



Cent. Eur. J. Energ. Mater. 2020, 17(4): 552-565; DOI 10.22211/cejem/131804

Article is available in PDF-format, in colour, at:

http://www.wydawnictwa.ipo.waw.pl/cejem/Vol-17-Number4-2020/CEJEM_01125.pdf



Article is available under the Creative Commons Attribution-Noncommercial-NoDerivs 3.0 license CC BY-NC-ND 3.0.

Research paper

The Effect of Detonator Shell Materials on Detonation Calorimetry Results

Ondřej Němec¹, Tomáš Musil², Martin Künzel^{1,*}

¹ OZM Research, Blížňovice 32, Hrochův Týnec, Czech Republic

² Austin Detonator, Vsetín, Czech Republic

*E-mail: kunzel.martin@gmail.com

Abstract: Detonation calorimetry is a method for the determination of the heat released by the detonation of an explosive charge. Compared to classical combustion calorimetry, detonation calorimetry requires an inert atmosphere, a large sample mass and a detonator for its initiation. This detonator releases some energy for which the results must be corrected. Four types of detonator have been tested in the calorimeter alone and also in combination with explosive charges of PETN. It was found that the aluminium shell of the detonator considerably increases the apparent heat of detonation of the PETN samples in a vacuum, while the presence of combustible (polymeric) components has the opposite effect. Pressurization of the calorimetric vessel with nitrogen gas only partially suppresses these effects. The preferred technique is to use copper or glass confinement in a high pressure inert atmosphere.

Keywords: detonation calorimetry, detonator, PETN, heat of detonation, bomb calorimetry

1 Introduction

Detonation calorimetry is an important method in explosives research. It measures the overall heat released by the detonation of an explosive. The basic principle and construction of the detonation calorimeter is similar to a common combustion calorimeter. The explosive charge is detonated inside a thick-walled vessel ("bomb") submerged in a water bath. The released heat is determined from the change in water temperature caused by the tested explosive, compared with that caused by a standard sample. However, a detonation reaction has limits compared to burning. The detonation can only proceed when the explosive charge diameter is greater, and the initiator has its shockwave impulse higher, than the critical values for the tested explosive material. Therefore the pressure vessel of the calorimeter must be large and thick-walled enough to withstand detonations of explosive charges larger than the critical diameter.

Experiments had already been performed into studying the effects of charge confinement [1, 2], density [3], specific elemental composition [3, 4], and initial pressure inside the bomb [5]. Little attention had been paid to the effect of the detonator on the calorimetric results. The very best way to deal with the effect of the detonator is to use an all-gold exploding bridgewire detonator [1], where the only excess energy comes from the detonator's base charge and the bursting bridgewire. However, this approach is hardly applicable for regular work. Other researchers have been using the more readily available industrial or military detonators [2, 6, 7], which typically consist of a high explosive base charge, a primary explosive charge, a bridgewire igniter with a pyrotechnic fusehead, several plastic parts, and a metallic shell. A detailed description of detonators is commonly omitted from available publications [2, 8, 9]. A correction for the heat introduced by the detonator has reportedly been determined by extrapolation of a series of experiments with varying sample masses to the zero mass value [6], or from a blank test with one or more detonators initiated simultaneously [2, 7]. Our preliminary testing of a DCA 25 calorimeter showed significant inconsistency between these two types of detonator corrections when using common industrial electric detonators with aluminium shells. We considered that this inconsistency is caused by the presence of the aluminium shell or some polymeric components. This paper describes our efforts to reveal the influence of potentially reactive detonator components on detonation calorimetry results.

2 Materials and Methods

2.1 Detonation calorimeter

The calorimetric measurements presented in this work were performed using a DCA 25 detonation calorimeter produced by OZM Research. It is an automatic isoperibolic calorimeter, *i.e.* it has the calorimetric bath surrounded by a constant temperature jacket. The autonomous measurement cycle starts after lowering the bomb into the calorimetric bath. The bomb is made of stainless steel and equipped with a single gas valve and two insulated feed-throughs for electric ignition. It has an internal volume of 5.3 dm³. In our measurements, the jacket temperature was held at 28 °C and the initial bath temperature at 25 °C. The bath was maintained for 60 min before initiation of the sample and 50 min afterwards. The instrument was calibrated using benzoic acid pellets (2 g mass, p.a. grade) burned in an oxygen atmosphere. The calorimetric constant of the system was 80.51 ± 0.15 kJ·K⁻¹, *i.e.* the heat measurement uncertainty was <0.2%.

The bomb was evacuated before each test using a rotary vane vacuum pump and then filled with oxygen gas (2 MPa, 99.995% O₂) for calibrations or eventually nitrogen gas (2 MPa, 99.95% N₂) for some of the sample tests. In the case of a vacuum experiment, the gas pressure was measured using an inbuilt vacuum gauge, while in the case of a nitrogen experiment and a calibration run, the pressure was checked using pressure regulator gauges on the gas cylinders. The estimated pressure measurement error was below 1%.

2.2 Detonators

Four types of electric detonators have been involved in this study. They differed by the mass of the base charge and by the shell, plug and wire insulation materials as listed in the Table 1. A schematic diagram of the detonator is shown in the Figure 1. The base charge was composed of pentaerythritol tetranitrate (PETN) pressed to a density of about 1.6 g·cm⁻³. The common industrial detonators (A1, C1) and customized detonators (C2, C3) were supplied by Austin Detonator. Except for the parts listed in the Table 1, all of the detonators contained a steel reinforcing element (approximately 2 g), a primary charge of 50 mg of lead(II) azide and an electric igniter with a pyrotechnic fusehead.

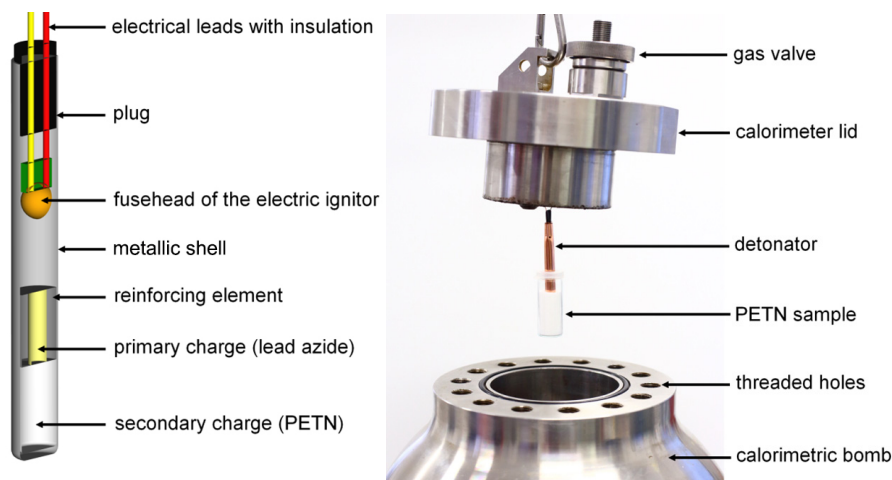


Figure 1. Schematic diagram of a detonator (left) and photograph of the sample (PI-V-C3) before closing the bomb

Table 1. Description of the tested detonators

Detonator	A1	C1	C2	C3
Mass of PETN [g]	0.72	0.99		
Shell material	Al	Cu		
Shell mass [g]	1.81	6.62		
Plug material	PVC ^a	PVC	Silicone	Ceramic
Electrical leads insulation	PVC	PVC	PVC	none

^a polyvinylchloride

2.3 Explosive samples

Pentaerythritol tetranitrate (PETN) was used in the form of pressed pellets with a density of $1.66 \text{ g} \cdot \text{cm}^{-3}$ or as a crystalline powder ($0.9 \text{ g} \cdot \text{cm}^{-3}$), designated PETN ND, both produced by Explosia a.s. Three principal types of charges were tested:

- pressed PETN pellets unconfined (PU),
- powdered PETN with inorganic confinement made of a glass vial or 0.02 mm thick copper foil (PI),
- powdered PETN with polymeric confinement made of a 3d-printed polylactide container or 0.02 mm thick polyamide “sausage” shell (PP).

These charges were tested with aluminium and copper shell detonators in two different atmospheres – a technical vacuum (V) or nitrogen gas compressed to 2 MPa (N). When the glass vial was used, it was closed by a polyethylene lid which was not in direct contact with the explosive. The explosive charges were fixed

to the detonators using short lengths of 0.1 mm diameter copper wire to prevent unintentional disconnection during the bomb manipulation and gas filling. All of the samples were weighed using an electronic balance with 0.001 g resolution.

2.4 Calculation of the detonation parameters

The detonation heats of PETN and its model mixtures with metals were calculated using the EXPLO5 V6.05 thermochemical code [10], the most recent version of the original EXPLO5 [11]. The Exp-6 equation of state was used for the detonation products [12, 13]. The model compositions were calculated assuming a density of $1.6 \text{ g}\cdot\text{cm}^{-3}$. The equilibrium compositions of the reaction products were taken from the last available point of the isentropic expansion calculation at 298 K [14]. The water was assumed to be in the liquid state and the aluminum oxide and the unreacted aluminum or copper in the solid state, to comply with the conditions at the end of a calorimetric experiment. All of the other energetic components of the system, including the primary filling and the fusehead, were neglected in the calculations.

3 Results and Discussion

The tests have only been performed with PETN because it is a well-known explosive with a low critical diameter and high sensitivity to initiation. The heat of detonation of PETN had been determined under strictly controlled conditions by Ornellas [1], whose result is taken as a reference value ($\Delta H_{\text{PETN}} = 6.27 \text{ kJ}\cdot\text{g}^{-1}$). PETN is almost oxygen balanced (10.1%), so the specific heat of detonation does not change by much with charge confinement or sample density [15]. The composition of the reaction products and the heat of detonation of unconfined charges of oxygen-deficient explosives detonated under vacuum are altered by low pressure, high temperature re-equilibration of the detonation products caused by reflected shockwaves [3]. To limit these effects, we performed most of the experiments under a compressed nitrogen atmosphere, as has been suggested [5].

The experimental results obtained in this work are compared by means of the apparent specific heat of detonation, $\Delta H_{\text{PETN-ap}} [\text{kJ}\cdot\text{g}^{-1}]$, which was calculated according to Equation 1.

$$\Delta H_{\text{PETN-ap}} = Q_c / (m_s + m_d) \quad (1)$$

where Q_c is the detonation heat measured in a given test and m_s and m_d are the

corresponding masses of the PETN sample and the detonator, respectively. The presence of any other components was neglected. This quantity makes sense only when the detonator filling is of the same material as the charge being tested. This allows a comparison of the results from different test arrangements without using any detonation correction factors. We assumed that in the ideal case, the value of this quantity should be close to the actual value of ΔH_{PETN} and also to the reference value. Wherever applicable, the value of ΔH_{PETN} [$\text{kJ}\cdot\text{g}^{-1}$] is also shown, which is defined as the slope of the linear regression equation of the detonation heat (Q) vs. sample mass (m_s) data:

$$Q = \Delta H_{\text{PETN}} m_s + Q_{\text{d-extp}} \quad (2)$$

The intercept, $Q_{\text{d-extp}}$ [kJ], is the heat output of the detonator and may be compared with the independently determined values of $Q_{\text{d-meas}}$ from plain detonator tests. The regression equations are shown in the graphs. The coefficients of determination are not shown in Figures 2 and 3 as they are all higher than 0.999.

At least two tests were performed under each set of experimental conditions (bomb pressure, type of detonator, confinement). The average difference between the pairs of tests was less than 0.5%. When more than two test results were available, uncertainty is shown in the tables as twice the standard deviation.

3.1 Experiments in a vacuum

The first experiments were performed in a vacuum as we assumed it would highlight the differences between the particular test arrangements. We wanted to quantify the worst case of the aluminium shell reaction and also to select one of the available types of copper shell detonators for the subsequent experiments.

The results from the vacuum experiments are shown in Figure 2 and Table 2. It can be seen that the heat output of the plain A1 detonators is 32% higher compared to the value obtained by extrapolation of the sample tests. On closer inspection, the heat-mass dependence in this case is not exactly linear. The value of $\Delta H_{\text{PETN-ap}}$ is 13% higher than the ΔH_{PETN} determined from the same tests and 25% higher than the reference value. The value of ΔH_{PETN} resulting from the sample tests with the A1 detonators is 10% higher than the reference value.

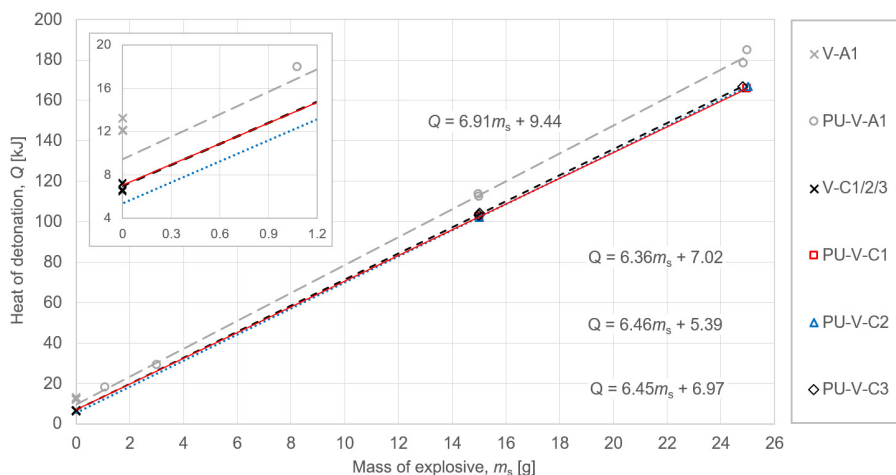


Figure 2. The detonation heats of detonators and unconfined PETN samples, tested under vacuum

Table 2. Comparison of the heat produced by the tested detonators, and the specific heat of detonation of PETN determined with them, in a vacuum (samples PU-V-A1/C1/C2/C3). The literature value of ΔH_{PETN} is $6.27 \text{ kJ} \cdot \text{g}^{-1}$ [1]

Test	Units	V-A1 PU-V-A1 PI-V-A1	V-C1 PU-V-C2	V-C2 PU-V-C2	V-C3 PU-V-C3
$Q_{\text{d-meas}}$	[kJ]	12.49 ± 1.05	6.66	6.58	6.98 ± 0.72
$Q_{\text{d-extp}}$	[kJ]	9.44	7.02	5.39	6.97
ΔH_{PETN}	[kJ·g ⁻¹]	6.91	6.36	6.46	6.45
$\Delta H_{\text{PETN-ap}}$	[kJ·g ⁻¹]	7.82 ± 2.04	6.40 ± 0.02	6.41 ± 0.02	6.48 ± 0.04

The tests with copper shell detonators revealed much better consistency compared to the aluminium ones. In this case, the extrapolated results match with the single detonator results to within 6% and the $\Delta H_{\text{PETN-ap}}$ matches with the ΔH_{PETN} to within 1%. The resulting ΔH_{PETN} from the tests with the three types of copper detonators is on average 2.4% greater than the literature value (Table 2). The copper shell detonators seem to have almost the same heat output regardless of the detonator construction, with the largest difference being 3% between C1 and C3. Nevertheless, we decided to use the C3 detonator in the following experiments as it has the least amount of potentially reactive constituents.

3.2 Experiments under a nitrogen atmosphere

In the following set of experiments, the aluminium and copper shell detonators and their combination with PETN samples have been tested under a compressed nitrogen gas atmosphere at 2 MPa. The nitrogen atmosphere is being used as an alternative to the heavy confinement which is otherwise necessary to obtain correct calorimetric results with explosives having a negative oxygen balance. We hypothesized that the nitrogen atmosphere might also be able to reduce or eliminate the aluminium reactivity by diluting and cooling the detonation products. In these tests, powdered PETN confined in glass vials or copper foil was used. No influence of these inorganic confiners on the resulting $\Delta H_{\text{PETN-ap}}$ was found, so all of these results were grouped with the results of the unconfined charges.

From Figure 3, it can be seen that the presence of compressed nitrogen gas reduces the aluminium contribution to the heat released compared to the vacuum experiments (Figure 2). This difference is also evident from the photographs of the detonator remains, where the shards from the nitrogen plain detonator test (Figure 4(b)) are glossy but those from the vacuum test (Figure 4(c)) shows some surface erosion. Moreover, the heat-mass dependence is in this case linear and the $\Delta H_{\text{PETN-ap}}$ matches the ΔH_{PETN} from the same tests (Table 3). However, it is clear from Table 3 that the effect of an aluminium shell is not eliminated completely as the value of ΔH_{PETN} is still 6.2% higher than the reference value. The values of $\Delta H_{\text{PETN-ap}}$ and ΔH_{PETN} obtained with the C3 detonators are also identical and only 1.3% off the reference value.

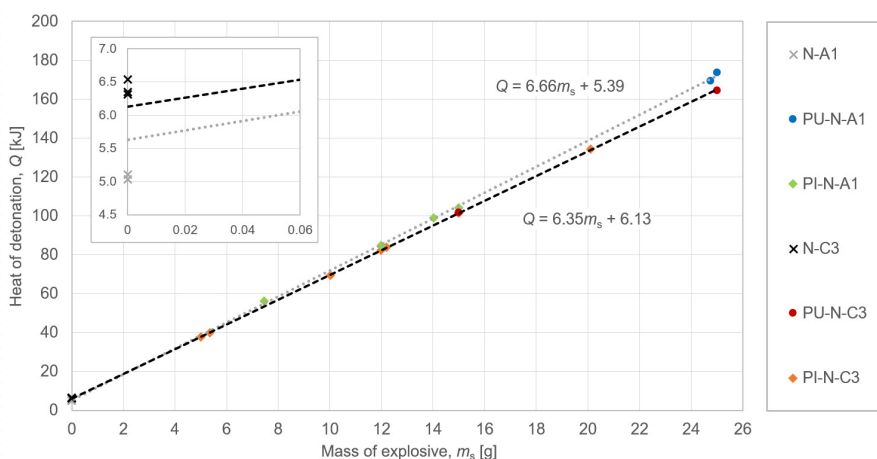


Figure 3. The detonation heats of detonators and PETN samples tested under a compressed nitrogen atmosphere. The PETN samples were either unconfined or with inorganic confinement

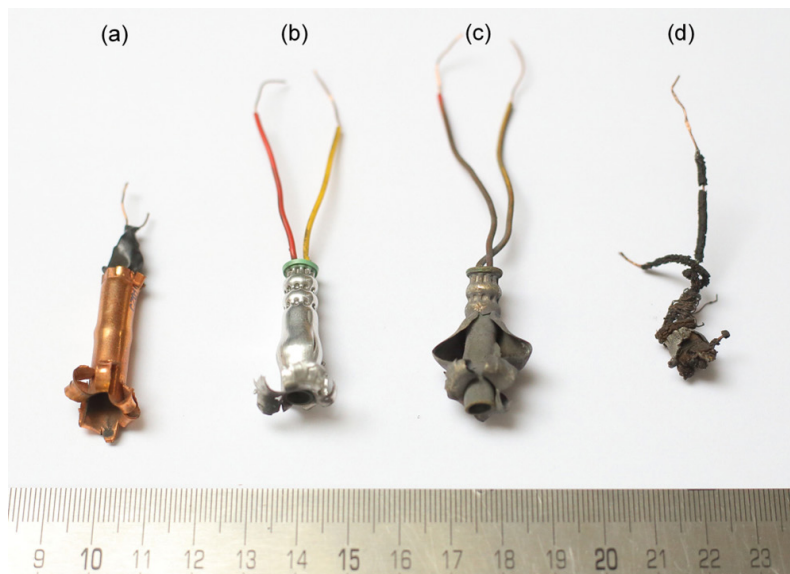


Figure 4. Remains from tests V-C3, N-A1, V-A1, PU-N-A1 (left to right)

Table 3. Comparison of the heat produced by the tested detonators, and the specific heat of detonation of PETN determined with them, under a nitrogen atmosphere; the literature value of ΔH_{PETN} is $6.27 \text{ kJ} \cdot \text{g}^{-1}$ [1]

Test	Units	N-A1 PU-N-A1 PI-N-A1	N-C3 PU-N-C3 PI-N-C3
$Q_{\text{d-meas}}$	[kJ]	5.07 ± 0.07	6.45 ± 0.2
$Q_{\text{d-extp}}$	[kJ]	5.39	6.13
ΔH_{PETN}	[kJ·g ⁻¹]	6.66	6.35
$\Delta H_{\text{PETN-ap}}$	[kJ·g ⁻¹]	6.69 ± 0.15	6.35 ± 0.04

3.3 The effect of polymeric confinement of explosive samples

It may sometimes be required to perform detonation calorimetry on powdered samples. Such samples must be somehow confined and it is tempting to do so using readily available polymeric materials. Experiments with polymeric charge confinements were therefore performed and compared to the previous results (Figure 5).

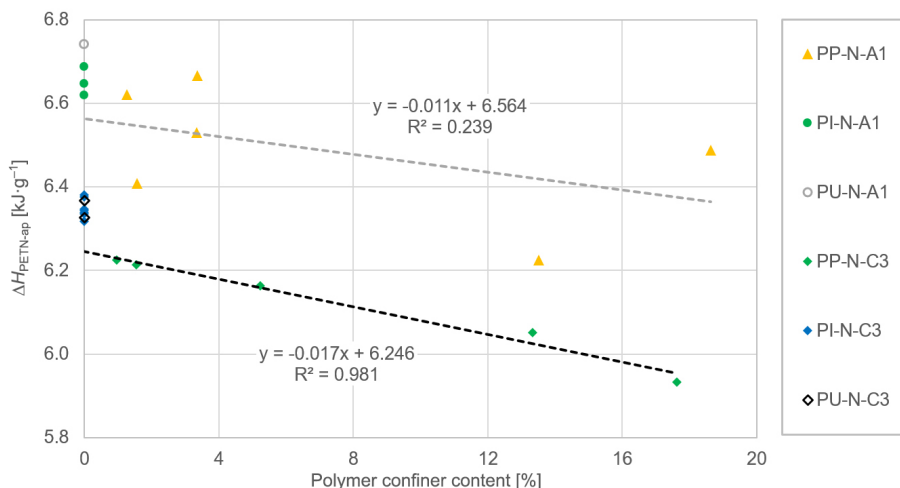


Figure 5. The apparent specific heat of detonation of PETN samples with varying amounts of polymeric confiner materials compared to the samples with inorganic confinement; all of these results were obtained in a compressed nitrogen atmosphere

In the case of the copper detonator tests, there is a linear trend of decreasing apparent detonation heat with increasing polymer content. It can be seen that even a small amount of polymer decreases the apparent detonation heat by ~2% compared to the unconfined material while the inorganic confiners (glass vial or copper foil) have no impact on it. Two additional tests (not shown) have been performed in a vacuum and resulted in values a further 10% lower. The results obtained with the A1 detonators seem to follow a similar trend, but they are higher by about 5% over the C3 detonator, *i.e.* by about the same amount as in the tests without polymeric confiners. The extreme scatter of the A1 data is caused by the presence of a second variable, the aluminium content, because of the varying charge masses. In specific cases, the simultaneous presence of aluminium and polymer may cancel out their effects leading to an ostensibly correct result.

These results suggest that a polymeric confiner of the charges easily equilibrates with the detonation products, consuming a part of the available heat in its endothermic decomposition. It also effectively reduces the overall oxygen balance, making the mixture sensitive to the re-equilibration phenomenon. It should be noted that the effect of polymer addition would be the opposite to classical combustion calorimetry as the polymer would burn in oxygen, increasing the heat released. Polymeric confiners should therefore be omitted in detonation calorimetric measurements.

3.4 Predictions using thermochemical calculations

Thermochemical calculations using the EXPLO5 code have been performed to estimate the heat released from the reaction of the shell material with the detonation products from PETN. The calculations are obviously a large simplification of the problem as they assume thermal and chemical equilibrium of the reaction products. However, comparison with the experimental data may show situations where the equilibrium is close to being established.

A series of model compositions were calculated to simulate changes in the heat released with increasing portions of the shell material being consumed, taking into account the overall mass of PETN and metal in the system (Figure 6). The experimental points are also shown, the extreme right point representing a plain detonator. The experiments with the A1 detonators match the calculations at the lowest and highest aluminium contents, *i.e.* where there is a large excess of either detonation products or aluminium, respectively. After the PETN sample tests of 15 g or more, no shards can be found implying complete reaction of the aluminium. At a medium Al content (~5 g sample mass), the amount of heat is probably not sufficient to melt all of the aluminium and therefore it cannot mix with the products and reach the equilibrium state. In the plain detonator experiments, just a small part of the aluminium shell disappears with a major portion remaining intact (Figure 4(c)). There is a clear nonlinear trend of increasing apparent specific heat with increasing aluminium content.

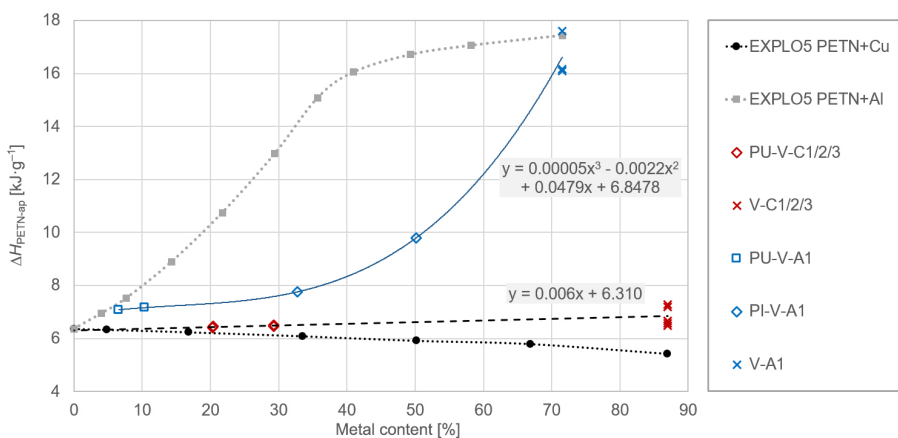


Figure 6. The apparent specific heat of the model mixtures of PETN with metals, compared to experimental results. The metal content for the experimental points was calculated based on the total masses of PETN and the metallic shell; all of these experimental results were obtained under vacuum (the dotted lines between the EXPLO5 points are there as a visual aid)

Figure 7 shows how the concentrations of the important reaction products change with increasing aluminium content. The water contained in the detonation products is completely consumed by reaction with aluminium, forming aluminium(III) oxide and hydrogen, in the mixtures with more than 29% Al. This percentage corresponds to a PETN sample mass of approximately 4 g. Beyond this point, aluminium may only react with carbon monoxide and a portion of the aluminium is left unreacted. According to the model, 78.5% of the Al shell mass should remain intact in the case of a plain Al detonator test. Copper was found to be non-reactive in all of the mixture ratios.

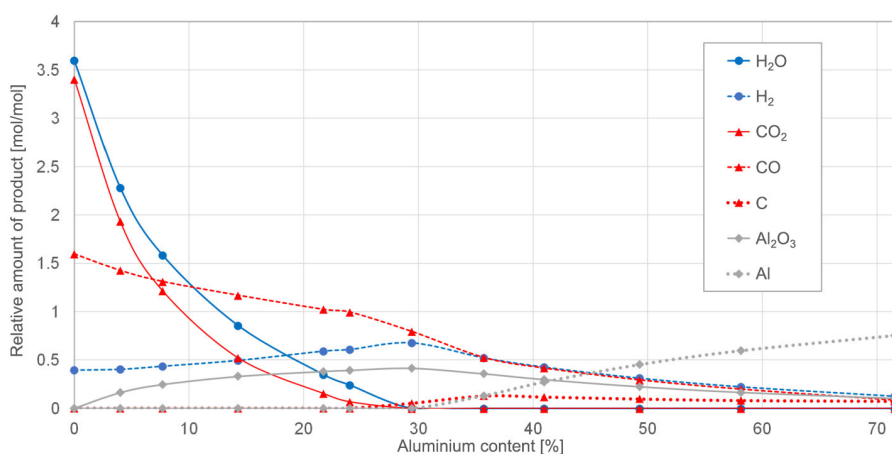


Figure 7. The concentrations of equilibrium reaction products of the model mixtures calculated by the EXPLO5 code; the concentrations are shown in moles per mole of the mixture (the lines between the points are there as a visual aid)

4 Conclusions

The effect of detonator shell materials on the detonation heat of PETN has been evaluated based on EXPLO5 calculations and experimental results obtained with a DCA 25 calorimeter. It was found that the aluminium shell of a detonator considerably reacts with the detonation products and that the reacted amount increases non-linearly with increasing sample mass in the tests under vacuum. When the tests are carried out under a compressed nitrogen atmosphere, the aluminium contribution is reduced but not eliminated. According to the thermochemical calculations, the aluminium primarily reacts with the water in

the reaction products, so it may influence the results for almost all explosives regardless of their oxygen balance. Simple detonator corrections applied for aluminium shell detonators may therefore introduce a systematic error of 5-10% to the detonation calorimetry results.

On the contrary, a copper shell can be safely considered to be inert. The corrections for the copper detonators can be determined either by extrapolation of a series of sample shots or by single detonator experiments, with a negligible impact on the final results.

Plastic materials, used as a charge confinement material, do have a considerable negative effect on the measured heat release, so the use of glass, copper or another non-reactive inorganic confinement material is necessary.

References

- [1] Ornellas, D.L.; Carpenter, J.H.; Gunn, S.R. Detonation Calorimeter and Results Obtained with Pentaerythritol Tetranitrate (PETN). *Rev. Sci. Instrum.* **1966**, 37(7): 907-912.
- [2] Tongchang, Y.; Menchao, Y.; Jianling, W. Determination of Heats of Detonation and Influence of Components of Composite Explosives on Heats of Detonation of High Explosives. *J. Therm. Anal.* **1995**, 44: 1347-1356.
- [3] Ornellas, D.L. The Heat and Products of Detonation of Cyclotetramethylenetetranitramine, 2,4,6-Trinitrotoluene, Nitromethane, and Bis[2,2-dinitro-2-fluoroethyl]formal. *J. Phys. Chem.* **1968**, 72(7): 2390-2394.
- [4] Ornellas, D.L. The Heat and Products of Detonation in a Calorimeter of CNO, HNO, CHNF, CHNO, CHNOF, and CHNOSi Explosives. *Combust. Flame* **1974**, 23: 37-46.
- [5] Trzciński, W. On Some Methods of Determination of the Detonation Energy of Explosives. *New Trends Res. Energ. Mater., Proc. Semin.*, Pardubice, Czech Republic, **2006**, pp. 748-755.
- [6] Cudziło, S.; Trębiński, R.; Trzciński, W.; Wolański, P. Comparison of Heat Effects of Combustion and Detonation of Explosives in a Calorimetric Bomb. *Int. Annu. Conf. Fraunhofer ICT*, Karlsruhe, Germany, **1998**, pp. 150/1-150/8.
- [7] Pepekin, V.I.; Gubin, S.A. Heat of Explosion of Commercial and Brisant High Explosives. *Combust., Explos. Shock Waves (Engl. Transl.)* **2007**, 43(2): 212-218.
- [8] Kiciński, W.; Trzciński, W.A. Calorimetry Studies of Explosion Heat of Non-ideal Explosives. *J. Therm. Anal. Calorim.* **2009**, 96: 623-630.
- [9] Makhov, M.N.; Gogulya, M.F.; Dolgoborodov, A.Y.; Brazhnikov, M.A.; Arkhipov, V.I.; Pepekin, V.I. Acceleration Ability and Heat of Explosive Decomposition of Aluminized Explosives. *Combust., Explos. Shock Waves (Engl. Transl.)* **2004**, 40(4): 458-466.

- [10] Sućeska, M. *Explo5 Version 6.05/2018 User's Guide*. ed. 2018, OZM Research, Hrochuv Tynec, Czech Republic, **2018**.
- [11] Sućeska, M. Calculation of the Detonation Properties of C-H-N-O Explosives. *Propellants Explos. Pyrotech.* **1991**, 16(4): 197-202.
- [12] Sućeska, M.; Braithwaite, C.H.; Klapötke, T.M.; Stimac, B. Equation of State of Detonation Products Based on Exponential-6 Potential Model and Analytical Representation of the Excess Helmholtz Free Energy. *Propellants Explos. Pyrotech.* **2019**, 44(5): 564-571.
- [13] Brown, W.B. Analytical Representation of the Excess Thermodynamic Equation of State for Classical Fluid Mixtures of Molecules Interacting with α -Exponential-six Pair Potentials up to High Densities. *J. Chem. Phys.* **1987**, 87(1): 566-577.
- [14] Sućeska, M. Evaluation of Detonation Energy from EXPLO5 Computer Code Results. *Propellants Explos. Pyrotech.* **1999**, 24(5): 280-285.
- [15] Ornellas, D.L. *Calorimetric Determinations of the Heat and Products of Detonation for Explosives: October 1961 to April 1982*, Lawrence Livermore National Laboratory, Report UCRL-52821, **1982**.

Received: February 25, 2019

Revised: December 17, 2020

First published online: December 28, 2020