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Small-Scale Safety Testing of Ammonium Nitrate and Mixtures

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Abstract: Ammonium nitrate (AN), gunpowder (GP), and an ammonium nitrate gunpowder mixture (AN/GP) were studied for impact sensitivity by four laboratories using the drop hammer apparatus. Bruceton and Neyer methods were used as experimental protocols and for data reduction. The results are presented as 50 % probability of reaction (DH_{50}). For AN, the DH_{50} values are widely varied among the participants, from sensitive to completely insensitive (limit of the equipment), with no real correlation among results. GP and the AN/GP mixture exhibited much more sensitivity overall and were in some cases within statistical values extrapolated from previous studies of RDX. The variability in results for the AN data is attributed to the difficulty in determining a positive reaction event for AN, as detailed by Neyer experiments and photography during positive reactions. Variability in results for the GP and AN/GP mixtures is attributed to equipment environment and detection criteria. This work was performed by the Integrated Data Collection Analysis (IDCA) program, a multi-laboratory effort to standardize safety testing of improvised or homemade explosives funded by the Department of Homeland Security.

Keywords: Safety testing · Ammonium nitrate · Gunpowder · Impact sensitivity · Ammonium nitrate mixtures

1 Introduction

The Integrated Data Collection Analysis (IDCA) Program recently conducted a round-robin type proficiency test for Small-Scale Safety and Thermal (SSST) testing of standard and improvised or homemade explosives (HMEs). During that test, 19 materials were subjected to impact, friction, spark, and thermal testing by up to five different laboratories that routinely handle energetic materials – three Department of Energy and two Department of Defense. One series of materials of interest tested was a combination of ammonium nitrate (AN) and double base gunpowder (GP) as well as the components themselves. AN and, to a lesser extent, the mixture of AN/GP, exhibited challenges to obtaining reliable SSST testing data. Particularly affected was the impact sensitivity. This communication shows the issues behind the discrepancy in impact results among the participants of the proficiency test.

2 Experimental

The materials, testing equipment, and test protocols have been presented elsewhere [1]. The AN was Fisher Brand, Catalog Number A676, Lot #086459 and was dried at 60 °C for 16 h, then stored in a dessicator until use. The GP (Bullseye® smokeless powder) was from Alliant Powder Company. The composition (according to the manufacturer) is nitroglycerin (NG) 40 %, nitrocellulose (NC) 58 %, ethyl centralite (stabilizer) 1 %, modifier and graphite 1 %. The material was packaged in May, 2003 (the manufacturer suggested the stabilizer level be checked once every 5 years). The particle size distribution has been previously presented [1]. For the gunpowder, the distribution extends from 500 to 1000 μm (10 % 530 μm, 95 % 970 μm). The average particle size is

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753 ± 153 μm. For the AN (dried), the distribution extends from 200 μm to over 1500 μm (10% 364 μm, 95% 1573 μm). The average particle size is 724 ± 401 μm. A full listing of the results can be obtained as Supporting Information from the author [2–4].

The impact sensitivity was measured using Type 12 equipment – LLNL, LANL, IHD, ERL; AFRL, MBOM modified for Type 12. The data were taken by the modified Bruceton method [5] or the Neyer method protocols and reduced to DH_{50} values [6]. The DH_{50} (in cm) is the height for 50% probability of reaction. Values in Table 1 are averages of at least three independent data sets unless otherwise stated.

3 Results

Four laboratories tested the AN, GP, and AN/GP for impact sensitivity using Type 12A methods. The standard sandpaper to hold the sample inplace for the testing was 180-grit garnet dry sandpaper. LLNL also used 120-grit Si/C wet/dry sandpaper. These methods have been reviewed previously, including the characterization of the sandpaper [1,7]. Table 1 shows the DH_{50} values for the three materials tested.

3.1 Ammonium Nitrate

Concentrating on the AN results only shows that the participants do not agree on the magnitude of the DH_{50} values. Results span the range from sensitive (AFRL) to completely insensitive (LANL). LANL could not measure sensitivity to the limit the drop height of the equipment (320 cm) using the Bruceton method. Using the Neyer method, LANL was able to record sensitivity, but the sensitivity is still quite low. LANL tested the AN before (as received from manufacturer) and after drying at 60 °C for 16 h. For the Bruceton method, no difference in sensitivity was seen [8]. In addition, LANL tested some aged dried material using the Neyer protocol and found no difference in impact sensitivity than with the dried material. LLNL tested the AN using two different sandpapers, 180-grit garnet and 120-grit Si/C. The DH_{50} values for these measurements exhibited large differences in sensitivity. This has been seen previously for several materials where using 180-grit sandpaper in the drop hammer yields a more sensitive material than using 120-grit sandpaper in the drop hammer [1].

Table 1. DH_{50} values for AN, GP, and AN/GP mixtures by Bruceton and Neyer methods.

Laboratory	Conditions[a)]	DH_{50} [cm]
LLNL	AN, dried, 120-grit Si/C, B	157 ± 1
LLNL	AN, dried, 180-grit Garnet, B	82 ± 8
LANL	AN, dried, 180-grit Garnet, B	> 320
LANL	AN, AR[b)], 180-grit Garnet, B	> 320
LANL	AN, dried, 180-grit Garnet, N	304.2 ± 9.2
LANL	AN, old, 180-grit Garnet, N[c)]	304.5 ± 16.7
IHD	AN, dried, 180-grit Garnet, B	201 ± 29
AFRL	AN, dried, 180-grit Garnet, B	60.5 ± 2.5
LLNL	GP, AR[b)], 180-grit Garnet, B	54.2 ± 4.9
LANL	GP, AR[b)], 180-grit Garnet, B	20.7 ± 1.0
LANL	GP, AR[b)], 180-grit Garnet, N	21.0 ± 1.2
IHD	GP, AR[b)], 180-grit Garnet, B	12.3 ± 0.6
LLNL	AN/GP, dried[d)], 120-grit Si/C, B	85.8 ± 18.1
LLNL	AN/GP, dried[d)], 180-grit Garnet, B	46.8 ± 1.8
LANL	AN/GP, dried[d)], 180-grit Garnet, B	29.0 ± 0.5
LANL	AN/GP, dried[d)], 180-grit Garnet, N	28.2 ± 3.3
IHD	AN/GP, dried[d)], 180-grit Garnet, B	21.3 ± 2.3

a) Material tested, pretreatment, sandpaper, data reduction method (B = Bruceton, N = Neyer). b) As received from manufacturer. c) Dried but left to sit one month. d) AN dried, GP as received from manufacturer.

3.2 Gunpowder

Table 1 shows the DH_{50} values for GP. The GP data overall shows a much more sensitive material to impact than the AN. Unlike the AN data, the GP data shows much better agreement among the participants. LANL and IHD values are within application of statistical values determined in a previous study [7]. The LLNL value indicates a much less sensitive material. Again, the LANL values by the Bruceton and the Neyer methods agree.

3.3 Ammonium Nitrate and Gunpowder Mixture

Table 1 also shows the impact sensitivity values for the AN/GP mixture. The mixture data overall shows a sensitivity that is slightly less than the GP. The wide variation among the participants seen for the AN data is not seen in this case either. Based on the DH_{50} values, mixture sensitivity seems to be dominated by the GP. LANL and IHD measured values are within application of statistical values determined in a previous study [7]. LLNL measured values indicate a much less sensitive material with the 180-grit sandpaper than the other participants, and indicate even a more insensitive material when the 120-grit sandpaper is used. As in previous measurements, the LANL Bruceton derived value agree with the Neyer derived value.

4 Discussion

4.1 Drop Hammer Test of Ammonium Nitrate

Table 1 shows a large discrepancy in the impact sensitivity values among the participants. Some discrepancies have been reported previously in the proficiency test [1] and have been attributed to a variety of factors, such as sandpaper and detection equipment differences among the participants. It has to be noted that it is not due to differences in the materials, pretreatment or sample mixing as the IDCA had specific protocols for these operations. However, the variation in results for the impact sensitivity of AN is some of the largest reported in the proficiency study.

RDX has been studied by the IDCA multiple times in the proficiency test. From these tests, there has been sufficient data collected to perform statistical analyses [7]. For RDX, the order of drop hammer sensitivity was found to be LLNL < LANL < IHD < AFRL. However, some analyses indicate that LLNL and LANL results are statistically the same and that AFRL is statistically different (more sensitive) and IHD bridges in between. In this study on AN, although not evaluated statistically, the order for drop hammer sensitivity was found to be LANL < < IHD < < LLNL < AFRL, where the magnitudes of the differences are much more than in the RDX case. Temperature and humidity are probably not the reason because the orders do not follow either parameter. For temperature, the order is LANL > AFRL > LLNL > IHD; for humidity the order is LANL < LLNL < IHD = AFRL.

A key to the understanding the differences in the DH_{50} values can be found in a more detailed examination of the drop hammer experiment of AN using the Neyer protocol. LANL used this protocol along with the Bruceton method for all the materials examined in the proficiency test. The correlation between the two methods for those materials has been discussed previously [1] and was found to be essentially one to one, although PETN was an outlier. Not all the AN data was included in that comparison because of the issues with the Bruceton results (greater than the height of the drop weight).

Table 2 shows the individual determinations using the Neyer method for AN. The March 2011 data shows no sensitivity. However, the April 2011 data shows marginal sensitivity (for not dried and dried), contrary to the March data. Examining the standard deviations for the April determinations, show a very large variation as well as very high deviations. Typical Neyer testing deviations are around 2 cm for these types of materials, so the AN deviations show very large spread in the positive reaction level.

A potential source for these differences in results can be found in the positive/negative reaction ("go-no/go") determination process. AN appears to be a very difficult material to test in the drop hammer experiment. The problem seems to be with the determination of a positive/negative event based on sound. At large drop heights, materials that yield little noise when reacting are difficult to discern because the background noise is so great. Figure 1 shows the positive/negative determination graph for a Neyer determination on AN. Twenty five trials were performed on the AN (180-grit garnet sandpaper, 35-mg samples). The detection method used was a sound threshold over background. A green "x" marks a positive reaction and a red "o" marks a negative reaction. Clearly the range of positive and negative events is very large. There are positive events as low as 200 cm and negative events as high as 320 cm (upper limit of the equipment). This material has very low sensitivity and as a result, the background from the high drop height can interfere with determining a positive and negative event. For the sound meter, the drop hammer produces 110 dB on the average for a negative reaction and 122 dB on the average for a positive reaction.

Table 2. Drop hammer date by Neyer method for AN.

Test date	T [°C]	RH[a] [%]	DH_{50} [cm]	S[b] [cm]
3/16/11[c]	19.5	< 10	> 320	NA[e]
3/17/11[c]	18.9	< 10	> 320	NA[e]
3/18/11[c]	18.5	< 10	> 320	NA[e]
4/7/11[d]	22.0	24.5	293.7	8.8
4/7/11[d]	21.2	21.0	311.0	26.2
4/7/11[d]	21.0	20.8	307.9	12.8
4/7/11[c]	21.2	22.3	323.5	67.1
4/7/11[c]	21.4	20.9	298.2	10.0
4/7/11[c]	21.2	18.1	291.9	23.0

a) RH = relative humidity. b) Standard deviation. c) Dried. d) As received from manufacturer. e) Not applicable.

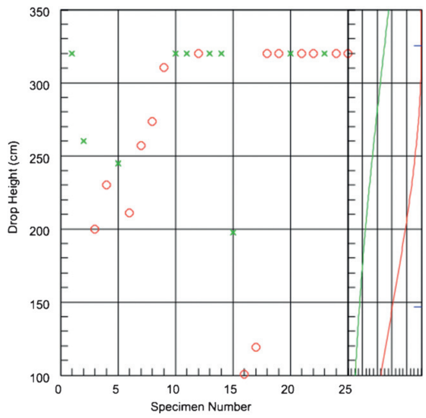

Figure 1. Testing of AN by Neyer method (x = positive event, o = negative event).

To illustrate the issue further, Figure 2 shows photographs of two tests that were considered a positive event. The photographs were taken in the dark with the aperture wide open (f1.8) and with maximum speed (6400). The photograph on the top of the figure shows an event selected as positive by sound. This clearly shows light of reaction. However, the photograph on the bottom of Figure 2 was also identified by sound as a positive event, but no light was visible. Visibly, it would be considered a negative or no-go, but was recorded by sound as a positive event. Many of the events that were considered positive did not exhibit light. Higher order was verified in some cases by inspection of the sandpaper after the test, but results sometimes conflicted.

This alone exhibits considerable challenge to the operator for determining a positive event. Most operators use light, sound, smell, and detection equipment. When one system, in this case light emission, does not agree with the other systems, this case sound, the operator has to make a subjective assessment which could lead to the questionable result. Add to this the variation seen in Figure 1 for

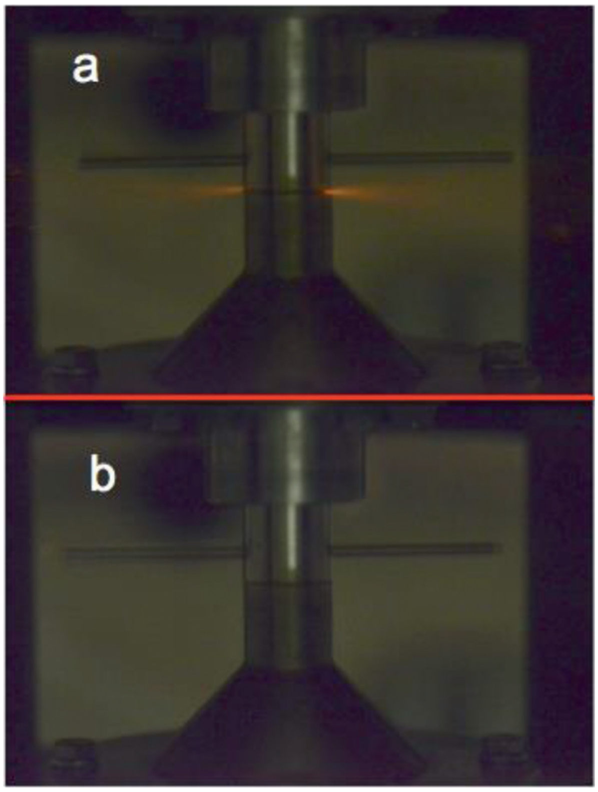

Figure 2. Photographs of positive events in the drop hammer testing of AN, Neyer method; both were considered a positive event by sound: (a) shows visible evidence (b) does not.

a positive event can lead to the variation seen in the results in Table 1 for AN.

4.2 Impact Sensitivity of Ammonium Nitrate/Gunpowder Mixture

The data in Table 1 for the AN/GP mixture indicate results that agree with previous proficiency test results – LANL and IHD results agree and LLNL results generally rate materials less sensitive than the other participants [1]. Other BAM friction and ESD measurements have also shown this. These differences are generally due to equipment configuration issues. For the BAM friction case, the LLNL friction tester is located in a glove box with a HEPA filter as a separate venting system, making positive reaction events more difficult to hear [1,7] compared to the other participants that have only sucker hoses for venting systems. For the ESD measurements, the LLNL equipment is custom built and includes a 510-Ω resistor to mimic the human body, greatly modifying the current response compared to the ABL systems of the other participants.

To complicate matters among participants, the positive/negative determination is not uniformly conducted. LANL uses a sound detection system with a microphone that is one meter away. Assessment of positive or negative can be overridden by other input, such as personal decisions by the operator and/or by photography. LLNL uses a different type of microphone that is 15.24 cm from the anvil. Assessment of a positive or negative event can be overridden by personal decisions by the operator. IHD and AFRL use operator only decision-making. The microphone issue is likely the reason for the LLNL results indicating less sensitive materials.

4.3 Sandpaper Effect

Table 1 shows for the LLNL data there are sandpaper effects. This has been reported previously in the proficiency test and has accounted for major differences in testing results among the participants. Although 180-grit garnet sandpaper was used as the standard for the proficiency test, 120-grit Si/C wet/dry and 150-grit garnet dry were also used on occasion. For the 19 materials tested, the biggest differences were measured between 120-grit and 180-grit sandpapers for the improvised binary mixtures, for example, $KClO_3$/sugar. Military materials such as RDX, PETN, and HMX exhibited less sensitivity difference when studied with both sandpapers. The origin of the differences in sensitivities measured by the different sandpapers is not known, although grit-size and hardness has been verified as responsible for non-shock initiated reactions [9], other sandpaper properties, such as paper thickness and glue, have to be considered.

5 Conclusions

This work addresses the difficulty in obtaining agreeing results from different laboratories that have similar equipment and protocols testing identically prepared materials. These differences can be attributed to two sources: (1) the specific AN material, and (2) differences in environmental and detection configurations. AN appears to be very difficult to determine a true positive reaction. This detection may also be controlled more by the environmental factors, such as sound insulation, and detection criteria, such as microphone placement. Issues such as these account for the wide differences in results presented here. They also highlight the need for a standard method of detection in the testing community.

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