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DETECTION AGENTS FOR EXPLOSIVES

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Abstract

DSC measurements have been used to investigate the thermal stability of each of four specific detection agents, prescribed by the International Civil Aviation Organization for incorporation into explosives at the point of manufacture. Additionally, the compatibility of these agents with a number of commercial explosives has been assessed. DSC results for a complete study of mixtures of the agents with the explosive, tetryl are specifically described. The thermograms are compared with those of the pure agents and tetryl, the thermal decomposition of which has been previously characterized.

Keywords: explosives

Introduction

An international effort is underway to develop methods for easily detecting explosives that are being transported in a concealed fashion. The International Civil Aviation Organization (ICAO) is sponsoring this effort and the ICAO has in place a Convention [1] specifying certain detection agents for incorporation into 'flexible or malleable' explosives at the point of manufacture. These detection agents are ethylene glycol dinitrate (EGDN), 2,3-dimethyl-2,3-dinitrobutane (DMNB) and the nitrotoluenes, *o*-MNT and *p*-MNT.

Some member countries of the ICAO are undertaking research and development studies in this area. In Canada, the National Research Council (NRC) is developing means for detecting these agents, primarily gas chromatographic methods, and our laboratory is studying the properties of the ICAO detection agents and the effects of the addition of the detection agents on the properties of the explosives.

Properties of an ideal detection agent for explosives

An ideal detection agent for incorporation into plastic explosives should have the following desirable properties:

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(i) easily prepared and purified,
(ii) sufficient volatility for ease of detection,
(iii) low hazard rating as determined by mechanical/sensitivity testing,
(iv) low toxicity,
(v) odorless and colorless (i.e. presence in plastic explosive not immediately and obviously discernable),
(vi) solid at processing temperature (see vii)
(vii) compatible with all potential plastic explosives, easily mixed during manufacturing process and does not separate from, vaporize from or react with explosive during manufacture, storage or transportation i.e. no thermal events or 'aging problems'.

General properties of ICAO detection agents

Some of the general properties of the ICAO detection agents are summarized in Table 1.

Table 1 General properties of ICAO detection agents

Detection Agent	State[a]	p/μbar[a]	H_{50}/cm[b]	TLV/ppm[c]	Mass % in explosive[d]
EGDN	liquid	78	20	0.2	0.2
DMNB	solid	2.2	100	>10	0.1
o-MNT	liquid	150	>150	5	0.5
p-MNT	solid[e]	41	>150	5	0.5

[a]at 298 K; [b]$H_{50}(TNT)$/cm = 30 (impact sensivity); [c] threshold limiting value; [d]as prescribed by Convention [1]; [e]melts at 323 K

Comparison of these properties with those listed for the ideal detection agent, indicates that DMNB is the preferred choice. Additionally, the NRC has found that DMNB has properties that render it particularly suitable.

Since the detection agent will be added during the manufacture of the plastic explosives, DMNB has the notable advantage that it is the only material that is solid at typical processing temperatures i.e. >350 K, for plastic explosives. A detailed description of the thermal properties of DMNB is given in the following paper.

Properties of detection agent/explosive mixtures

Compatibility of the detection agent with the explosive in question is an important criterion for establishing the utility of a particular detection agent. Thermal and mechanical/sensitivity properties of the detection agent/explosive mixtures provide useful information about compatibility when these properties are compared with the same properties for the individual agent and explosive. A number of thermoanalytical studies, namely differential scanning calorimetry (DSC) and accelerating rate calorimetry (ARC) measurements, and impact sensitivity tests have been conducted in our laboratory (Table 2), using a variety of 'molecular' and commercial plastic explosives, containing the various detection agents at concentration prescribed by the Convention [1]. These studies formed part of the international program.

Table 2 Combinations of detection agent* and explosives tested

Explosive	EDGN	DMNB	*o*-MNT	*p*-MNT
RDX	–	x	–	–
PETN	–	x	–	–
TNT	–	x	–	–
Tetryl	x	x	x	x
C-4	x	x**	x	x
NSP-71[1]	–	x	–	–
NSP-72[1]	–	x	–	–
NSP-86[1]	–	x	–	–
NSH-71[1]	–	x	–	–
Semtex H[2]	–	x	–	–
Nitropenta[3]	–	x	–	–
Primasheet	–	x	–	–

[1]Swedish [2]Czech [3]Swiss
*at levels prescribed by Convention [1] (Table 1)
**aged samples have also been tested

It has previously been shown [2] that DSC measurements are a useful tool for compatibility testing of explosives. These measurements can be used to assess potential thermal hazards and, specifically, the effect of an additive on the temperature at which decomposition of the explosive starts i.e. thermal stability. In particular, experiments on explosive compositions containing quantities of detection agents at levels above those prescribed by the Convention [1] (Table 1) should help clarify the effect of the detection agent on the decomposition of the energetic material.

Moreover, compositions at these levels may simulate the worst case scenario in the manufacturing process in which the detection agent is incorporated, thereby indicating potential thermal hazards arising from the composition.

Table 3 Thermodynamic properties of the detection agents and tetryl

Material	$\Delta_f H$/J g^{-1}			ΔH/J g^{-1}		
	Solid	Liquid	Gas	Vaporization	Fusion	Sublimation
o-MNT	–	–71±28[a]	284[b]	348[b]	–	–
		–70[b]		420[c]		
m-MNT	–	–230±24[a]	125[b]	354[b]	–	–
		–228[b]		486[c]		
p-MNT	–351±21[a]	–223[b]	226±28[a]	415[b]	134[b]	563±14[b]
	–351[b]		226[b]	541[c]	112[f]	577±18[g]
				340[c]	123[h]	
EGDN	–	–1.60 10^3 [d]	–	485±3[c]	–	–
DMNB	–1768±3[a]	–1684±12[a]	–	–	84±15[a]	533[c]
					165±34[c]	
Tetryl	92±12[a]	–	–	–	79.9[d]	

[a]Reference [4] [b]Reference [5] [c]estimated from vapour pressure or solubility data Reference [6] [d]Reference [7] [f]Reference [9] [g]Reference [10] [h]Reference [11]

Thermodynamic and thermal information for ICAO detection agents and tetryl

This paper includes the results of DSC measurements of the thermal properties of (i) the ICAO detection agents, (ii) tetryl and (iii) mixtures of the ICAO detection agents with tetryl. The thermal properties of tetryl are compared with those published previously [3].

The thermodynamic properties of the detection agents and tetryl are summarized in Table 3. This Table also includes the properties of *m*-MNT in order to complete the MNT series.

While there have been extensive studies of 'molecular' explosives using DSC [12], the ICAO detection agents have not, in general, received much attention. DSC studies on condensed phase *p*-MNT [11] have revealed the presence of a metastable solid. Thermal decomposition studies of the MNTs in the vapour phase between 570 and 620 K [13] have yielded kinetic results. Additionally, onset temperatures and energies for the decomposition of the MNTs have been recorded in a compilation of pressure DSC results for a series of reactive chemicals [14]. No DSC results for the decomposition of condensed phase EGDN or DMNB were found in the literature, although DTA studies on DMNB at temperatures below decomposition have been reported [15].

In contrast, there have been several investigations of the thermal decomposition of tetryl by both ARC and DSC methods (for a summary of the results see [3]). Tetryl is known to decompose in a two step consecutive reaction of the type

$$A \rightarrow B \rightarrow C$$

and the kinetic parameters have been determined, since the steps in the reaction occur at widely different temperatures and can therefore be readily separated.

Experimental

Chemicals

DMNB and the MNTs were purchased from the Aldrich Chemical Co. These chemicals were claimed to be at least 98 mol% pure and were used without further purification. Samples of DMNB additionally purified by sublimation or recrystallization showed no discernible difference in the DSC from those untreated. EGDN was kindly donated by *L.* Elias of the NRC, where it was prepared by careful nitration of ethylene glycol, followed by washing with alkaline solution, water and subsequent drying. The resultant oily product was claimed to be at least 96 mol% pure and it was used without any further purification in the thermoanalytical studies described here. Tetryl was kindly supplied by DREV (Defence Research Establishment at Valcartier) who, in turn, obtained this material from the Los Alamos National Scientific Laboratory (LASL). The properties of LASL tetryl have been described [17]. The sample of tetryl was claimed to be at least 95 mol% pure and it was used without further treatment.

Measurements

Standards, samples of detection agents and tetryl and the mixtures were sealed in glass microampoules (closed system) as described in the following paper. In some cases, experiments were repeated using hermetically sealed aluminum pans. The loaded microampoule was placed in a DSC 910 – TA 2100 System (TA Instruments) with a carrier gas of oxygen-free dry nitrogen at a flow rate of 50 cm^3 min^{-1} for the DSC measurements. The instrument was calibrated for temperature and heat flow using an appropriate pair selected from the standards gallium, indium, tin, zinc and lead. Calibration was checked by running another standard with an intermediate melting temperature. A heating rate of 5 K min^{-1} and sample size of less than 1 mg were used.

Results and discussion

Detection agents and tetryl

The thermoanalytical curves for the detection agents and tetryl are shown in Figs 1 to 4 and 6. Table 4 provides a list of the peak temperatures and transformation energies for each of these materials. For *p*-MNT, the onset temperature of 322.6±0.5 K and enthalpy of fusion of 117±4 J g^{-1} can be compared with the values of 325.7±0.1 K and 122.6±0.7 J g^{-1} (Table 3) obtained from earlier DSC measurements [12]. Some variation in the latter results were noted as a result of the appearance of a 'meta stable phase'.

For DMNB, the value of 475 K is in satisfactory agreement with the reported melting point of 480 K [16]. There are, however, large differences between the ΔH recorded in Table 4 and the two values listed in Table 3 for the fusion of DMNB. Onset temperatures for the low temperature endotherms are in excellent agreement with those published previously [15], but the ΔH value for the endotherm at 388 K in Table 4 differs significantly from the reported value of 131 J g^{-1}.

The values of 398±2 K and 78±6 J g^{-1} in Table 4 for tetryl compare closely with the reported melting point of 403 K and the enthalpy of fusion of 79.9 J g^{-1} [7] (Table 3).

The thermoanalytical curves for *o*-MNT and *p*-MNT show that decomposition in the liquid phase occurs at similar temperatures to those at which the earlier vapour phase decomposition kinetics were determined [13]. The results of the publis-hed [14] pressure DSC results for *o*-MNT and *p*-MNT are also recorded in Table 4 for comparison.

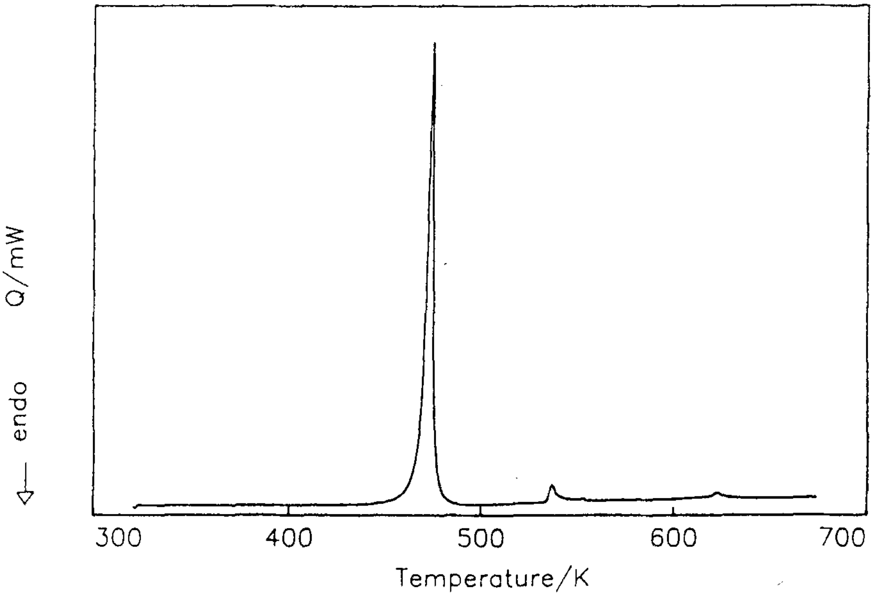

Fig. 1 DSC curve for EGDN

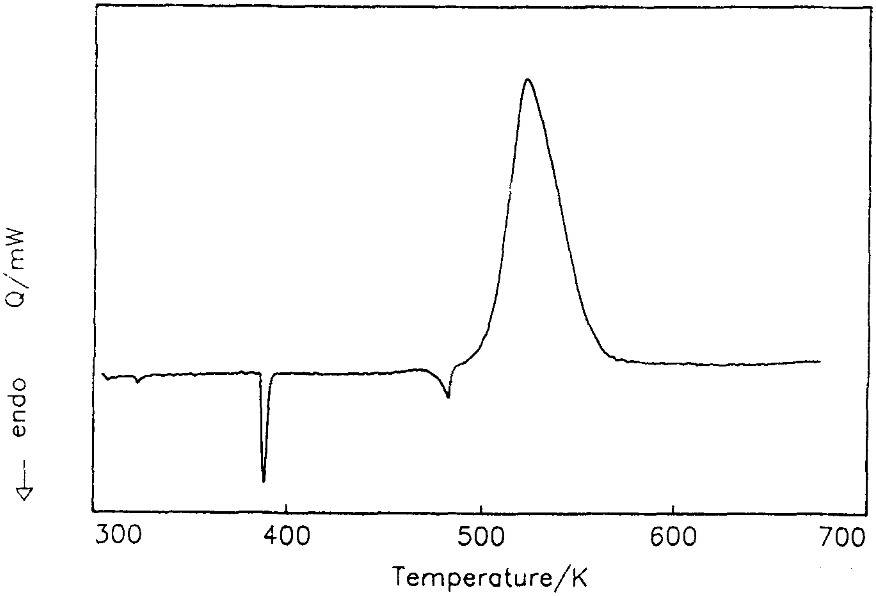

Fig. 2 DSC curve for DMNB

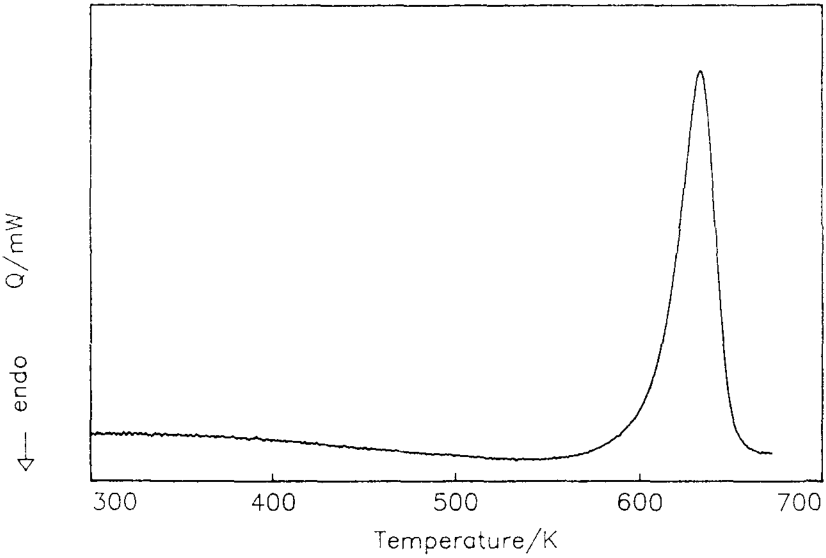

Fig. 3 DSC curve for *o*-MNT

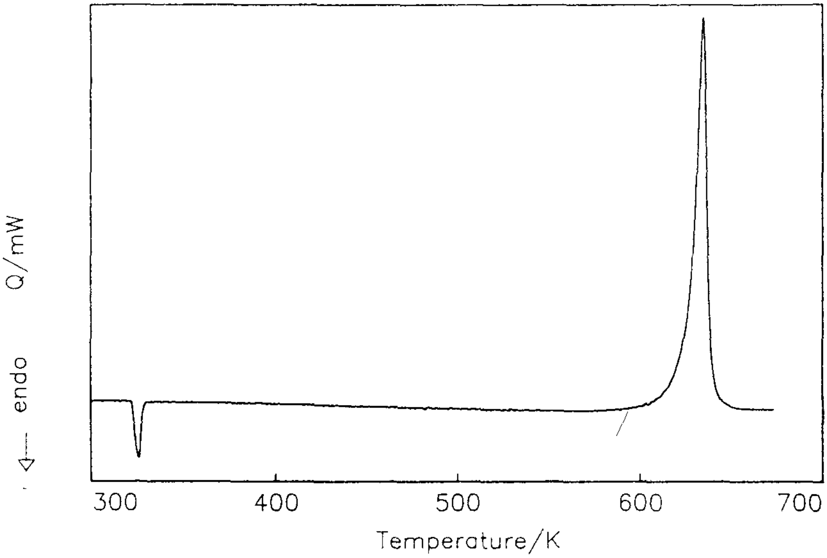

Fig. 4 DSC curve for *p*-MNT

EGDN shows the characteristic behaviour of a highly energetic material in that its exotherm peak in the thermogram leans to the high temperature side. This is an indication that the temperature increase resulting from decomposition exceeds that provided by the instrumental heating rate for that time period. Since EGDN has a 'heat of explosion' of 7.3 kJ g [7], the large decomposition energy (Table 4) observed in the DSC measurements is not unexpected. The small exotherms occurring after the main decomposition peak are believed to be indicative of secondary decomposition processes.

Table 4 Peak temperatures and apparent ΔH values for the ICAO detection agents and tetryl

Material	Endotherms		Exotherms	
	T/K	ΔH/J g^{-1}	T/K	ΔH/kJ g^{-1}
EGDN	–		475±1	4.28±0.15
			535±2	0.25±0.05
DMNB	322*	5.7±1.1	521.0±0.5	3.08±0.27
	388*	103±9		
	475*	34±6		
o-MNT	–		632.6±0.1	2.10±0.12
			611**	1.33**
p-MNT	322.6±0.5*	117.0±3.5	635.3±0.2	1.98±0.13
	326.1±0.2		639**	1.56**
tertyl	398±2*	78±6	470.7±0.3	1.77±0.03
	401.0±0.5		556.9±0.9	2.92±0.10

*onset **Reference [14] at 35 bar

The thermoanalytical curve for tetryl shows the separation of the two exotherms resulting from the consecutive steps of the thermal decomposition as described earlier. The energy change in the first step is about 60% of that of the second step. Further, it is clear, under the experimental conditions, that (i) there is some overlap in the peaks characterizing these steps and (ii) an additional event occurs at the end of the second step [3], resulting in a broad tail in the thermogram. Peak separation of 86±2 K occurs at a heating rate of 5 K min^{-1}. From preliminary results at a heating rate of 20 K min^{-1}, the activation energies for the two steps are approximately the same, in contrast with the published results [3]. Additional experiments at lower heating rates may provide additional peak separation, thereby permitting expanded kinetic studies.

Detection agent/tetryl mixtures

The thermoanalytical curves for the mixtures of detection agents with tetryl are shown in Figs 5 to 8. The peak temperatures and apparent ΔH values for these mixtures are recorded in Table 5. Where multiple overlapping peaks and shifting baselines occur, assignment of a ΔH value was arbitrarily done by dropping a perpendicular between the peaks. For the purpose of comparison of the decomposition energy with that for the separate detection agent and tetryl, the total energy is often useful.

The combination of EGDN and tetryl shows an exotherm at the same peak temperature as for pure EGDN with an energy value significantly larger than expected on the basis of composition. A secondary peak at 545 K occurs with an energy approximately 50% that for pure tetryl with a reduced peak separation, apparently initiated by the secondary decomposition process in EGDN which occurs at 530 to 540 K.

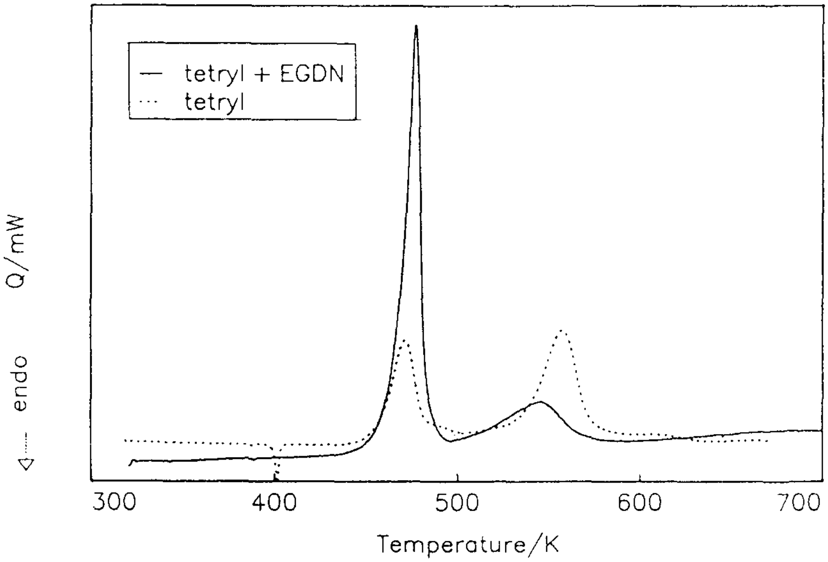

Fig. 5 DSC curve for tetryl +EGDN

In the mixture of tetryl and DMNB, the melting point of tetryl has been depressed from about 400 to about 375 K and this transition overlaps with the phase transition of DMNB occurring at 388 K. As for the exotherms in this mixture, it is noted that (i) the peak temperature of the first step is the same as that for pure tetryl and (ii) the energy change is approximately 50% that for pure tetryl, as expected. Thus, the first step of the decomposition of tetryl appears to be unaffected by the presence of DMNB. Conversely, the second step of the tetryl decomposition is shifted to lower temperatures as a result of the early decomposition of DMNB. The absence of the 'tail' characteristic of the tetryl decomposition also suggests an altered mechanism for this process.

Similar to the above results for DMNB, *o*-MNT does not affect the first step of the decomposition of tetryl. The second peak apparently includes the decomposition of *o*-MNT, shifted to a lower temperature, since the energy is larger than expected from the composition.

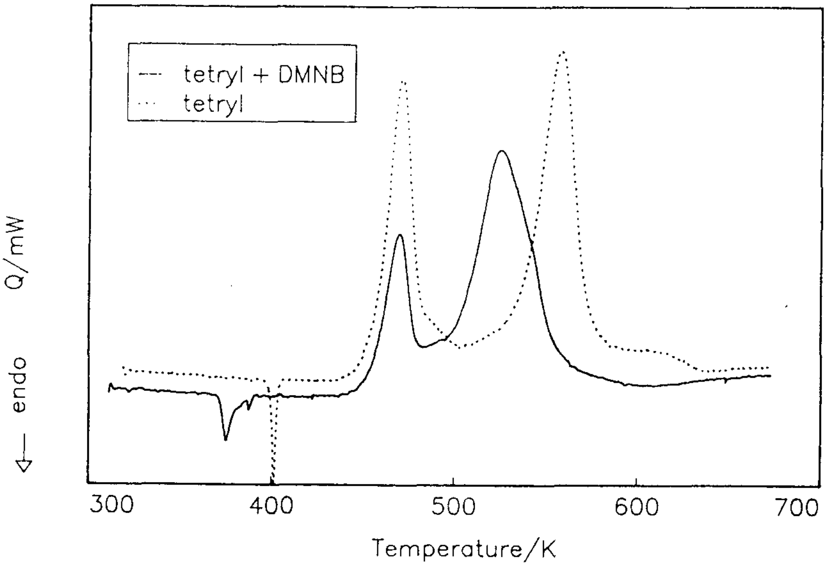

Fig. 6 DSC curve for tetryl +DMNB

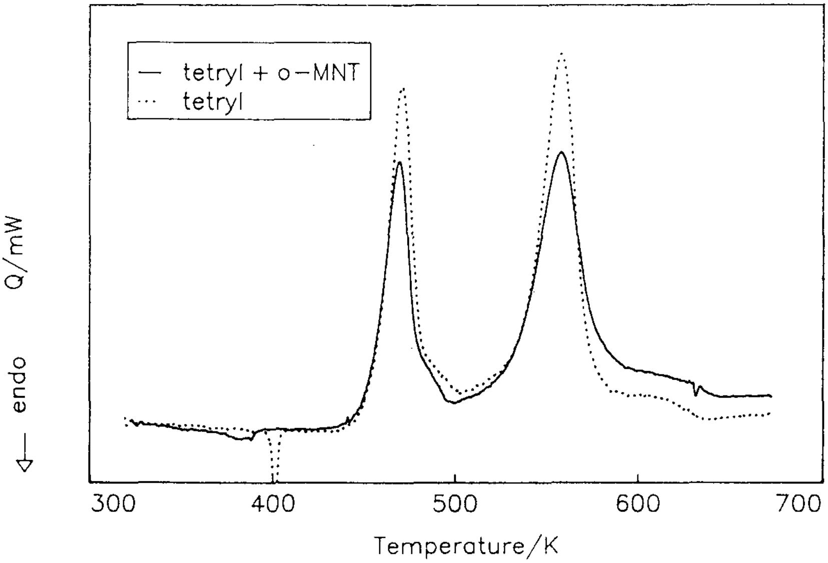

Fig. 7 DSC curve for tetryl +*o*-MNT

Finally, the mixture of *p*-MNT and tetryl shows thermal behaviour which is quite different from that of the mixture of *o*-MNT and tetryl. There are three

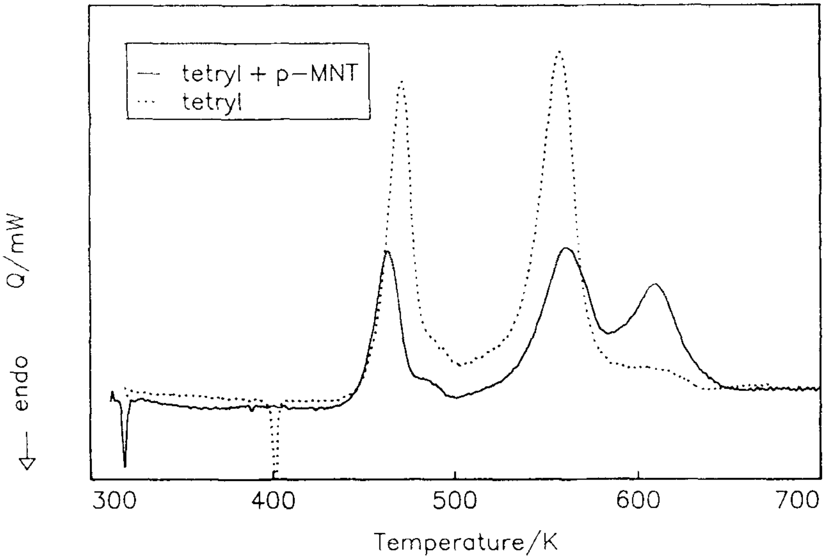

Fig. 8 DSC curve for tetryl +*p*-MNT

Table 5 Comparison of the peak temperatures and apparent ΔH values for the detection agent +tetryl mixtures with those values for tetryl

	Endotherms		Exotherms	
	T/K	ΔH/J g^{-1}	T/K	ΔH/kJ g^{-1}
tetryl	401.0±0.5	78±6	470.7±0.3	1.77±0.03
			556.9±0.9	2.92±0.10
tetryl +EGDN	389±1	2.0±0.3	477±1	3.75±0.13
50:50*			545±1	1.30±0.17
tetryl +DMNB	375.0±0.4	100±10	469.9±0.2	0.84±0.01
50:50	387.5±0.1	8.0±2.0		3.09±0.25
tetryl +*o*-MNT	383±5	68±2	469.3±0.2	1.36±0.02
67:33			557.7±0.1	2.77±0.07
tetryl +*p*-MNT	318.6±0.1	53±2	461.8±0.6	0.59±0.08
50:50	388.0±0.1	2.05±0.13	562.4±1.4	0.98±0.13
			616.6±1.6	1.26±0.02

*mass ratio

peaks in the thermogram with the first peak occuring at a temperature significantly lower than that for pure tetryl and with a decomposition energy reduced from that expected on the basis of concentration. The second peak occurs at a temperature somewhat higher than the second peak for pure tetryl and with about 30% of the energy. Lastly, the third peak appears to represent the major part of the decomposition of *p*-MNT occurring at a significantly lower peak temperature and with slightly greater than the expected energy.

Because of the difficulty in assigning energies for the individual overlapping peaks, the weighted sums of the energies for the pure components were compared with the observed values. An energy balance, within the estimate of the uncertainty, was obtained for all mixtures except *p*-MNT/tetryl, the latter case showing excess energy beyond that expected, suggesting chemical incompatibility.

Conclusions

The first results for the direct DSC analysis of the decomposition of the condensed phase ICAO detection agents using a closed system are given here. This same system has been used to confirm that the decomposition of tetryl proceeds via at least two consecutive and separable steps.

The compatibility of the detection agents with the explosive, tetryl has been tested using DSC measurements. For all cases except that for the system containing *p*-MNT the onset of the decomposition of tetryl is unaffected by the presence of the detection agent. However, the second step of the decomposition of tetryl is clearly affected, with the DSC results suggesting an altered mechanism.

In the mixture containing *p*-MNT and tetryl, there is evidence for incompatibility from the following observations: (i) an onset temperature lower than that for pure tetryl and (ii) failure of this system to adhere to an energy balance, in contrast with the other combinations of detection agent +tetryl.

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Zusammenfassung — Mittels DSC-Messungen wurde die thermische Stabilität von vier speziellen Nachweismitteln untersucht, die von der Internationalen Organisation für Zivilluftfahrt zur werkseitigen Einbringung in Explosivstoffe vorgeschrieben wurde. Zusätzlich wurde die Verträglichkeit dieser Mittel mit einer Anzahl handelsüblicher Explosivstoffe beurteilt. Die DSC-Ergebnisse einer kompletten Untersuchung von Gemischen der Mittel und dem Sprengstoff Tetryl wurden ausführlich beschrieben. Die Thermogramme werden mit denen der reinen Mittel und dem von Tetryl verglichen, dessen thermische Zersetzung zuvor charakterisiert wurde.