



Blast Wave Parameters of Liquid Esters of Nitric Acid: Propane-1,2,3-triyl Trinitrate, Propane-1,2-diyl Dinitrate, Ethane-1,2-diyl Dinitrate and Methyl Nitrate

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Abstract: A knowledge of blast wave parameters generated by detonating explosives is important for the evaluation of protective measures, modelling validation and post blast analysis. The relevant data are available for solid military explosives, but not for liquid or homemade explosives. In this contribution we present comparison of experimental incident blast wave parameters for bare charges, weighing from 100 g to 1 kg, of liquid esters of nitric acid, including propane-1,2,3-triyl trinitrate (NG), propane-1,2-diyl dinitrate (PGDN), ethane-1,2-diyl dinitrate (EGDN) and methyl nitrate (MeN), amongst themselves and with TNT charges of approximately the same size. The TNT equivalents, determined from both the incident overpressures and the impulse of the positive phase of the blast wave, were above 100% and showed relatively high scatter. The strongest blast wave parameters under otherwise identical conditions were observed for charges of methyl nitrate.

Keywords: nitric ester, blast wave, TNT equivalent, liquid explosive, shock wave in air

1 Introduction

A detonation wave passing through an explosive generates a shock wave in the surrounding medium. When the medium is air the shock wave is often called

a blast wave. Its parameters depend on the type of explosive, or more precisely on the amount of energy it contains and the rate at which it can be released. Different types of explosives therefore generate shock waves with different parameters. However the general shape remains similar, which allows the effects of different types or sizes of explosive charges to be compared [1].

The strength of an explosive is often defined by relating some of its output parameters to a well-known standard using appropriate scaling methods [2, 3]. In the case of air blast parameters the most common method uses TNT (2-methyl-1,3,5-trinitrobenzene) as the standard. Even though it is one of the worst choices for a standard, the blast wave parameters of a studied explosive are evaluated by comparing them to the blast wave parameters of an equivalent charge of TNT. For a simple and easy to interpret comparison, the term “TNT equivalence” was introduced and is defined as the ratio of weight of TNT to the weight of the tested explosive that would produce the same overpressure (or impulse) at the same distance [4]. Explosives generating effects greater than the same amount of TNT have a TNT equivalent above one (or 100%) and those generating lower effects have a value below one.

It seems logical to use the blast wave parameters for defining the TNT equivalency when comparing the effect of detonation of some explosives in air rather than their other properties. The two parameters of choice are often the overpressure and impulse. The arrival time or positive phase duration may be scaled as well, but they are not commonly used for the determination of TNT equivalency [5]. It would seem from the definition of the TNT equivalent that it does not depend on the distance from the charge, or more generally on the scaled distance; however that is not the case [6-8]. The entire TNT equivalency concept therefore needs to be used carefully with its limitations in mind.

We believe that the best way to compare the ability of the detonating explosive to create a strong shock wave in air is to conduct the experiments with the investigated explosive under the same conditions as used previously for experiments with TNT. The TNT equivalent should then be evaluated as a function of scaled distance. The methodology we used for scaling is based on the usual cube root scaling approach and is described in detail in the experimental section below. It is slightly different from our earlier publication [9] in which we fitted the experimental TNT data by a simple exponential relation.

Blast wave data are available for a number of military explosives and for some of them is nicely summarized in Ref. [10]. Data for less common explosives are to the best of our knowledge not openly available. In the case of the liquid nitric esters considered in this study we were able to find blast wave data only for nitroglycerine [11]. The objective of this article is therefore aimed at providing

experimental results that enable a comparison of the four selected liquid esters of nitric acid in terms of their blast wave parameters in air.

2 Material and Methods

Propane-1,2,3-triyl trinitrate (more commonly known as nitroglycerine, NG) is a well-known explosive used in dynamites. The other esters are similar in chemical composition to NG, which has three carbon atoms and three $-O-NO_2$ groups; propane-1,2-diyl dinitrate (more commonly known as propyleneglycol dinitrate, PGDN) has the same number of carbon atoms but only two $-O-NO_2$ groups, ethane-1,2-diyl dinitrate (more commonly known as nitroglycol, EGDN) has two carbon atoms and two $-O-NO_2$ groups, and finally methyl nitrate (MeN) has just one carbon atom and one $-O-NO_2$ group. Some of their published [12] parameters are summarized in Table 1, showing that NG has the highest density and detonation velocity and MeN the lowest. The detonation velocities were taken from Refs. [12] and [13], which are both encyclopedias and not the original research papers. Table 1 also includes our own experimental results.

Table 1. Selected properties of the investigated esters of nitric acid [12]

| | | NG | PGDN | EGDN | MeN |
|--------------------------|------------------------|-------|----------|-------|-------|
| Molecular mass | [g·mol ⁻¹] | 227.1 | 166.1 | 152.1 | 77.0 |
| Density | [g·cm ⁻³] | 1.591 | 1.368 | 1.480 | 1.217 |
| Oxygen balance | [%] | +3.5 | -28.9 | 0.0 | -10.4 |
| Nitrogen content | [%] | 18.49 | 16.87 | 18.42 | 18.19 |
| Detonation velocity | [km·s ⁻¹] | | | | |
| - data from literature | | 7.6 | 6.9 [13] | 7.3 | 6.3 |
| - our experimental data* | | 7.58 | 7.04 | 7.45 | 6.64 |

* tested in polyvinylchloride (PVC) pipes with internal diameter 36 mm and 2 mm wall thickness. The initiation of the charges was by a 10 g booster of Semtex 1A.

a. Preparation of the nitric esters

Propane-1,2,3-triyl trinitrate was provided by the company Explosia a. s. and was used as provided; the other esters of nitric acid were synthesized by standard routes from the corresponding alcohol, nitric acid and sulphuric acid (Figure 1) and were analyzed by HPLC and determination of their refractive indexes. Propane-1,2-diyl dinitrate (PGDN) was prepared according to the Matignon *et al.* procedure [14]. Approximately 520 g PGDN were prepared in one batch. The average yield among the batches was 88% (analysis: n_D^{25} 1.4405

(n_D^{20} 1.4420 [15]), HPLC (210 nm): over 99% @ 6.021 min). Ethane-1,2-diyl dinitrate (EGDN) was synthesized by the procedure published by Naoum [16]. About 520 g EGDN batches were prepared with an average yield of 90% (analysis: n_D^{30} 1.4435 (n_D^{25} 1.4454 [15]), HPLC (210 nm): 98% @ 5.022 min). Methyl nitrate (MeN) was prepared according to Desseigne [17] with 65 wt.% nitric acid instead of the 98% nitric acid used in the original procedure. The mass ratio of the reactants (methanol/nitric acid/sulphuric acid) was also changed to 1/2.8/3.6. Batches of about 520 g MeN were prepared with an average yield of 76% (analysis: n_D^{25} 1.3725 (n_D^{20} 1.3743 [15]), HPLC (210 nm): over 99% @ 2.108 min).

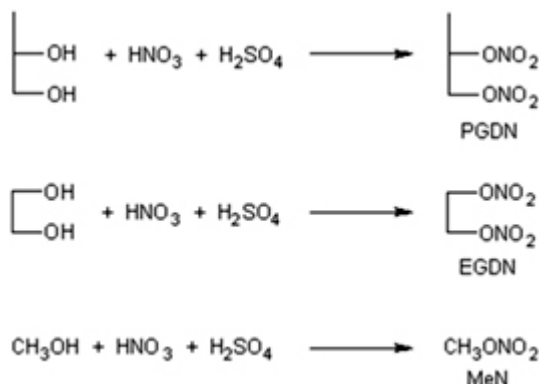


Figure 1. Scheme for the synthesis of PGDN, EGDN and MeN

The refractive index was determined for all of the prepared samples using an Optech Abbé RMI refractometer. The purity was further verified by liquid chromatography using an Agilent 1200 chromatograph. Standard isocratic elution using acetonitrile/water 60/40 mobile phase with a flow rate of $1 \text{ mL} \cdot \text{min}^{-1}$ was used. The injection volume was $10 \mu\text{L}$, the column material was BDS Hypersil C-18 with particle size $5 \mu\text{m}$ and pore size 12 nm , column dimensions were $250 \text{ mm} \times 4.6 \text{ mm}$. The column temperature was held constant at $30 \text{ }^\circ\text{C}$. A DAD detector was used to check the spectra from 200 nm to 800 nm . The quantitative evaluation was made from the absorbance at 210 nm . The peak area was evaluated as a percentage of the total peak areas.

b. Preparation of the charges

The blast wave parameters for TNT were obtained in earlier experiments carried out at our institute [18]. Standard cylindrical pressed charges weighing from 27 g to 267 g were used. The density of the TNT charges varied from $1.566 \text{ g} \cdot \text{cm}^{-3}$

to $1.660 \text{ g}\cdot\text{cm}^{-3}$. Two additional charges were cast weighing 560 g and 616 g TNT and tested to expand the low scaled distance region. A booster consisting of 20 g of Semtex 1A was used for initiation because of the low sensitivity of cast TNT to standard blasting cup. The equivalent of Semtex 1A was taken as 1.3 and the charges were therefore evaluated as 586 g and 642 g of TNT.

An appropriate amount of the liquid ester was poured into a polyethylene bottle (PET) with the top conical part cut off. The shots with 100 g were performed using 500 mL bottles and the shots with 500 g and 1000 g using 1.5 L bottles. The detonator was inserted from the top with its secondary charge immersed just under the surface of the liquid explosive. The charges were initiated while standing on the ground surface. Industrial instantaneous detonators with initiating strength exceeding the standard No. 8 detonator were used. The contribution of the detonator was not corrected for and the results therefore correspond to the entire charge including the secondary explosive in the detonator (0.72 g of PETN).

c. Blast wave measurements

The measurement of the blast waves was performed using ICP 137A23 pencil pressure sensors produced by PCB Piezotronics Inc. Four sensors were connected to a four-channel Tektronix oscilloscope, model DPO3014, *via* the ICP sensor signal conditioner PCB Piezotronics Inc., model 482a22. The sensors were mounted on tripods and the height of the sensing element was 90 cm. The four measuring probes were positioned 3 m, 4 m, 5 m and 6 m from the charge for the first round of shots and at 7 m, 8 m, 9 m and 10 m for the second round of shots. The distance was measured from the charge directly to the sensing element by tape-measure. Charges of nominal weight 100 g, 500 g and 1 kg were shot twice for each mass and range of sensors. When some of the sensors failed to acquire a usable signal (due to the limitations of the 8 bit depth of the oscilloscope), the test was repeated. The overall number of shots was over 50, including partial failures, resulting in 190 usable signals. The combination of various distances and weights enabled us to determine the influence of the charge mass at the same scaled distance in the range from $3 \text{ m}\cdot\text{kg}^{-1/3}$ to $22 \text{ m}\cdot\text{kg}^{-1/3}$. The central part of this range was covered by all three charge sizes, enabling a comparison of the resulting overpressures and impulses at the same scaled distances.

The test site is located 220 m above sea level, the temperature on the days of the tests was 5-15 °C. The pressure-time signals were therefore taken as measured without pressure or temperature correction and were not post processed by any type of signal filter.

2.1 Scaling of the experimental data

The scaling of the blast wave radius and impulse was done according to the following equations [2-4]:

$$Z = \frac{R}{W^{1/3}} \quad (1)$$

$$\zeta^+ = \frac{I^+}{W^{1/3}} \quad (2)$$

where Z ($\text{m} \cdot \text{kg}^{-1/3}$) is the scaled distance, R (m) is the real distance from the charge surface to the sensor, W (kg) is the weight of the charge, I^+ ($\text{Pa} \cdot \text{s}$) and ζ^+ ($\text{Pa} \cdot \text{s} \cdot \text{kg}^{-1/3}$) are the absolute and scaled impulses of the blast wave's positive phase.

In order to compare the blast wave parameters of the esters with some standard it is necessary to know the behaviour of the blast waves generated by detonation of that standard. TNT has been historically chosen as such a standard and blast wave parameters have been measured for charges ranging from grams to kilotons. Scaling all of the parameters resulted in the formulation of the dependence of pressure and impulse on the scaled distance. These dependencies were published and can be used as a baseline for comparing any explosive to TNT. Such an approach is convenient as it does not require one to measure the TNT behaviour, however it does not take into account possible issues resulting from charge size (scaling validity) or experimental arrangement. We therefore decided to use our own TNT data which were obtained under very similar conditions as the data for the esters.

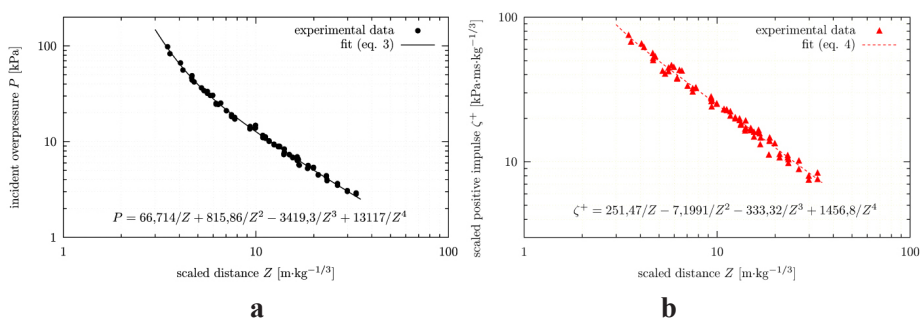


Figure 2. The experimental incident maximum overpressure (a) and scaled impulse (b) vs. scaled distance for TNT. The equations in the graphs are fits of the experimental data and are shown as lines in the graphs

The experimentally determined dependencies of TNT overpressure and scaled impulse on scaled distance are shown in Figure 2. In our previous work

[9, 18] we have fitted the data to a simple exponential function according to the procedure of McCovan [19]. This approach can be justified only for a relatively narrow range of scaled distances, because an unrealistic dependency of the TNT equivalency on scaled distance is obtained when applied to a broader range. We were correctly advised to use more complex types of fitting equations and based on a review of the forms used in the past, summarized in [20], we decided to use the following:

$$P_{\text{TNT}} = \frac{A_P}{Z_{\text{TNT}}} + \frac{B_P}{Z_{\text{TNT}}^2} + \frac{C_P}{Z_{\text{TNT}}^3} + \frac{D_P}{Z_{\text{TNT}}^4} \quad (3)$$

$$\zeta_{\text{TNT}} = \frac{A_\zeta}{Z_{\text{TNT}}} + \frac{B_\zeta}{Z_{\text{TNT}}^2} + \frac{C_\zeta}{Z_{\text{TNT}}^3} + \frac{D_\zeta}{Z_{\text{TNT}}^4} \quad (4)$$

The parameters A , B , C and D in the above equations were fitted to our TNT data using the Levenberg-Marquardt algorithm. The resulting values of the fitting parameters are summarized in Table 2 and shown in Figure 2 as curves through the data.

Table 2. The coefficients obtained by fitting Equations 3 and 4 to experimental TNT data and the corresponding coefficients of determination R^2

| | A | B | C | D | R^2 |
|---|--------|---------|---------|--------|---------|
| Overpressure [kPa] | 66.714 | 815.86 | -3419.3 | -13117 | 0.99622 |
| Scaled impulse [kPa·ms·kg ^{-1/3}] | 251.47 | -7.1991 | -333.32 | 1456.8 | 0.98683 |

2.2 Method of TNT equivalency determination

The TNT equivalent from the peak overpressure is defined as the ratio of charge weights of TNT and the sample explosive (Equation 5) that would each generate the same peak overpressure, at the same distances from the charges [11].

$$k_{\text{TNT}}^P = \left(\frac{W_{\text{TNT}}}{W_{\text{ester}}} \right)_{P,R} \quad (5)$$

where k_{TNT}^P is the overpressure-based TNT equivalent, W_{ester} is the weight of the ester charge leading to a certain incident overpressure P at a particular distance R and W_{TNT} is the weight of TNT leading to the same overpressure at the same distance.

Substituting the weight from Equation 1 and having equal radial distances results in:

$$k_{TNT}^P = \frac{W_{TNT}}{W_{ester}} = \frac{\left(\frac{R_{TNT}}{Z_{TNT}}\right)^3}{\left(\frac{R_{ester}}{Z_{ester}}\right)^3} = \left(\frac{Z_{ester}}{Z_{TNT}}\right)_P^3 \quad (6)$$

where Z_{ester} is the scaled distance of the ester leading to a certain incident overpressure P and Z_{TNT} is the scaled distance for TNT leading to the same overpressure. In this manner, for a particular (P, Z) pair of the ester, we find the corresponding Z for TNT at the same pressure from Equation 3, and apply Equation 6 to obtain the TNT equivalent.

The TNT equivalent based on impulse is the ratio of charge weights of TNT and the sample explosive that will result in the same positive impulse, at the same radial distances from either of the two charges.

From Equation 1, applied to both the ester and TNT, we have:

$$Z_{ester} W_{ester}^{1/3} = R_{ester} \quad \text{and} \quad Z_{TNT} W_{TNT}^{1/3} = R_{TNT}$$

and from Equation 2, also applied to both the ester and TNT:

$$I_{ester}^+ = \zeta_{ester}^+ W_{ester}^{1/3} \quad \text{and} \quad I_{TNT}^+ = \zeta_{TNT}^+ W_{TNT}^{1/3}$$

From the definition of TNT equivalent, the impulses must be equal:

$$\begin{aligned} I_{ester}^+ &= I_{TNT}^+ \\ \zeta_{ester}^+ * W_{ester}^{1/3} &= \zeta_{TNT}^+ * W_{TNT}^{1/3} \\ \left(\frac{\zeta_{ester}^+}{\zeta_{TNT}^+}\right)^3 &= \frac{W_{TNT}}{W_{ester}} \end{aligned} \quad (7)$$

Substituting the weight from Equation 1 and having the radial distances equal results in:

$$k_{TNT}^{I^+} = \frac{W_{TNT}}{W_{ester}} = \frac{\left(\frac{R_{TNT}}{Z_{TNT}}\right)^3}{\left(\frac{R_{ester}}{Z_{ester}}\right)^3} = \left(\frac{Z_{ester}}{Z_{TNT}}\right)^3 = \left(\frac{\zeta_{ester}^+}{\zeta_{TNT}^+}\right)^3 \quad (8)$$

The above can be simplified to:

$$\left(\frac{Z_{ester}}{Z_{TNT}} \right) = \left(\frac{\zeta_{ester}}{\zeta_{TNT}} \right) \quad (9)$$

$$\frac{\zeta_{ester}}{Z_{ester}} = \frac{\zeta_{TNT}}{Z_{TNT}}$$

In the $\zeta^+ = f(Z)$ plane, the above ratios represent slopes, and since they must be equal, they represent the same line. Intersections of this line with $\zeta^+_{TNT} = f(Z_{TNT})$ and $\zeta^+_{ester} = f(Z_{ester})$ gives (ζ^+, Z) pairs for equal impulses at equal radial distances. In the normal coordinate system this line does not have a constant slope for all (ζ^+, Z) pairs, however it crosses the origin as shown in Figure 3. Converting the coordinate system to a log-log scale (Equation 10) results in slopes having 45° for any of the corresponding pairs (provided the scale on both axes is of the same length per decade) as shown in Figure 3.

$$\left(\frac{Z_{ester}}{Z_{TNT}} \right) = \left(\frac{\zeta_{ester}}{\zeta_{TNT}} \right)$$

$$\log \left(\frac{Z_{ester}}{Z_{TNT}} \right) = \log \left(\frac{\zeta_{ester}}{\zeta_{TNT}} \right) \quad (10)$$

$$\log Z_{ester} - \log Z_{TNT} = \log \zeta_{ester} - \log \zeta_{TNT}$$

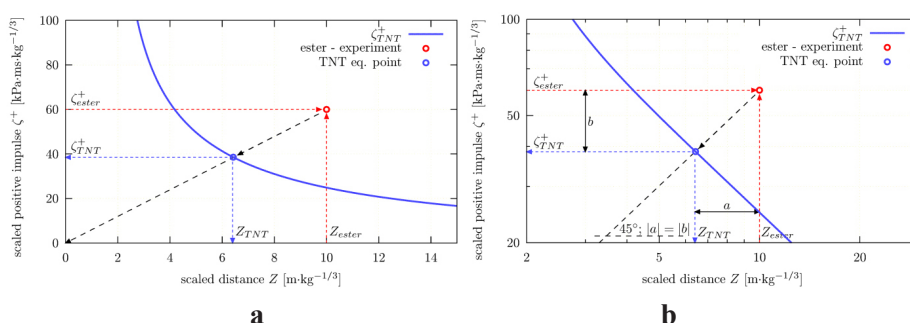


Figure 3. Determination of the scaled distance and scaled impulse of TNT corresponding to the experimentally determined scaled distance and the scaled impulse of the tested ester in normal (a) and logarithmic (b) coordinates

3 Results and Discussion

An example of the measured pressure-time histories recorded by four probes positioned at different distances (3 m, 4 m, 5 m and 6 m) from the NG charge and the corresponding integral curves is presented in Figure 4. All of the measured signals showed a relatively sharp peak with a shorter than 20 ms rise time, and it was therefore decided not to extrapolate the back slope of the blast wave and to simply take the peak maximum as an overpressure. The impulse of the positive phase was determined from the corresponding difference between the baseline and the maximum of the integral curve. The integration was done on raw data without any filtering or fitting of the expansion part of the wave.

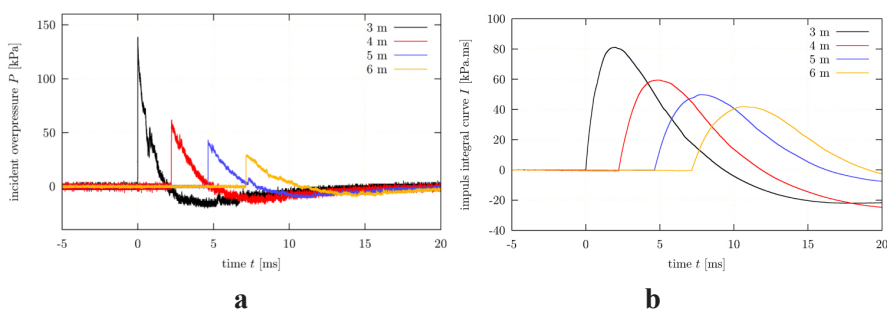


Figure 4. An example of a measured incident pressure-time history for a 1 kg NG charge (a) and the corresponding integral curves (b)

Table 3. Summary of the TNT equivalents determined from the overpressure (k_{TNT}^P) and impulse (k_{TNT}^{I+})

| | k_{TNT}^P | k_{TNT}^{I+} | k_{TNT}^P | k_{TNT}^{I+} |
|-------------------------------------|---|-----------------------|---|-----------------------|
| | for | | for | |
| | $3 < Z < 22 \text{ m} \cdot \text{kg}^{-1/3}$ | | $6 < Z < 10 \text{ m} \cdot \text{kg}^{-1/3}$ | |
| Propane-1,2,3-triyl trinitrate (NG) | 1.0-1.8 | 0.9-1.4 | 1.2-1.7 | 1.0-1.35 |
| Propane-1,2-diyl dinitrate (PGDN) | 1.2-1.7 | 1.1-1.4 | 1.3-1.6 | 1.1-1.25 |
| Ethane-1,2-diyl dinitrate (EGDN) | 1.0-1.8 | 1.0-1.4 | 1.3-1.6 | 1.1-1.35 |
| Methyl nitrate (MeN) | 1.2-2.1 | 1.1-1.6 | 1.6-2.1 | 1.1-1.55 |

The maximum incident overpressure and scaled impulse of the positive phase of the blast wave were plotted as a function of scaled distance in Figure 5 and the corresponding TNT equivalents from pressure and impulse are plotted in Figures 6 and 7, respectively. The results are summarized in Table 3. The first two columns show the results for the entire range of scaled distances and

the following two columns show results in the scaled range where all of the charge sizes overlap.

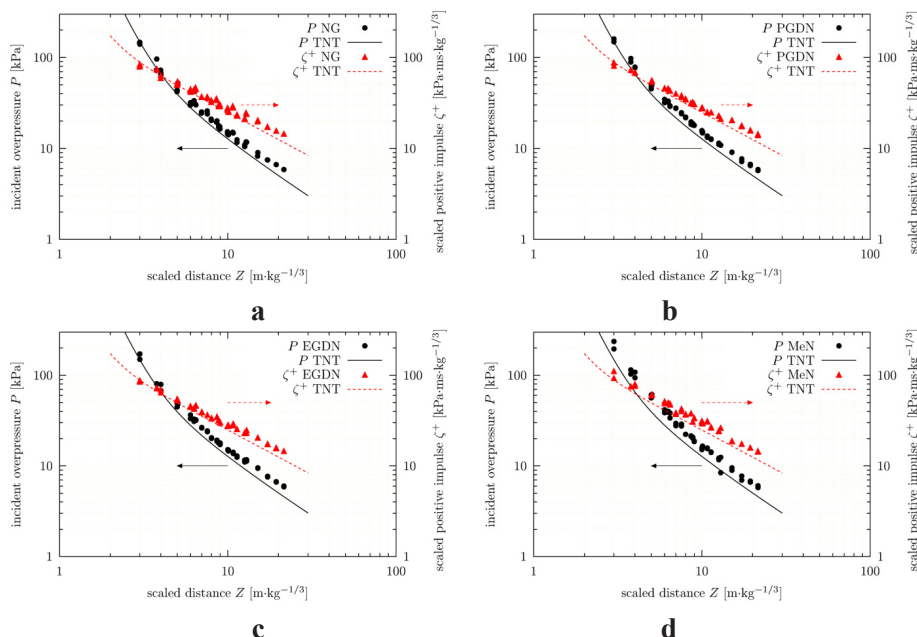


Figure 5. The incident maximum overpressure and scaled impulse vs. scaled distance for NG (a), PGDN (b), EGDN (c) and MeN (d)

The range of the TNT equivalents obtained may at first seem somehow wide but a similar scatter was observed by Swatosh and Napadensky for NG [11]. A few observations were made when evaluating the equivalents as a function of the scaled distance:

- k_{TNT}^P and k_{TNT}^{I+} tended to be lowest at low scaled distances and highest at high scaled distances.
- for 1 kg charges the values of k^P and k^I tended to increase with scaled distance for NG, PGDN and EGDN. This trend was not clearly observed for MeN.
- for 100 g and 500 g charges the values of k_{TNT}^P and k_{TNT}^{I+} tended to show constant values, independent of scaled distance, however with relatively high scatter,
- k_{TNT}^P and k_{TNT}^{I+} determined for different charge sizes but falling into the same scaled distance range (6-10 $\text{m}\cdot\text{kg}^{-1/3}$) were, in the cases of NG and EGDN, following a trend where the highest values of both overpressure and impulse based TNT equivalents were found for the small 100 g charges, and the

lowest values for the 1000 g charges. The results obtained for PGDN and MeN did not follow this trend.

The above mentioned observations pose two questions:

- why do the TNT equivalents show a dependence on scaled distance?
- why do the equivalents depend in some cases on charge weight?

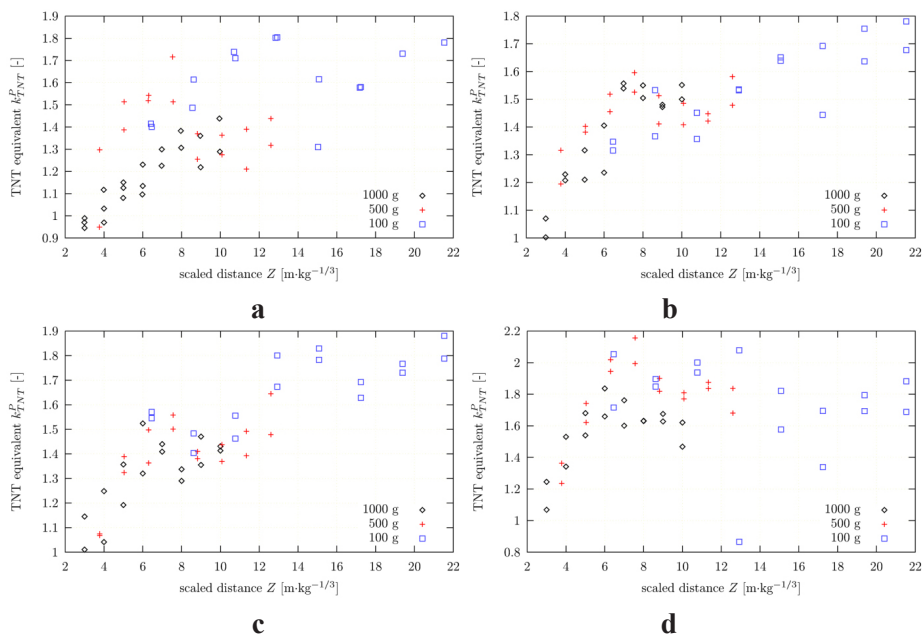


Figure 6. TNT equivalency of NG (a), PGDN (b), EGDN (c) and MeN (d) determined from the overpressure as a function of scaled distance

At the present time we can only speculate about the causes. It seems possible, that both of the above issues may be related to the nature of the explosives. TNT is highly oxygen deficient ($OB = -74\%$) and relatively insensitive to shock wave initiation compared to the liquid esters.

The high oxygen deficiency of TNT results in the formation of detonation products containing solid carbon and a carbon monoxide rich mixture that is quite different from the composition of the detonation products of the esters (the PGDN and MeN have only a slightly negative oxygen balance, EGDN is balanced and NG is positive). This could result in different expansion behaviour and therefore influence the attenuation behaviour of the blast wave.

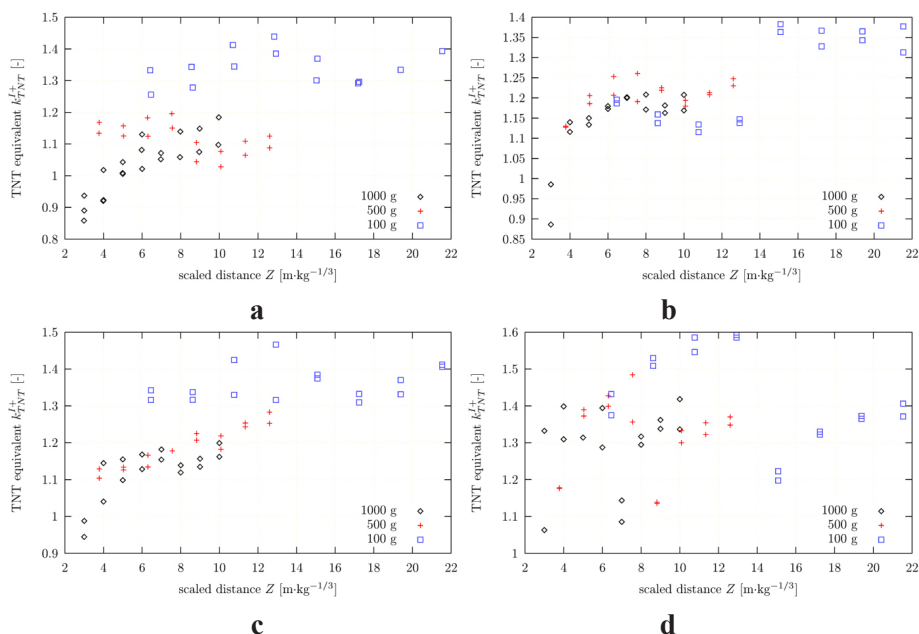


Figure 7. TNT equivalency of NG (a), PGDN (b), EGDN (c) and MeN (d) determined from the impulse as a function of scaled distance

Up until now we have assumed that even the small charges of our pressed TNT fully detonated after initiation by a detonator. This assumption was supported by the overlap of the pressures and scaled impulses of different charge sizes. If however the full detonation of TNT was not achieved, the observed pressures and impulses would be lower, which would lead to higher equivalencies of the esters, assuming they too fully detonated. An investigation into the detonation behaviour of small TNT charges will clarify this issue in future.

The comparison summarizing the experimental values for overpressure and impulse of the positive phase of the incident blast waves of the investigated esters of nitric acid are summarized in Figures 8 and 9, showing that all of the nitric esters outperform TNT and do not differ that much from each other. A bit of a surprise was the fact that MeN slightly, but clearly outperformed the other three, despite having the lowest density and detonation velocity of all four of the esters.

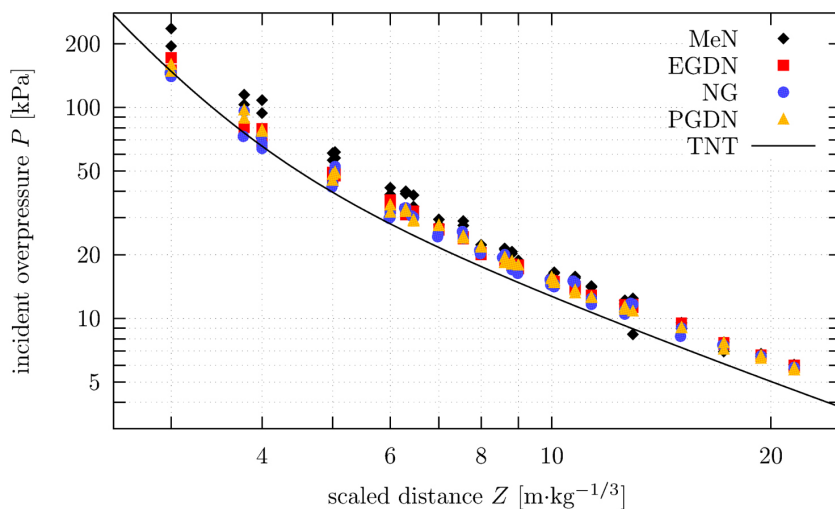


Figure 8. Comparison of the maximum incident overpressure of the tested nitrate esters vs. the scaled distance

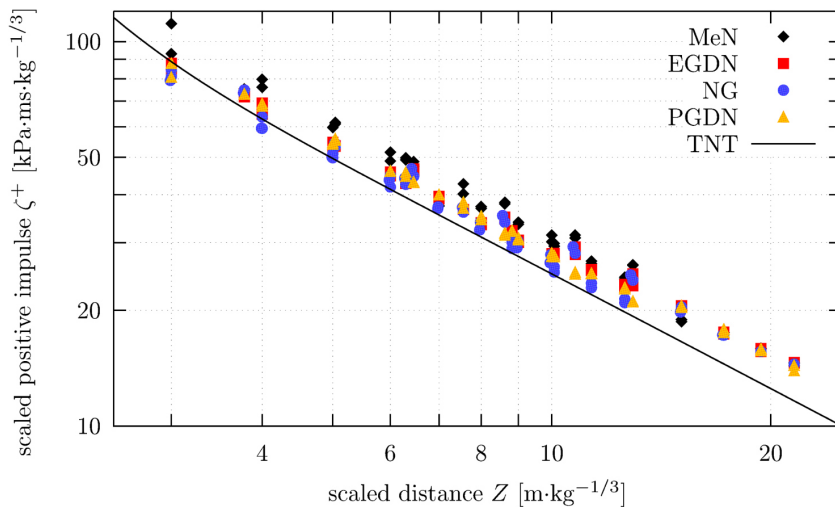


Figure 9. Comparison of the scaled positive impulse of the tested nitrate esters vs. the scaled distance

4 Conclusions

This article provides previously unpublished experimental data of the blast waves generated by small scale charges of NG, PGDN, EGDN and MeN. Charges of 100 g, 500 g and 1000 g were fired at distances from 3 m to 10 m. The blast waves resulting from the detonation of such charges were measured using PCB pencil probe gauges. The results were compared to TNT charges similar in size and shape and the TNT equivalents were calculated from the experimental values of overpressure and impulse.

Detonation of any of the four nitric esters results in the generation of a shock wave in air that has a higher overpressure and impulse than a TNT charge of the same mass. The TNT equivalents, determined from the impulse of the blast wave's positive phase, show relatively high scatter, which was in the case of NG and EGDN found to be dependent on charge size. Relatively surprisingly, MeN outperformed all of the other nitric esters, despite its low density and detonation velocity.

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