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Comparison of Test Results from Typical Explosive Properties Screenings, such as the Closed Pressure Vessel Test (CPVT) and the Glass Cylinder Deflagration Test

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A fast and reliable screening for explosive properties of organic substances is a crucial and ongoing topic for the fine chemicals industry. However, many test systems require large amounts of material, especially for the evaluation of detonative properties, e.g. the BAM 50/60 Steel Tube Test, which may not be available in early stages of development.

Therefore, a CPVT with high-resolution pressure measurement (1 kHz) was implemented, based on Adolf Kühner's mini-autoclave system as described in Whitmore et al. (1999). To evaluate the violence of the decomposition reactions, the CPVT was calibrated according to a procedure as suggested in Knorr et al. (2007), which is based on comparing the maximum pressure rise rate and peak temperature data of standard materials with known explosive properties. Variations of this system are already implemented in some companies and proved its usefulness (Bodman & Chervin, 2004).

The use of this type of stability testing of energetic, organic materials was accompanied by parallel testing of the sample materials with several other screening tests, such as the Glass Cylinder Deflagration Test (VDI 2263-1, 1190), the UN Time/Pressure Test (UNDG MTC, 2015) and also by more simple screenings such as dynamic runs in DSC and in the Lütolf Oven (VDI 2263-1, 1990).

This work compares and discusses the different test results, i.e. detonation and deflagration behaviour.

1. Introduction

In chemical process development there is a strong demand for a fast and reliable screening of explosive properties of energetic organic compounds. The handling of material with explosive properties is not just associated with legal challenges but also technical issues, e.g. processing in larger scale may become inefficient and thus game-changing decisions are required as early as possible in the development phase. However, in such early stages only small amounts of sample material are available for safety testing. Typically, the screening criteria as outline in the Orange book (UNDG MTC, 2015) are applied to exclude explosive properties. These criteria are very conservative leading to numerous false positive results. The UN screening scheme refers mainly to the heat of decomposition as pivotal criterium and is based on thermal stability screening tests such as DSC (Differential Scanning Calorimetry). If the screening criteria indicate potential explosive properties, it is prudent to treat the material as such until proven otherwise. The CPVT and its criteria are intended to reduce the number of false positives.

The aim of this project was to compare results from different screenings tests and to evaluate the recently implemented Closed Pressure Vessel Test (CPVT) in regard to experimental effectiveness. The materials used for testing were mainly standard lab samples with suspected explosive properties. Only one reference material (Azodicarbonamide) as mentioned in the Orange book (UNDG MTC, 2015) was integrated in the test program.

2. Screening tests and evaluation schemes

The following screening calorimeters and tests were used to characterise the thermal stability and explosive properties of samples.

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2.1 Calorimetric screenings (DSC and Lütolf Oven)

The initial test performed was a dynamic DSC measurement up to 400°C using gold plated high pressure crucibles and a heating rate of 4 K/min according to ASTM E 537.
For the evaluation the typical threshold values as mentioned in Appendix 6 of the Orange book (UNDG MTC, 2015) were used:

(i) exclusion of self-reactive properties (UN Division 4.1) when the exothermic decomposition energy is < 300 J/g,
(ii) exclusion of explosive properties (UN Class 1) when the exothermic decomposition energy is < 500 J/g,
(iii) exclusion of detonation propagation (UN Class 1) when the exothermic decomposition energy is < 800 J/g.

Another thermal stability test performed was the dynamic measurement in the Lütolf Oven using open glass test tubes with 2 g samples and a heating rate of 2.5 K/min according to VDI 2263-1 (Figure 1a). The temperature difference (ΔT) between the sample tube and a graphite reference sample is recorded and plotted against the oven temperature (Figure 1b). Despite the rather old-fashioned test setup, energetic decomposition reactions can be followed even visually, which makes it a useful screening tool especially for deflagration reactions.
The criterium used to exclude deflagration behaviour, as determined in the Glass Cylinder Deflagration Test according to VDI 2263-1 (see more detailed description below), is: ΔT_{max} < 10 % of the left temperature limit of the exotherm peak (T_{Onset}) in °C. This criterium is applied within TÜV SÜD Process Safety and is an alternative to the above listed 300 J/g criterium for DSC measurements.

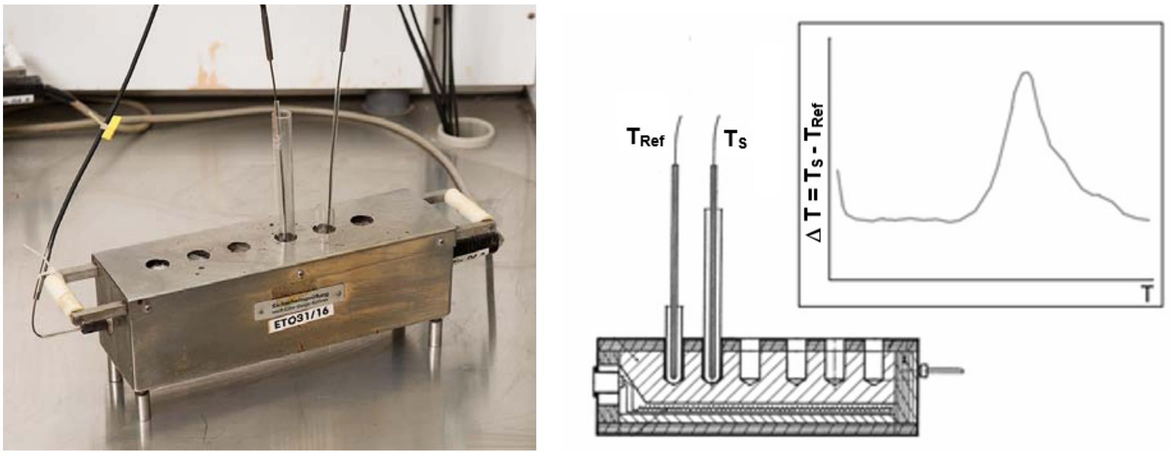

Figure 1: Picture of Lütolf Oven (1a) and cross-section with thermogram (1b)

2.2 Glass Cylinder Deflagration Test

The Glass Cylinder Deflagration Test according to VDI 2263-1 consists of a vertical glass tube (40 mm in diameter), filled with 200 ml of sample material, which is ignited by a glowing plug (about 800°C) either at the bottom or on top. The propagation of the decomposition front is monitored visually and with 3 thermocouples immersed in the sample at different heights. If a propagating deflagration front is observed, then the sample is considered capable of deflagration. Since deflagration is temperature and pressure dependent the sample is typically pre-heated prior to testing (to process temperature or 100 °C).
Many deflagration incidents observed in the Basel chemical industry were initiated by hot tramp material in dryers, mixers, mills, sieves and screw conveyers. Therefore, a classification system was developed by Fink and Zwahlen (1992), in which the deflagration behaviour is classified from GKD 1 to 3 for increasing violence (Table 1). Based on this deflagration risk class, unit operation specific recommendations regarding use of equipment and layout of safety measures, e.g. extinguishing systems, can be derived.

Table 1: Deflagration risk class GKD

Risk class	GKD 1	GKD 2	GKD 3
Operator (combination of the criteria below)	*and*		*or*
Decomposition energy	< 1000 J/g		> 1500 J/g
Combustibility index @ 100°C			6
Onset (left limit) in dyn. Lütolf or DSC	> 150 °C		
Ignition time (glowing plug)	> 60 s		≤ 20 s
Propagation velocity	≤ 1 cm/min	> 1 ≤ 3 cm/min	> 3 cm/min
Gas release	< 10 l/kg		> 50 l/kg
Reaction violence	Only smoke, no ejection of material		Material mainly ejected

2.3 Closed Pressure Vessel Test (CPVT)

The CPVT consists of a g-scale differential thermal analysis system with mini-autoclaves with a free volume of about 6 ml and is connected to a high-speed pressure transducer (kHz data capture). The autoclaves are filled with 1 g of sample material and heated with 2.5 K/min up to a maximum of 400 °C. Besides pressure the temperature difference (ΔT) between sample and reference (containing graphite) is recorded and plotted against the reference temperature. The system setup is illustrated in Fig. 2 and a detailed description is given in Whitmore et al. (1999).
Based on the maximum rate of pressure rise (MPR) and the peak temperature (T_P), which is defined as the reference temperature at peak maximum, an explosive rank may be assigned. The risk ranking was suggested by Whitmore et al. (2001) and is shown in Table 2.

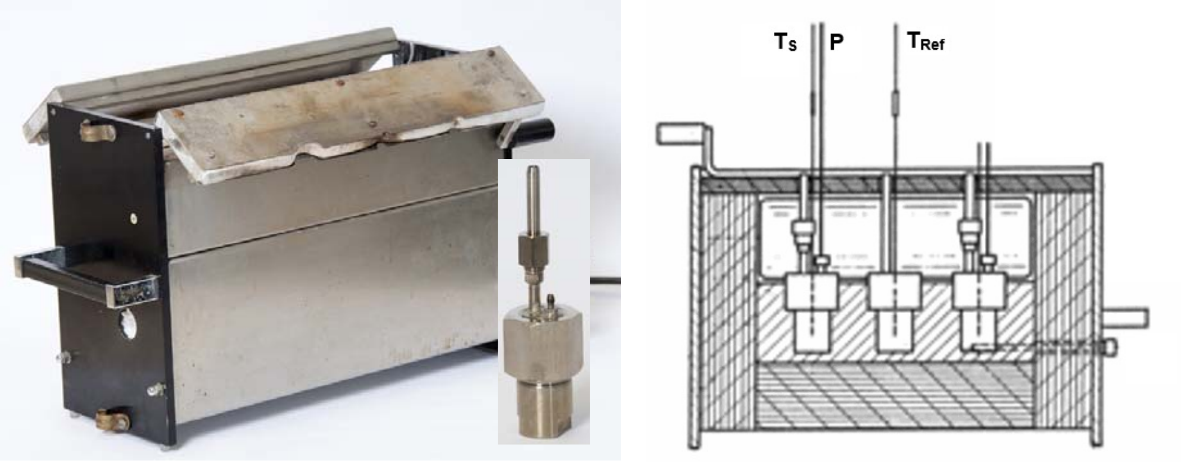

Figure 2: Picture of CPVT oven with single mini-autoclave (2a) and cross-section of CPVT (2b)

The boundaries for classification are shown in Fig. 3 and were based on the results of the three reference materials BPO75 (Dibenzoyl peroxide 75% with water), AIBN (2,2'-Azobis(2-methylpropanenitrile)) and MN (Malononitrile) following the calibration procedure as suggested by Knorr et al. (2007).

2.4 UN Tests

From the official UN tests the Time/Pressure Test and in two cases also the Koenen Test were used to compare the previously described screening test results. The UN Tests were performed according to the Orange book, Manual of Tests and Criteria (UNDG MTC, 2015).

Table 2: Explosive rank determined by the CPVT

Explosive rank	Severest property according to UN Class 1 tests	Correspondence to UN transport classification
A	Detonates (related to BAM 50/60 Steel Tube Test)	Potentially class 1
B	Deflagrates rapidly (related to Time/Pressure Test) and/or gives violent effect upon heating under confinement (related to Koenen Test)	Potentially class 1, but not detonable
C	Deflagrates slowly (related to Time/Pressure Test) and/or medium or low effect of heating under confinement (related to Koenen Test)	Not class 1
D	Does not deflagrate and shows no effect of heating under confinement	No explosive properties with respect to transport classification

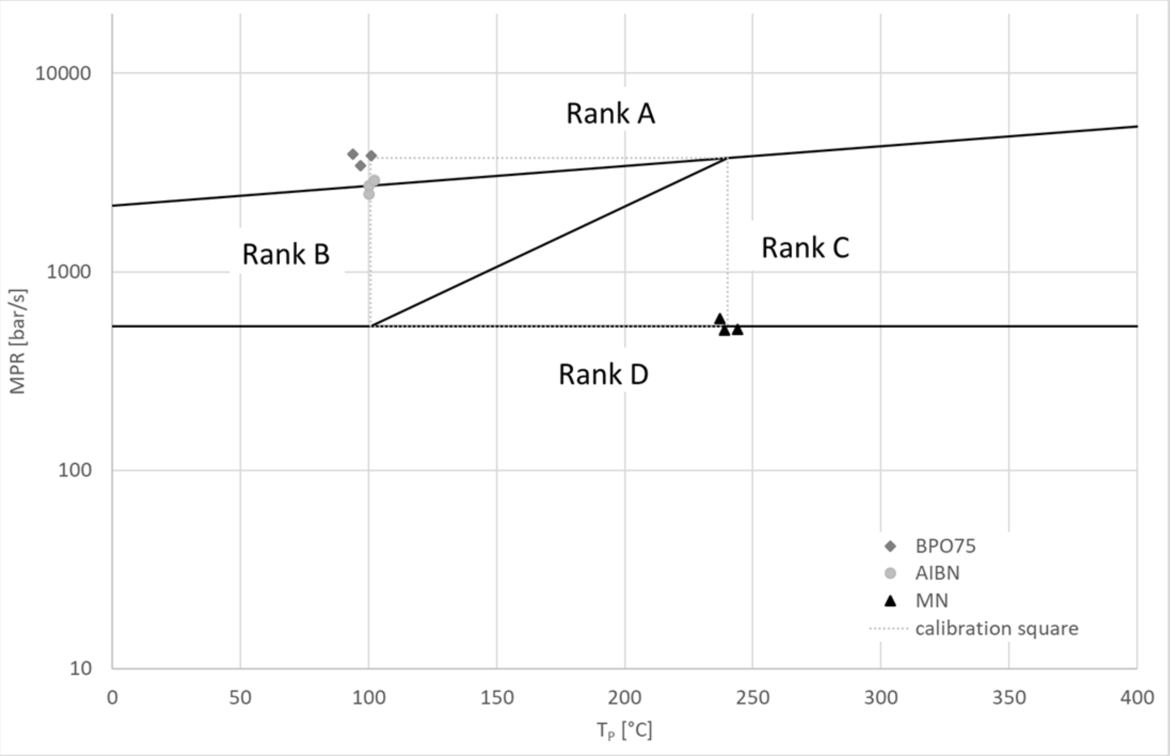

Figure 1: Explosive rank classification boundaries

3. Results and discussion

The test results for each test are listed in table 3a and 3b. The samples are listed in the order of increasing exothermic decomposition energy Q’ determined by DSC or, when not available, by increasing ΔT_{max} determined in the Lütolf Oven.

10 samples were tested negative and 5 positive in the Glass Cylinder Deflagration Test. Only those with Q’ > 1000 J/g (determined by DSC) led to positive results of the Glass Cylinder Deflagration Test. However, all positively tested samples showed very violent deflagrations, rated as GKD = 3, which explains the observed high threshold value of 1000 J/g, being more than 3 times the internal limit value of 300 J/g.

From the 10 negative Glass Cylinder Deflagration Tests all were false positive regarding the Q’ > 300 J/g criterium for DSC and 9 false positive regarding the 10% criterium for the Lütolf Oven.

False negative results could occur, because only samples were chosen which were suspected to be capable of deflagration, i.e. Q’ > 300J/g determined by DSC or the 10% criterium determined in the Lütolf Oven (ΔT_{max} > 10 % T_{Onset}).

Table 3a: Test results (Calorimetric screenings)

Sample	DSC			Lütolf Oven		
	T_{Onset} *[°C]*	T_P *[°C]*	Q' *[J/g]*	T_{Onset} *[°C]*	ΔT_{max} *[°C]*	10% criterium
1	106	241	309	180	19	pos.
2	157	224	332	181	19	pos.
3	181	225	531	140	35	pos.
4	116	224	601	200	92	pos.
5	220	251	617	200	33	pos.
6	112	231	618	180	18	pos.
7	276	328	735	211	132	pos.
8	198	265	758	199	69	pos.
9	192	249	778	200	100	pos.
10	294	367	1039	301	122	pos.
11	99	116	1118	98	53	pos.
12	159	210	1315	142	48	pos.
13	233	302	1359	240	24	pos.
14	75	135	1520			
15	99	169	1695			
16	215	242	2827	230	84	pos.
17				209	14	neg.
18				184	100	pos.
19				212	157	pos.

Table 3b: Test results (Glass Cylinder Deflagration Test, Time/Pressure Test, CPVT and Koenen Test)

Sample	Glass Cylinder Deflagration Test		Time/Pressure Test			CPVT			Koenen
	Result	GKD	P_{end} *[bar]*	$t_{6.9\text{-}20.7\ bar}$ *[ms]*	Result	MPR *[bar/s]*	T_P *[°C]*	Expl. rank	
1	neg.					<1		D	
2	neg.					<1		D	
3	neg.				neg.	<1	227	D	
4	neg.				neg.	<1		D	
5	neg.				neg.	<1		D	
6	neg.				neg.	<1		D	
7	neg.				neg.	8		D	
8	neg.					6		D	
9					neg.	2	229	D	
10	pos.	3			neg.	235	332	D	
11				21	fast	2274	91	B	
12	pos.	3	>20.7	63	slow	2529	179	B	limiting Ø = 1.5 mm
13	neg.				neg.	<1		D	
14			24.3	30	slow	2298	190	B	
15				182	slow	1558	141	B	
16	pos.	3		89	slow	5828	234	A	limiting Ø < 2.0 mm
17	neg.					<1	230	D	
18	pos.	3			neg.	<1	197	D	
19	pos.	3		429	slow	1179	198	C	

As expected, all negative results from the Glass Cylinder Deflagration Test were confirmed by the Time/Pressure Test. However, the 5 positive Glass Cylinder Deflagration Tests corresponded to two slow deflagrations in the Time/Pressure Test and 3 negative Time/Pressure Tests. The reason for this are the different criteria applied. The observation period in the Glass Cylinder Deflagration Test is in minutes (propagation velocity of > 3 cm/min for violent deflagrations), but it is milli-seconds for the Time/Pressure Test (pressure increase between 6.9 and 20.7 bar in < 30 ms), which is linked to the intended application (unit operations in production vs. transport classification).

The same holds true for the CPVT. All negative results from the Glass Cylinder Deflagration Test were confirmed by the CPVT. The 5 positive Glass Cylinder Deflagration Tests corresponded to one explosive rank A (detonation), one rank B (fast deflagration), one rank C (slow deflagration) and two rank D (no deflagration) in the Time/Pressure Test. The comparable classification outcome is not surprising, as the CPVT ranking criteria are derived from UN-Tests, incl. the Time/Pressure Test. The CPVT cannot be regarded as conservative for the evaluation of unit operations, as 2 rank D results (no deflagration) were obtained. The extrapolation of the criteria derived from UN tests for transport classification to other applications especially at elevated temperature is not possible. Further investigations would be required as it is not clear to what extent the higher temperatures affect the ranking. Anyway, the existing ranking system already uses temperature dependent boundaries.

All negative results from the Time/Pressure Test (9) were confirmed by the CPVT.

The 5 slow deflagrating substances, as tested in the Time/Pressure Test, corresponded to one rank A (detonation), three rank B (fast deflagration) and only one correct rank C (slow deflagration) in the CPVT. The one fast deflagrating substance, as tested in the Time/Pressure Test, got a correct rank B. Thus, for the limited amount of tested samples the CPVT always gave conservative results.

Only two samples could be tested with the Koenen test. Sample 12 showed a medium effect of heating under confinement (limiting Ø = 1.5 mm) and got a rank B in the CPVT (violent effect of heating under confinement) and sample 17 showed a medium effect or less (limiting Ø < 2.0 mm) and got a rank A (detonation). Though for both samples the CPVT gave conservative results.

4. Conclusions

In this test series the CPVT was a fast and reliable screening test, consuming small amounts of sample (2 x 1 g per test). It led to conservative assessments regarding explosive properties for transport classification, i.e. explosives of class 1 and self-reactive substances of division 4.1. Due to the limited number of samples this finding cannot be generalized. Further evaluation, preferably by round robin tests, is required to verify the ranking system and to confirm the conservative nature of the screen.

For the assessment of deflagration behavior in unit operations, e.g. drying processes, the CPVT test showed clear limitations, which are related to the actual ranking system.

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