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Evaluation of SSRT-Test by Classical Gravimetric Analysis and Optical Topographic Measurement: A Comparative Study

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Abstract: To establish a database of performance values in the small-scale shock reactivity test (SSRT), common secondary explosives based on organic nitrates (e.g. PETN) and nitramines (e.g. RDX and HMX) as well as aromatic (e.g. TNT), heteroaromatic (e.g. TKX-50 and MAD–X1) and open chain systems (e.g. FOX-7) were investigated. The evaluation of the test results was carried out by two different methods. On the one hand, manually by weighing out the resulting dents with sand, and on the other hand, optically with the aid of a profilometer. The two analysis methods were compared and evaluated with respect to their absolute results and absolute as well as relative standard deviations.

Keywords: Detonation Properties · Evaluation · Explosives · High Explosives · SSRT

1 Introduction

The small-scale shock reactivity test (SSRT) was developed in 2005 by *Bohl et al.* [1] and gives experimental insights on the explosiveness of secondary explosives, which can be transferred to the compounds' behavior in applications below their critical diameter. The test setup, which consists of a steel block with a bore and an aluminum block underneath, allows to measure the explosiveness of energetic materials in a practical way (Figure 1). It therefore shows advantages over the Trauzl lead block test, which requires a significantly higher quantity of testing substance. An equal volume of sample substance is always filled into the test device, by using the maximum density of the compounds. This method makes the results comparable with each other, referring to the filling level which is relevant for energetic materials research.

The small-scale shock reactivity test is a proven device for initial characterization of secondary explosives. The evaluation of this test is classically performed by filling the cavity in the aluminum block with sand and subsequent weighing. Since this evaluation can be very dependent on the operator and the selected sand (density, grain size, bulk density), it is difficult or even impossible to compare the obtained data between different working groups. The approach we follow in this study deals with

the optical topographic determination of the dent volume with the help of a profilometer. This method offers the advantage of an easy transferability, since the dent volume is determined independently of additional auxiliary substances. In addition, the measurements are very precise and can be carried out in a short time. Furthermore, we compare the results of the small-scale shock reactivity tests, evaluated by the gravimetric sand method and by the opti-

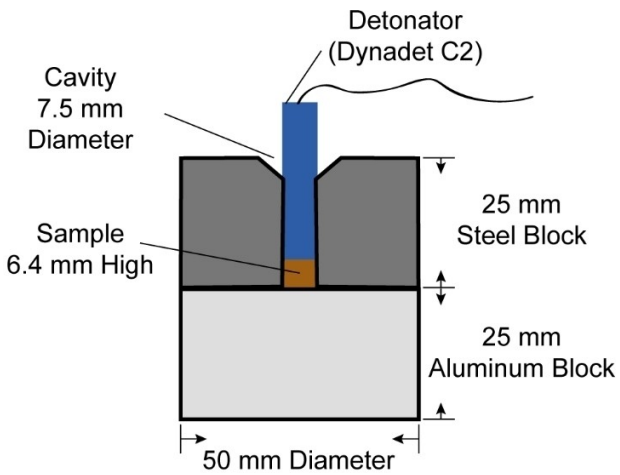

Figure 1. Schematic setup of a SSRT.

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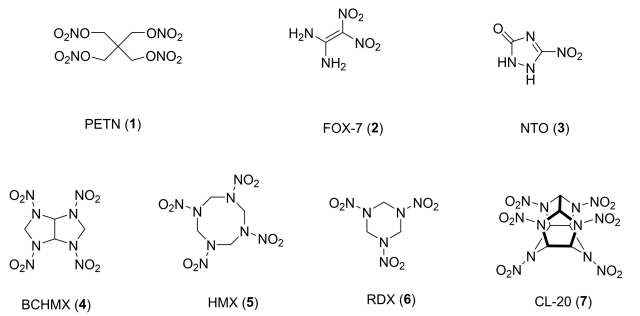
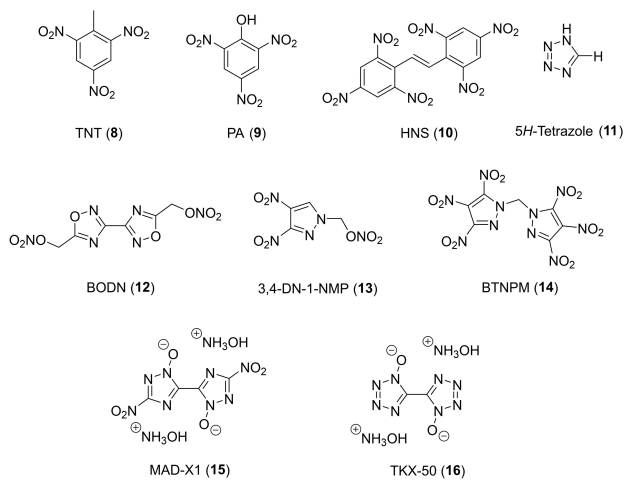
cal profilometer measurement, and thus create a small database for SSRT results, which can be used as a reference for further research.

2 Experimental Section

CAUTION! *All of the compounds which were investigated in this study are explosive energetic materials, showing sensitivities to various types of external stimuli (heat, friction, impact, electrostatic discharge). Therefore, respective safety precautions such as safety glasses, earthed equipment and shoes, leather jacket, ear plugs, Kevlar sleeves, Kevlar gloves and face shield should be used or worn throughout the entire handling.*



Scheme 1. Prepared non-aromatic high explosives: pentaerythritol tetranitrate (PETN, **1**), 1,1-diamino-2,2-dinitroethylene (FOX-7, **2**), nitrotriazolone (NTO, **3**), 1,3,4,6-tetranitrooctahydroimidazo[4,5-d]imidazole (BCHMX, **4**), octogen (HMX, **5**), hexogen (RDX, **6**), hexanitrohexaazaisowurtzitane (CL-20, **7**).



Scheme 2. Prepared aromatic high explosives: 2,4,6-trinitrotoluene (TNT, **8**), picric acid (PA, **9**), hexanitrostilbene (HNS, **10**), 5*H*-tetrazole (**11**), bis(1,2,4-oxadiazole)bis(methylene) dinitrate (BODN, **12**), 3,4-dinitro-1-nitratomethylpyrazole (3,4-DN-1-NMP, **13**), bis (trinitropyrazoyl) methane (BTNPM, **14**), bis-(hydroxylammonium) 3,3′-dinitro-5,5′-bis-(1,2,4-triazole)-1,1′-diolate (MAD–X1, **15**), bis-(hydroxylammonium) 5,5′-bistetrazole-1,1′-diolate (TKX-50, **16**).

For all three test blasts per compound the samples were used from the same batch in order to be able to avoid the differences in purity/composition. We did not include the grain size of the respective samples in the evaluation as these were pressed anyway. All samples for the SSRT tests were used as they were obtained from the synthetic manufacture. The selected compounds are depicted in Scheme 1 and Scheme 2.

Nitration of pentaerithritol (PE) using fuming nitric acid and neutralization with sodium bicarbonate solution yields PETN (**1**) [2]. FOX-7 (**2**) is obtained by nitration (mixed acid) of 2-methylpyrimidine-4,6-diol and a subsequent hydrolization of the nitration mixture in ice water [3]. NTO (**3**) was obtained by nitration of 1,2,4-triazol-5-on using concentrated nitric acid [4]. Potassium imidazo[4,5-d]imidazole-1,3,4,6-tetrasulfonate was prepared through condensation reaction of potassium sulfamate, formaldehyde and glyoxal. This respective tetrakis-potassiumsulfamat derivative was reacted to BCHMX (**4**) using fuming nitric acid [5]. HMX (**5**) and RDX (**6**) were synthesized by nitration of hexamine following the Bachmann process (due to the manufacturing process employed, RDX with an impurity of 7 % HMX was applied) [6–7]. CL-20 was prepared following a procedure of *Nielsen et al.* The protected hexaazaisowurtzitan backbone was obtained through condensation of benzyl amine and glyoxal solution under acidic catalysis followed by partial deprotection using H_2 and Pd/C. Subsequent anhydrous oxidation and nitration ($NOBF_4/NO_2BF_4$) yields ε-CL-20 (**7**) [8].

TNT (**8**) and PA (**9**) were obtained by nitration of the respective benzolic parent compound (toluene for TNT and phenol for PA) [9–10]. HNS (**10**) was obtained by oxidation of TNT using NaOCl [11]. 5*H*-tetrazole (**11**) was obtained by reaction of sodium azide, ammonium chloride and triethyl orthoformate in acetic acid [12].

BODN (**12**) was prepared by a procedure of *Sabatini et al* starting from diaminoglyoxime [13]. 3,4-DN-1-NMP (**13**) was produced via a five step procedure starting from 1*H*-pyrazole including *N*-nitration, nitro-rearrangement, *C*-nitration, *N*-hydroxymethylation and *O*-nitration [14]. BTNPM (**14**) was obtained through a five step reaction sequence starting from 1*H*-pyrazole [15]. MAD–X1 (**15**) and TKX-50 (**16**) were synthesized following literature known procedures starting from oxalic acid/aminoguanidinium carbonate and aqueous glyoxal solution, respectively [16–17]. The purity of all compounds was checked through ^{1}H NMR spectroscopy and CHNO elemental analysis.

3 Results and Discussion

To perform the test series, the synthesized compounds **1**–**16** were weighed and prepared for detonation in the SSRT setup as recently described [1, 17–19]. For the SSRT method, a constant volume of explosive is needed to be comparable within the other tested substances. The sample volume V_s is recommended to be 283 mm^3, which corre-

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sponds to a filling height of 6.4 mm for the required 7.5 mm of diameter of the drill hole in the steel block. The used sample mass m_s was calculated according to the formula given in Equation 1 [1,17,18].

$$m_s = 0.95 \times V_s \times \rho_{Xray} \quad (1)$$

This ensured that the identical fill level was used for all compounds investigated, whereby we always assumed the ideal crystallographic density of the substances. The calculated quantities of the respective substances can be found in the Supporting Information. Each substance was tested with three blasts in order to to obtain a reliable average value and to minimize the effect of outliers.

After the test was carried out and the aluminum block cleaned, all the blocks were evaluated using two different methods. On the one hand, an optical topographic measurement of the generated dents was performed using a Keyence profilometer (Keyence 3D profilometer VR-5200, KEYENCE DEUTSCHLAND GmbH, Siemensstraße 1, D-63263 Neu-Isenburg). The exact implementation of this measurement method can be found in detail in a recently published study [19]. On the other hand, a gravimetric method was used as originally proposed for the evaluation of the SSRT [1]. Commercially available, unground sand was used as the filler, which was poured into the dent of the corresponding aluminum block and smoothed with an object carrier to remove the excess sand. Using the empty aluminum block as reference, the mass of the poured sand was determined by weighing it out. This measurement was repeated ten times per block to obtain a good average with a reasonable standard deviation. The results of the various measurements are outlined in the graphs below.

The largest dent volumes were obtained with CL-20 and RDX, while PETN, HMX, BCHMX, DNNMP and TKX-50 show similarly high volumes (Figure 2). TNT, PA and HNS show lower volumes than the aforementioned, as could be expected from their performance parameters. Due to the high calculated performances, larger bulges were expected for numerous compounds (especially for TKX-50). However, this test setup aims to produce detonations below many compounds' critical diameter. Since this critical diameter is often not achieved (diameter of the cavity is 7.5 mm), the detonations cannot spread ideally and the test results are lower than expected. NTO, tetrazole and BODN show distinctly low dent volumes and tetrazole as well as BODN large error bars. This is due to the fact, that full initiation was not achieved for all blasts as can be seen in Figure 3. There are several possible reasons but, above all, the lower explosiveness and consequently, more difficult initiation of the two substances is noteworthy. All other compounds were initiated successfully with the used setup.

In comparison to each other, the three blasts show generally very similar data (Figure 3) except when initiation is not achieved like for tetrazole and BODN. Deviations between the blasts can result from small errors in the weighing and filling process e.g. from imperfect pressing of the compounds into the steel block cavity.

The values obtained by the gravimetric method agree with the values obtained by the optical topographic measurement and show a comparable error bar distribution. The results are depicted in Figure 4.

When comparing the values side by side (Figure 5) it can be seen, that especially low or high values can differ from one testing method to another. The gravimetric method shows a smaller difference between the highest (CL-20) and lowest (NTO) values than the topographic method. The dent depth of NTO compared to CL-20 is 32% for the gravimetric method and only 25% for the topographic method. To assess the quality of the obtained data for both methods, the relative standard deviation is a valuable tool, as it helps to visualize the size of the minimum measurement error for a given test setup (Figure 6).

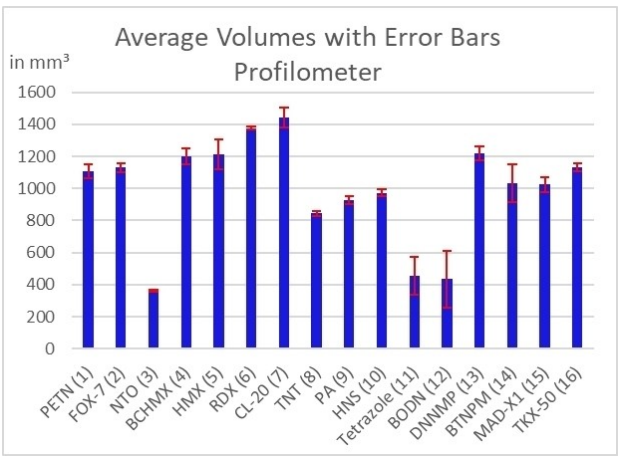

Figure 2. Average dent volumes in mm³ for compounds **1**–**16** with error bars, measured by the profilometer. Error bars are calculated using the averaged values for each blast.

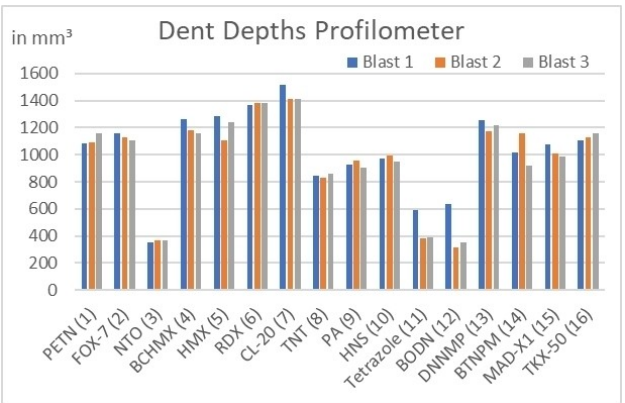

Figure 3. Dent volumes in mm³ for each blast performed for compounds **1**–**16**, measured by the profilometer.

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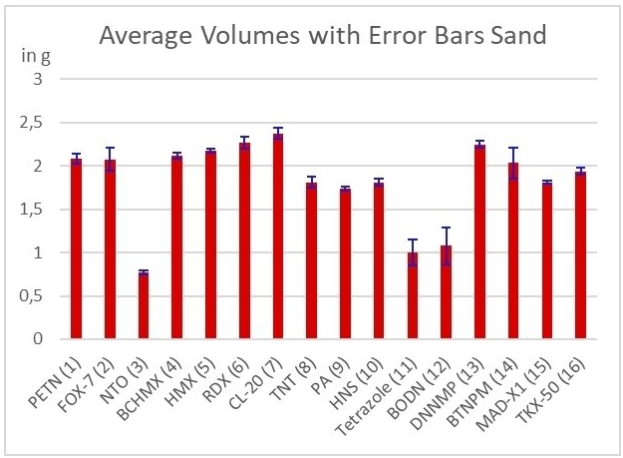

Figure 4. Average sand masses in grams needed for filling the dent in the aluminum block for compounds **1**–**16**, with error bars.

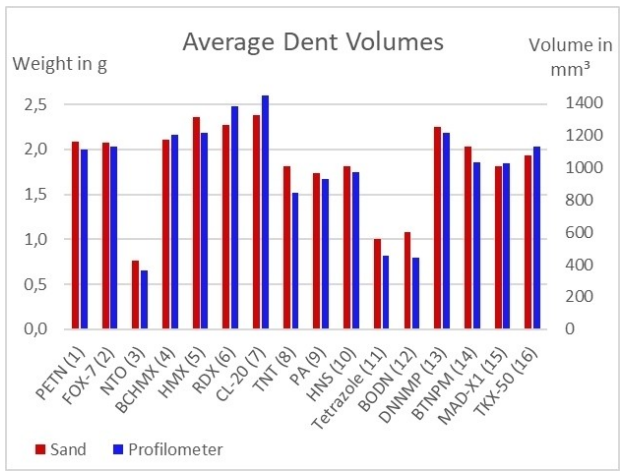

Figure 5. Average dent volumes for both measurement methods compared. Gravimetric method in red, profilometric method in blue.

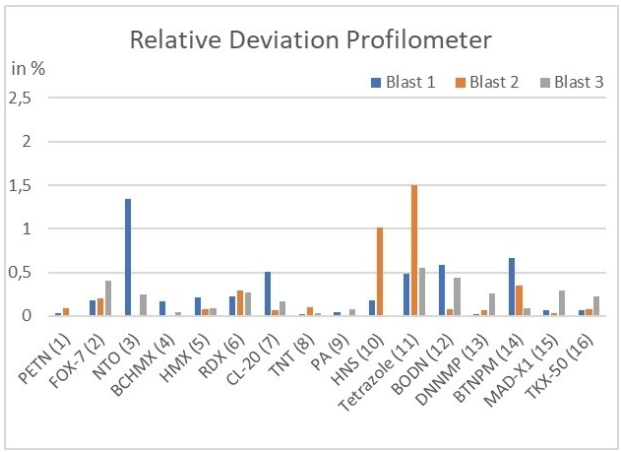

Figure 6. Relative deviation in % of the two profilometer measurements for each compound.

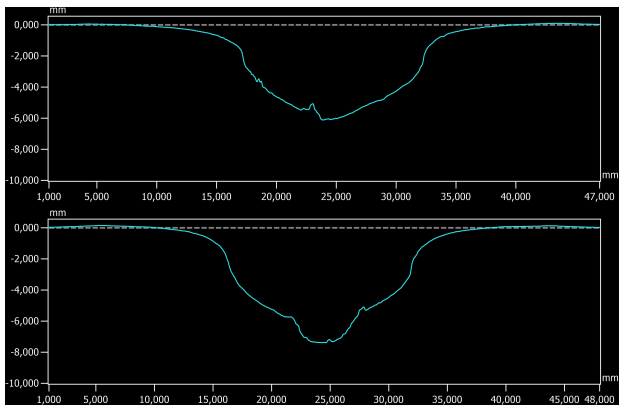

Figure 7. 2D profile measurements. a) HNS blast 1 with a convex tip in the profile; b) PETN blast 1 with concave hole in the profile.

The profilometer measurements were performed two times per blast to offset the impact of formed concavities or convexities in the overall dent profile of the witness block. The blocks were rotated by 90° in-between measurements to minimize the problem, but more measurements per block would give data with even higher accuracy. Nevertheless, the relative standard deviation is in the range of 0 % – 1.5 % with most measurements below 0.5 %. Up to six blocks can be measured in succession without further user interaction, reducing the actively spent time massively.

Figure 7 shows the result of the two topographic measurements with irregular dent shapes of HNS blast 1 (top) and PETN blast 1 (bottom). The measurement method with the profilometer, which is based on triangulation of polarized light, can lead to blind spots in certain areas of the block and thus to a serious error in the resulting volume values. This means that an increased number of measurements would have to be taken at different angles for each block in order to avoid this source of error. However, in the blocks investigated, there are only a few samples with extreme bulges (concavities or convexities), which we have already been able to average well with two measurements, which represents the volume with high accuracy.

The relative standard deviation graph (Figure 8) for the gravimetric method exposes a significant problem: operator-dependency. TNT and BTNPM show the highest deviations of up to 2.5 %, while the other compounds show a very similar deviation spread with values of around 0.25 %–0.5 %. TNT was the first and BTNPM the second compound to be measured by the operator. When a large amount of experiments is to be conducted, this flaw can be easily bypassed by refining the measuring process first. However, most SSRT experiments only compare a few selected compounds like RDX or PETN to the respective new compounds.

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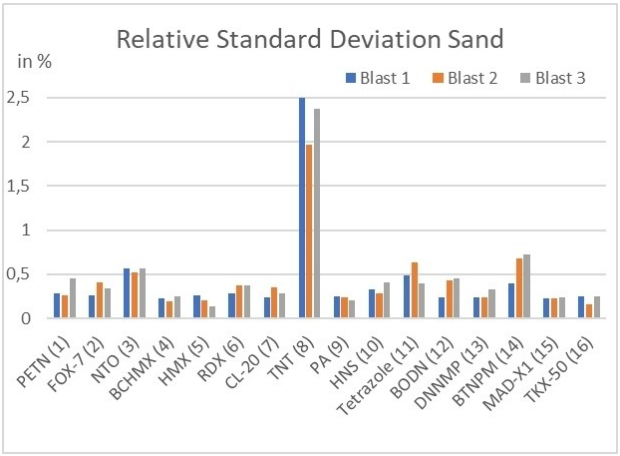

Figure 8. Relative deviation in % of the gravimetric measurements for each compound.

In addition to the measurement inaccuracy that occurs with an unestablished methodology, the measurement time is another disadvantage of the gravimetric method. Although the measurement duration is not as important for a few isolated samples, such as the analysis of a single compound, as it is for the preparation of a large collection of data, as in this study, it is nevertheless a factor that cannot be neglected. In our series of measurements, the time required to determine the mass of the sand for one compound (three tested blocks with ten dent measurements each) was approximately one hour. Compared with the 6 min for the profilometeric measurement of three blocks, there is a clear advantage for the digital measurement method.

4 Conclusion

In the present study, two evaluation methods for SSRT experiments were compared; the classical gravimetric analysis, which uses sand as a filling material of the dent, and an optical topographic measurement method, which generates its results through digital profilometer measurements. Basically, our two series of measurements yield similar results and trends. Nevertheless, we were able to gain some advantages from the measurement method with the profilometer. Among other things, the digital measurements are less time-consuming, more accurate, graphically better representable and reproducible independent of the operator. In addition, when evaluating with the profilometer, volumes are obtained as measurement results, which can be more easily compared with other measurement series than sand masses, which are the output of the gravimetric measurement method and are therefore dependent on the type and properties of the used sand. We present in our study the results of SSRT experiments for 16 common explosives, which can be used as reference value in the future.

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