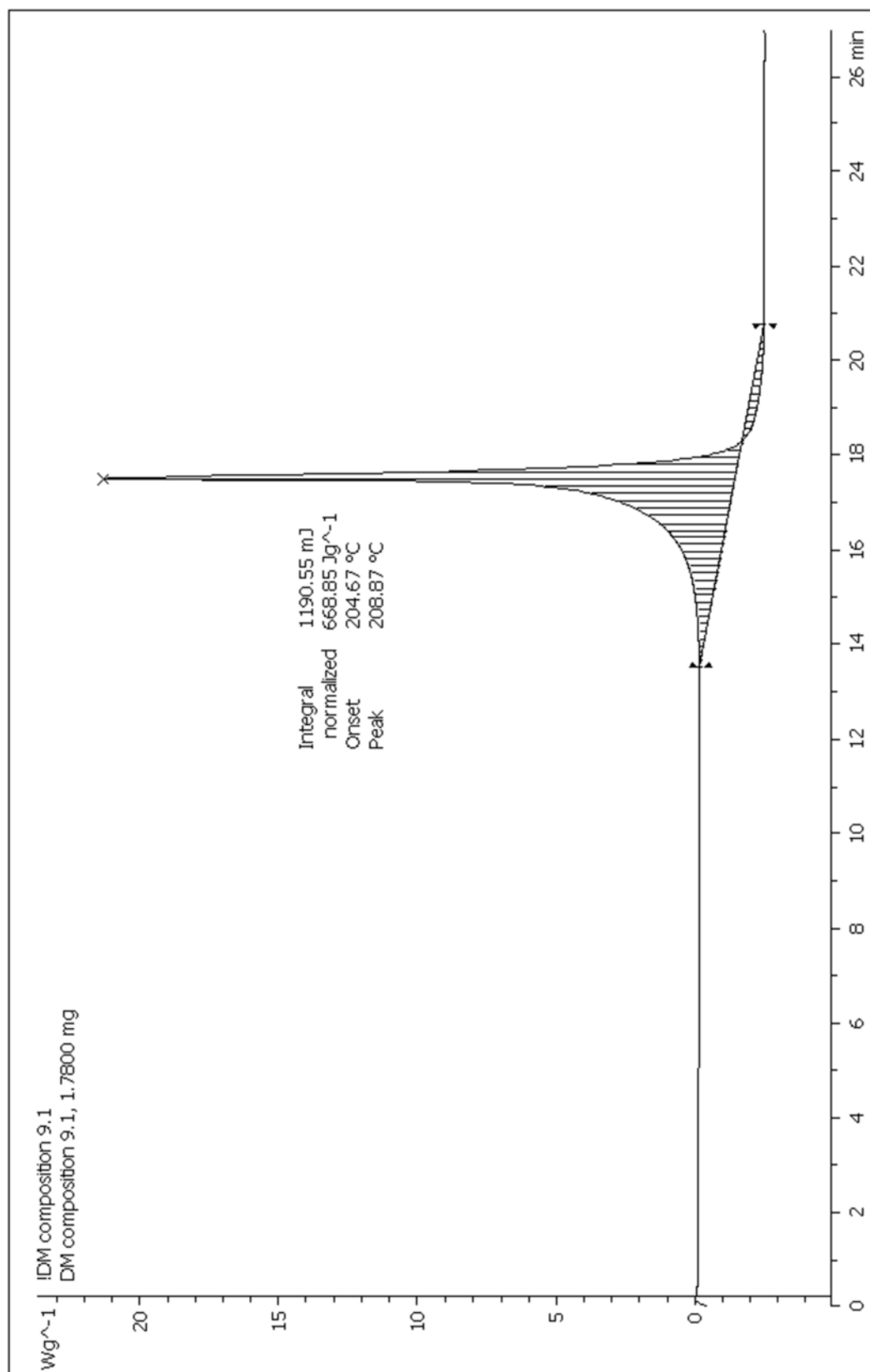


Figure 130: DSC measurement 1 of composition 9 (GuDN:PPZ 8:2)

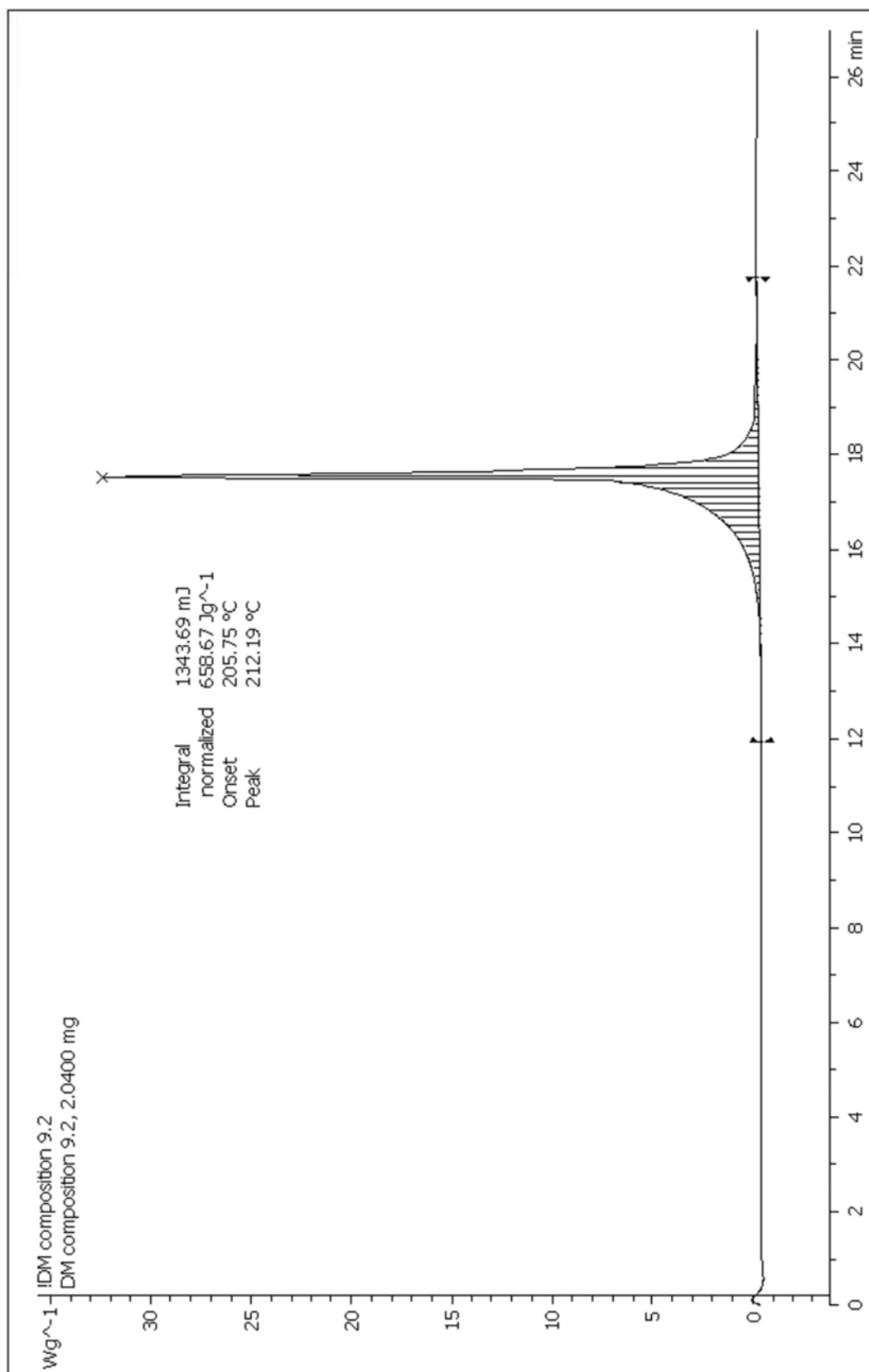


Figure 131: DSC measurement 2 of composition 9 (GuDN:PPZ 8:2)

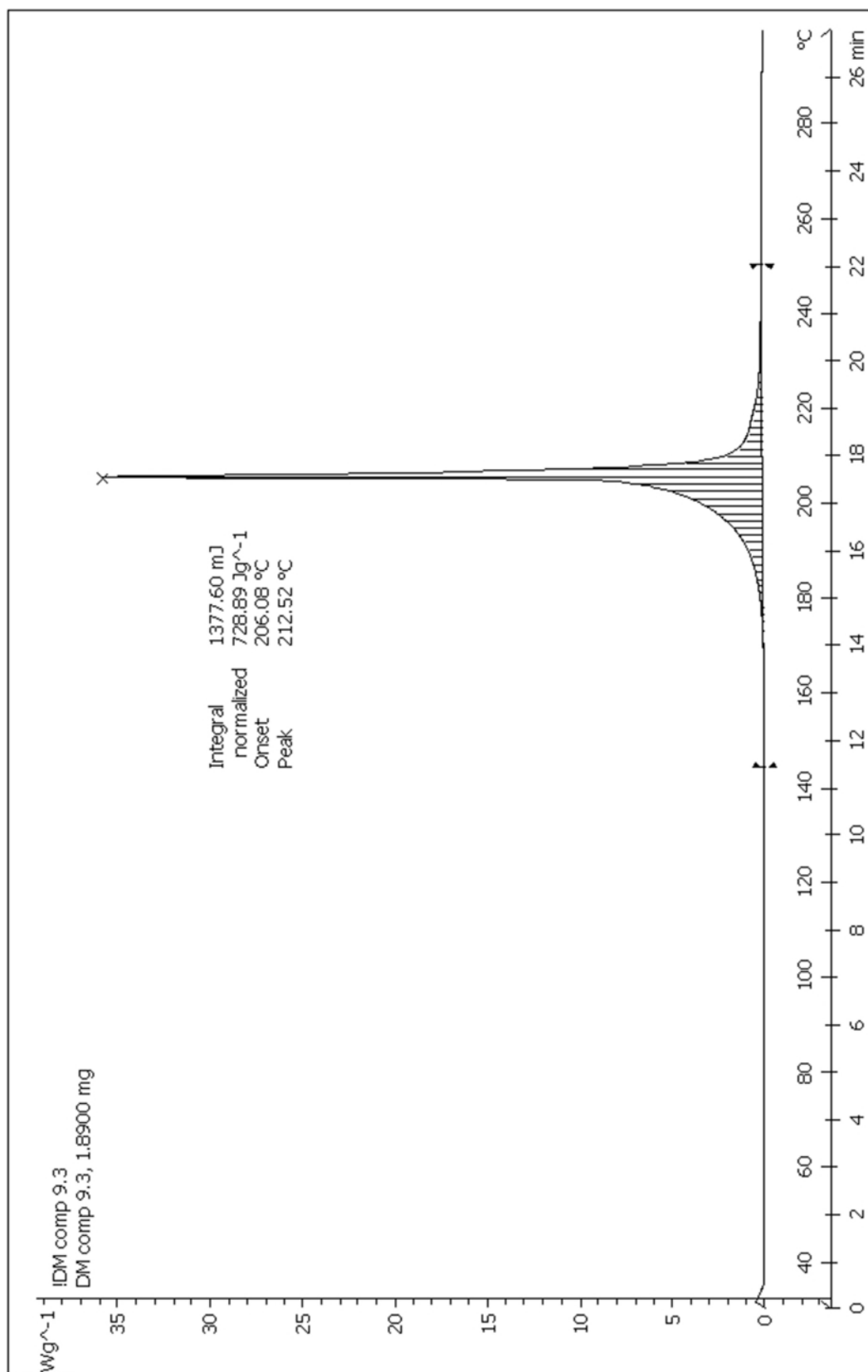


Figure 132: DSC measurement 3 of composition 9 (GuDN:PPZ 8:2)

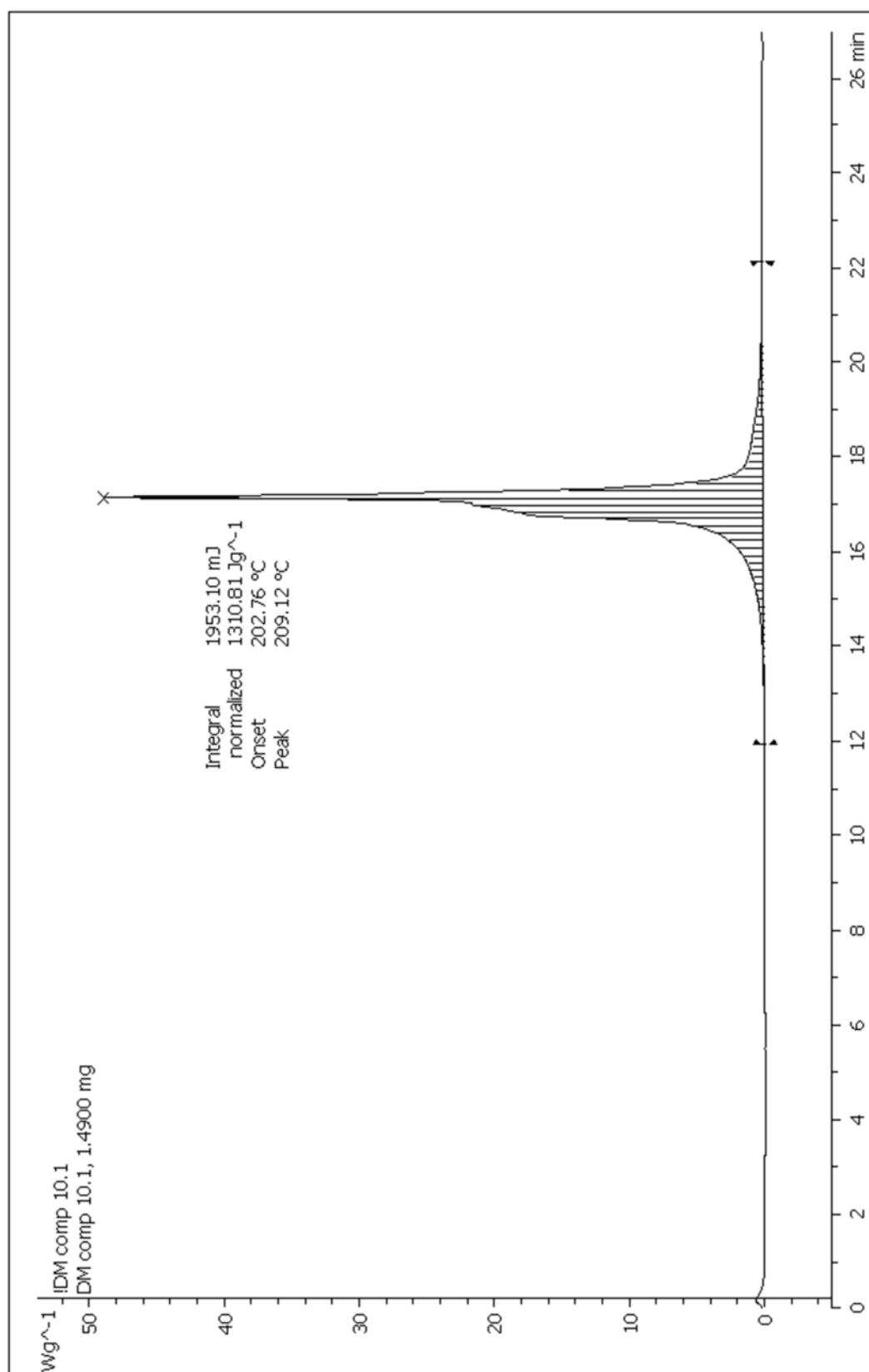


Figure 133: DSC measurement 1 of composition 10 (GuDN:PPZ 7:3)

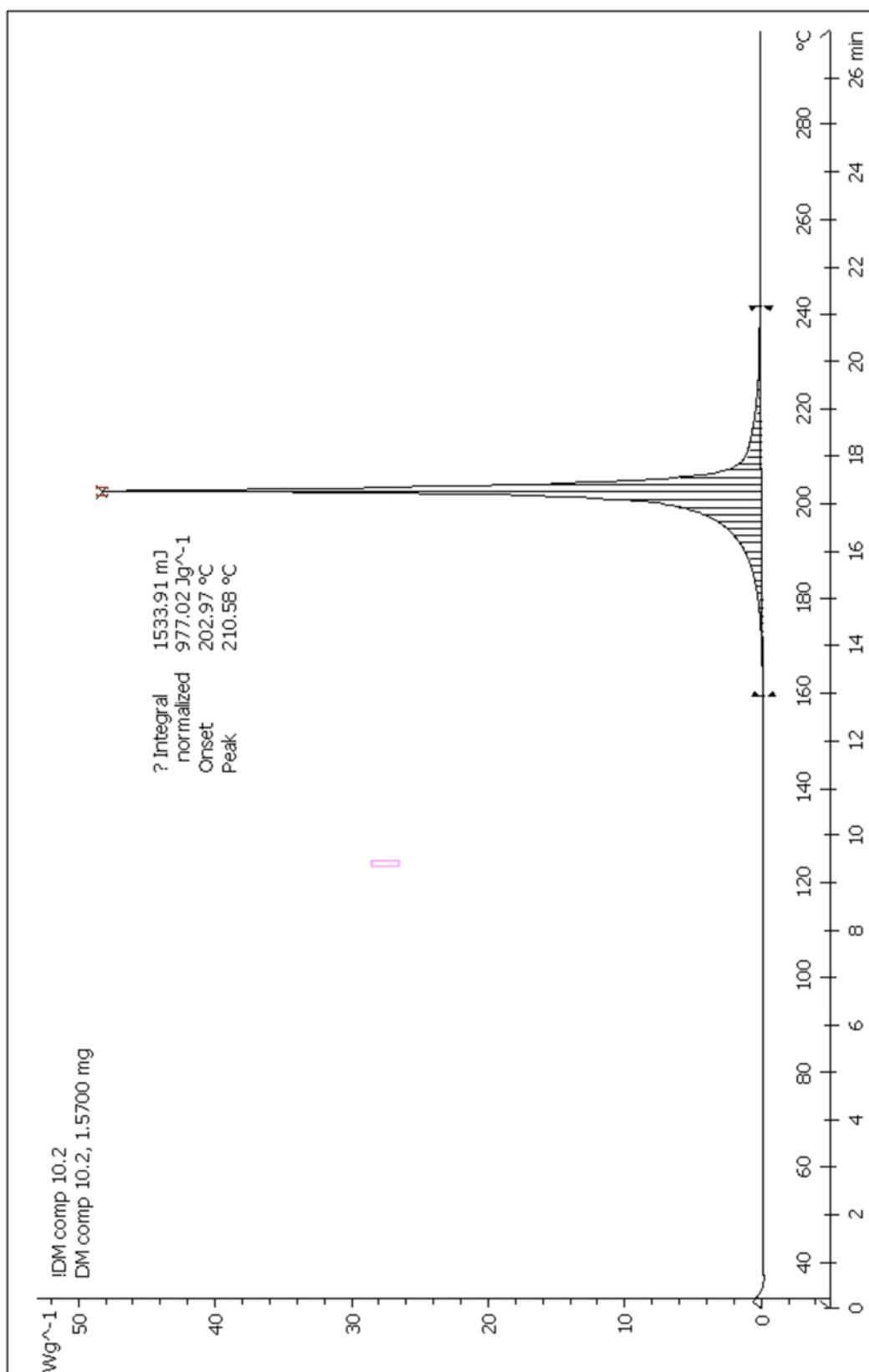


Figure 134: DSC measurement 2 of composition 10 (GuDN:PPZ 7:3)

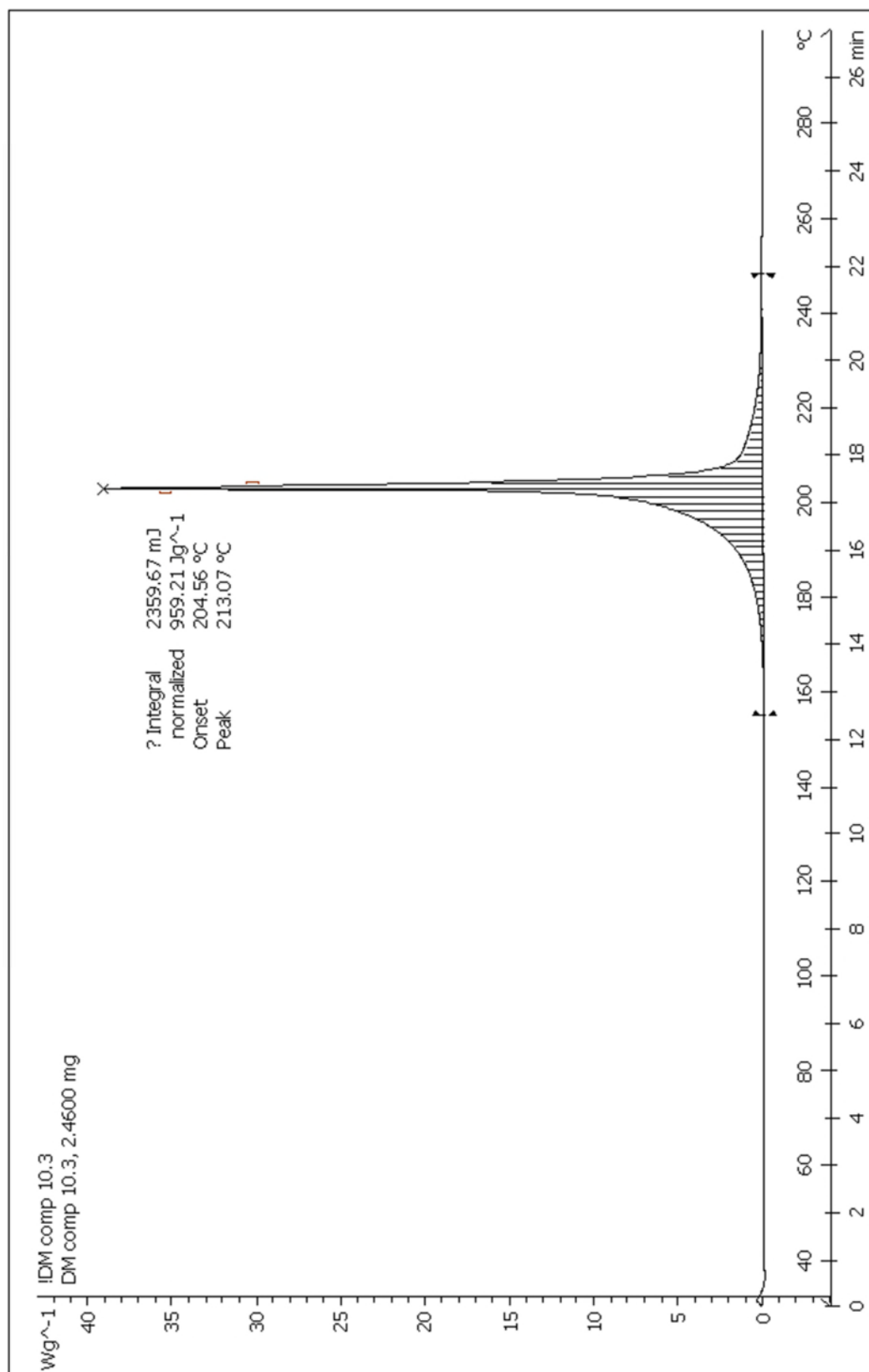


Figure 135: DSC measurement 3 of composition 10 (GuDN:PPZ 7:3)

8.9 Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectrometry (EDX)

SEM is a widely used technique that allows the visualisation of particles and surfaces on the scale of nm to μm . The SEM utilises an electron beam fired from an electron gun and focused through a series of lenses in an evacuated chamber to scan or raster a sample. A detector is used to collect information from the electrons emitted or “scattered” by the sample upon irradiation by the SEM beam, the information gathered is processed using a computer and a “live” image is displayed allowing the operator to select, magnify and capture any features of interest.

In general there are two types of electron emission that are detected and are used to generate an image of the surface. The first is known as a secondary electron. This is the product of a collision between an electron of the electron beam and an electron in the sample’s atomic orbitals. The electron ejected from the orbital is the particle detected and can be identified by its energy which is proportional to that of the electron beam. The second type of electron is known as a back-scattered electron. This electron is not released by the sample and is instead an electron from the electron gun beam that has been diverted through interactions with the sample’s positively charged atomic nuclei back towards the detector.

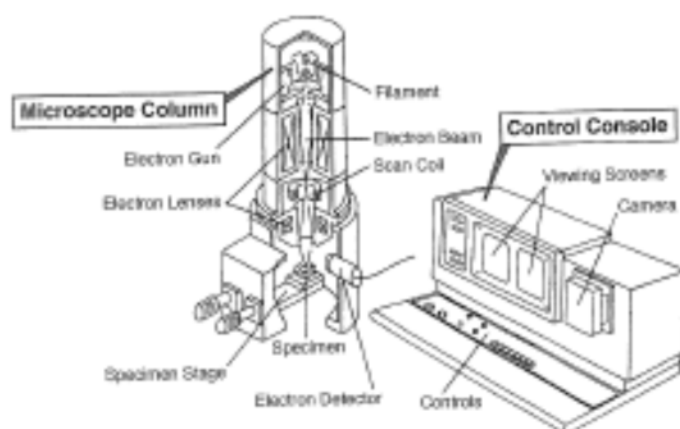


Figure 136: Simplified SEM apparatus¹²⁷

In addition to producing electrons from the sample orbitals, the electron gun can stimulate emission of x-rays. In this circumstance, the collision of an electron from the

electron beam with an inner shell electron produces an excited ion which may relax by one of two routes (Figure 137). In the first case an electron in a higher energy shell may relax to fill the unoccupied inner shell and in doing so release a photon. This photon if detected is to be observed in the x-ray region of the electromagnetic spectrum and the energy of this photon is characteristic of the element from which it was emitted. It is by the measurement of the number of the detected x-rays which allows the elemental mapping technique used here and referred to as EDX.

Auger electron spectroscopy (AES) is a complimentary technique that makes use of the alternative relaxation pathway. In this case the generation of an inner shell electron hole and the subsequent relaxation of an outer shell electron causes the emission of a photon which, instead of escaping from the atom, is absorbed by an electron in an outer shell and causes its excitation and exit from the orbital. This type of emitted electron is known as an Auger electron and gives its name to the technique which detects the characteristic energies of these electrons and provides quantitative elemental surface analysis.^{xxxviii}

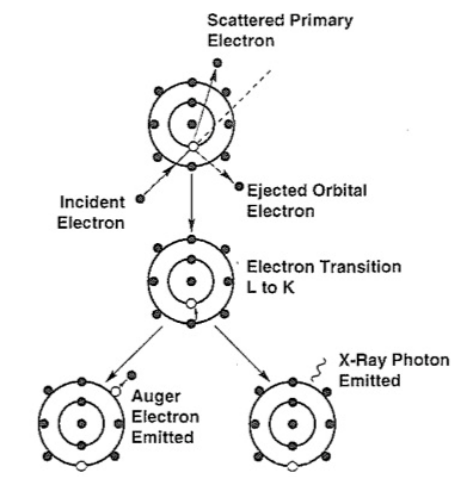


Figure 137: Transitions relating to Auger (left) and EDX (right)¹²⁷

^{xxxviii} For more information on SEM, EDX and AES please refer to “Scanning Electron Microscopy and X-Ray Microanalysis” by Goldstein et al.¹²⁷

8.10 Data Spread and Standard Deviation

The data collected for the firing replicates, DSC measurements and NMR integrals were collated and averages presented in the tables shown in chapters 5 and 6. As such the tables in chapter 5 were constructed to show the spread or standard deviation of the squib formulation performances and of the variation in the formulation compositions away from the mean values (which was used to imply the level of homogeneity). In all cases the spread was calculated using a standard deviation calculation (see Equation 14).

$$s = \sqrt{\Sigma \frac{(x - \bar{x})^2}{n - 1}}$$

Equation 14: Standard deviation calculation [where x = any variable from the data set, \bar{x} = the mean, n = the number of data points in the set]

8.11 Sensitivity Testing

8.11.1 Excerpt from “Explosive Effects and Applications”

Description of ERL and Type 12 Sensitivity Testing

“Impact

Impact testing determines whether impact (i.e., sudden compression) will initiate rapid decomposition of an energetic material. There are various configurations, but basically, a weight is dropped on a sample or a sample is impacted against a rigid target. One of the most common type of impact testers is the ERL (Explosive Research Laboratory) machine. It consists of a free-fall weight (2.5 kg or 5.0 kg), a striker and anvil (1.25 in. in diameter), and a supporting frame. Samples (30-40 mg) are placed in a dimple in the center of a 6.5 cm² sheet of 5/0 garnet paper (Type 12 configuration). A Type 12B configuration, without garnet paper, is also used on solids, while a third configuration, Type 13, is used for liquids. A standard test set consists of 20-30 shots performed by following the Bruceton “up-and-down” testing technique. Results are reported in terms of the height at which the event is obtained 50 % of the time (H_{50}). Although drop-weight impact testing is widely used for initial characterisation of small amounts of energetic materials, results can sometimes be misleading or inconsistent and are often operator-dependent...

...Friction

As with drop-weight impact testers, there are a number of friction sensitivity testing devices. In the ABL (Allegheny Ballistics Laboratory) sliding anvil test, a thin layer of powdered sample (~40 mg) is placed on a flat steel plate and slid by a nonrotating 0.3 m wide steel wheel at a [sic] initial velocity of 240 cm s⁻¹. The force between the plate and wheel is varied in 0.1 log (pound) intervals over the range of 10-1000 lbs. The results are reported in terms of the force at which initiation of the sample is probable 50 % of the time. Initiation is evidenced by production of a flash, smoke, or noise.

ESD

Sensitivity of an explosive to electrostatic discharge (ESD) is determined by subjecting a sample to a high-voltage discharge from a capacitor. The discharge energy is increased and decreased until the 50 % probability point is determined. The commonly used ESD apparatus holds a sample (3/16 in. diameter, ¼ in. high) on a steel dowel by means of a polystyrene sleeve. The sample is covered with lead foil. To induce a spark, a charged needle is moved down to penetrate the foil. Discharge takes place as the needle penetrates the foil. The discharge passes through the explosive to the grounded steel dowel. The needle, charged to varying degrees, is moved in and out of the sample until initiation is evidenced. Voltage, confinement, sample and particle size, temperature and moisture content can be varied.”⁶⁰

8.11.2 Excerpt from “Chemistry of High-Energy Materials”

Description of BAM Sensitivity Testing

“The impact sensitivity of solid, liquid or gelatinized explosives is determined by using the drophammer method. The drophammer essentially consists of a cast steel block with a cast base, a round anvil, a column fixed at the steel block, hardened, smoothed guide bars and the drop weight with retaining and releasing device. The heavy iron block is essential in order to absorb the shock waves caused by the falling weight. Both guide bars are attached to the column with three brackets. An adjustable metre rule allows an exact measurement of the drop height.

In this test the sample (approx. 40 mg) to be investigated is placed in the plunger assembly, consisting of two steel rollers, a hollow steel collar and a centring [sic] ring for fixation. The assembly is placed onto a small anvil. The impact energy (energy = work x distance = mass x acceleration x distance) can be varied by changing the drop-height (approx. 0.1-1 m) and the mass (approx. 0.1-10 kg). The minimum impact energy is determined by looking at which one had at least one out of five samples explode...

...In order to determine the friction sensitivity according to the BAM regulations, the sample is to be placed onto a rough porcelain plate (25 x 25 x 5 mm). This plate is to be clamped onto the moving platform of the friction apparatus. The friction force between the moving porcelain plate and a static porcelain peg (10 x 15 mm) (curvature radius 10 mm) causing sample initiation is determined...

...The electrostatic discharge sensitivity (electrostatic discharge sensitivity, ESD) is determined by using an ESD test apparatus. Different spark energies (usually between 0.001 and 20 J) can be set, by using variable capacitive resistances C (in Farad, F) and loading voltages”¹⁰²

8.12 Supporting Information

A CD is included with the thesis which contains data that was not readily presented within the format of a thesis but may prove useful to future researchers.

The CD contains:

- The unabridged down selection table, discussed in chapter 4
- The raw data from the firings, discussed in section 5.4
- The bridgewire resistance measurements, section 5.3.5
- Photographs of the fired squibs.

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