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Effect of Experiment Environment on Calorimetric Value of Composite Solid Propellants

Lalita S. Jawale, Chandrani Dey, Mehilal*, Manoj Gupta, and B. Bhattacharya

High Energy Materials Research Laboratory, Sutarwadi, Pune-411 021, India
**E-mail: drmehilal@yahoo.co.in*

ABSTRACT

The calorimetric value (cal-val) of solid rocket propellants and explosives is determined in the presence of inert atmosphere using industrial nitrogen gas. However, due to presence of trace amount of oxygen, the cal-val is not always correct. To avoid such inaccuracy in cal-val, a systematic study has been carried out by taking different types of solid propellant samples having burning rate in the range of 5 mm/s – 30 mm/s at different pressures. The data obtained were acquired using industrial nitrogen, ultra high pure nitrogen (UHP-N_2), ultra high pure argon (UHP-Ar), air and ultra high pure oxygen (UHP-O_2). The data reveal that cal-val is highest in the case of UHP-O_2 due to complete combustion while in the case of air and industrial nitrogen it is found to be substantially less. Moreover, the cal-val in the presence of UHP-N_2 and UHP-Ar meets the standard value with reproducibility. The results, further, confirm that for authentic cal-val, the most suitable environment is UHP-N_2/UHP-Ar.

Keywords: Calorific value, calorimetric value, composite propellant, bomb calorimeter, burning rate, cordite

NOMENCLATURE

Cal-val	Calorimetric value
UHP	Ultra high pure
Ar	Argon
r.t.p.	Room temperature and pressure
AP	Ammonium perchlorate
HTPB	Hydroxyl terminated polybutadiene

1. INTRODUCTION

Composite solid rocket propellants, heterogeneous in nature, basically contain ammonium perchlorate as an oxidizer along with aluminium powder as metallic fuel embedded in hydroxyl terminated polybutadiene (HTPB) binder being used extensively for space as well as missile applications[1]. The energetic of propellants, explosives and pyrotechnics play a vital role in their selection for a particular application. There are number of methods reported for the determination of energetic, viz.,

- Velocity of detonation (VOD) and blast effect in case of high explosives
- Specific impulse (I_{sp}), characteristic velocity (C*), etc. in the case of propellants
- Flame temperature/heat produced after combustion (pyrotechnics)
- Calorific value/calorimetric value (solid/liquid fuels)

However, these methods require large quantity of samples and are also cumbersome, whereascalorimetric value (cal-val) method is simple, fast and accurate. Thus, this method is obvious choice to determine energetic of propellants, explosives and pyrotechnics.

The literature survey reveals that little information on the effect of environment on cal-val is available for the determination of cal-val. Also, the role of specific environment on determined cal-val has not been studied exhaustively. Some basic works on the determination of cal-val using polystyrene, polyvinyl chloride and carboxyl terminated polybutadiene (CTPB) binder with ammonium perchlorate has been studied by Kishore[2], *et al.* Moreover, Jain[3], *et al.* have studied the cal-val of ammonium perchlorate based composite propellant in the presence of methyl ammonium perchlorate in ultra pure nitrogen medium.

The variation in cal-val has also been studied during the ageing of CTPB/Al and PVC/AP composite propellant in nitrogen atmosphere[4–5] and the data on cal-val of aged propellant decreases as ageing time increases. Also, a comparative study of cal-val of 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20), 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX), pentaerythritol tetranitrate (PETN), 2,4,6-trinitrotoluene (TNT) and hexanitro benzene (HNB) has been studied using Parr isothermally jacketed calorimeter without mentioning the type of environment[6] and their findings reveal that higher the oxygen balance of the energetic molecule higher the corresponding cal-val. The cal-val of energetic nitramines extruded double base propellant has been reported in the presence of air using Parr adiabatic bomb calorimeter and findings reveal that incorporation of nitramines in the composition enhances the cal-val[7].

In continuous to this work further, the cal-val of high

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energy propellants for advanced gun ammunition based on 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), glycidylazide polymer (GAP) and triaminoguanidinium nitrate (TAGN) has been studied on Julius Peters adiabatic bomb calorimeter[8]. However, this study does not reveal the exact nature of environment applied during the determination of cal-val. The successful attempts have also been made by other workers[9], where heat of combustion of new energetic thermoplastic elastomers based on GAP, polyNIMMO and polyGLYN were carried out in Parr calorimetric oxygen bomb at 3 MPa to co-relate the energy output of the prepared composition. On the same line, the cal-val of new non-toxic substances as stabilizer for nitrocellulose based propellants were also reported[10] in vacuum of constant volume at a temperature of 25˚C and heat output were compared with conventional stabilizers.

Moreover, the referred studies do not envisage the advantages or disadvantages of environment during the determination of cal-val. Therefore, a systematic study has been carried out to determine the cal-val in different environments and their comparison to the most accurate and reliable cal-val for the composite propellants having burning rates in the range of 5 mm/s to 30 mm/s at different operating pressures.

2. EXPERIMENTAL

2.1 Chemicals/Materials

Benzoic acid pellets, AR grade, was used as standard compound in the form of 1.0 g pellet each procured from Parr Co., USA (Make: National Institute of Standard and Technology, Washington, DC), having heat of combustion of 26.454 MJ/kg. Cordite, basically a double base propellant, cut into approximately 0.1 g square piece, procured from ordnance factory, Arvankadu. Different propellant compositions used to determine calorific and calorimetric values were processed *in-situ* and used as such. Other Chemicals like potassium hydroxide, potassium hydrogen phthalate and methyl orange (indicator), AR grade of Merck India were used without any further purification. Nichrome wire, used for ignition, having specific heat of 2.3 cal/cm was supplied along with the instrument by Parr Co. USA. The gases used in the present study were ultra high pure (UHP) oxygen, ultra high pure (UHP) nitrogen, ultra high pure (UHP) argon and industrial nitrogen, procured from M/s Sanghi Gases, Pune. All the UHP gases were 99.999 % pure with O_2 and moisture below 1 ppm and total hydrocarbon (THC) below 0.5 ppm. The industrial N_2 was of 99.6 % pure with 0. 4 % O_2 and traces of THC/moisture.

2.2 Instruments Employed

Calorific and calorimetric values were determined by Parr isoperibol bomb calorimeter, Model No. 6200 equipped with Parr water handling system Model No. 6510 supplied by M/s Parr Instruments, USA. The pH of bomb washings was determined by Mettler autotitrator, Model No. DL-50 using DG-111 electrode. Distilled water used for the preparation of solutions, washing of bomb and water handling system was obtained from M/s Millipore water purification unit, Model No.Elix-3, USA.

2.3 Procedure

2.3.1 Determination of Water Equivalent

1.0 g of standard benzoic acid pellet was accurately weighed and taken into the crucible. The crucible was placed in the bomb holder attached with the lid. After this, 10 cm long nichrome ignition wire was connected between the two electrodes touching the sample. The lid was tightly fitted with the S.S. bomb of 340 ml capacity and pressurized with oxygen at 30 atmospheric pressure. After pressurizing the whole set-up, it was kept in the bucket containing exactly 2 l of distilled water. The temperature of water in bucket was maintained in such a manner that it was 3 °C to 5 °C lower (i.e., 25 °C − 27 °C) than the jacket temperature (30 °C). Calorimeter lid was then carefully closed and sample was automatically fired. The total time taken for each experiment of the sample was 30 min with an accuracy of 0.0001 °C temperature. The water equivalent was obtained by burning benzoic acid in several experiments (at least 10). The exact handling of the instrument was conducted according to manufacturer's manual and the procedure described elsewhere[11]. The water equivalent of the calorimeter was determined by the following equation

$$W = \frac{H \times m + e_1 + e_2 + e_3}{T} \quad (1)$$

where,

W = Water equivalent of the calorimeter, cal/°C
H = Heat of combustion of the standard benzoic acid sample, cal/g (6318 cal/g)
m = Mass of standard benzoic acid sample, g
T = Temperature rise, °C
e_1 = Correction for heat of formation for nitric acid, cal
e_2 = Correction for sulfur present in the sample taken as 0
e_3 = Correction for heating wire (Nichrome wire–2.3 cal/cm)

2.3.2 Determination of other Correction Factors Correction for Heat of Formation of Nitric Acid or Acid Correction (e1)

After complete ignition, the bomb was washed with distilled water and the bomb washings were titrated against 0.0709 (N) potassium hydroxide solution already standardized with standard potassium hydrogen phthalate solution in the presence of methyl orange as an indicator. The titre values (ml) are the value of acid correction in the Eqn. (1).

Correction for heating wire or fuse correction (e_3)

After complete combustion of the sample, bomb was taken out from the bucket and opened carefully. The un-ignited wire piece was carefully collected and length was measured in cm and deducted from initial length, i.e., 10 cm. Heat of ignition of nichrome wire was calculated as 2.3 cal/cm and the value obtained was used in the Eqn. (1) as fuse correction.

2.3.3 Determination of Calorific and Calorimetric Values of Cordite

The calorific and calorimetric values of cordite were determined by the same instrument. The working principle and procedure was same as determination of water equivalent of the bomb.

During the determination of calorific and calorimetric value, a piece of cordite (accurately weighed) was pricked as pendant using the nichrome wire to ensure ignition of the propellant sample inside the crucible. The lid of the bomb was closed. Initially, the different gases like industrial N_2, UHP-N_2 and UHP-Ar were passed into the bomb sequentially by maintaining 30 atmospheric pressure, while measuring calorific value of the cordite, the bomb was pressurized with UHP-O_2 at 30 atmospheric pressure. The remaining procedures were same as per the determination of water equivalent. The cal-val of the cordite was determined by the following equation

$$h_1 = \frac{W \times T - e_1 - e_2}{m} \tag{2}$$

where,
h_1 = Cal-val of the cordite, cal/g
W = Water equivalent of the bomb used, cal/°C
T = Temperature rise observed,°C
e_1 = Heat produced by heating wire or fuse correction, cal
e_2 = Heat produced due to the formation of sulfuric acid from the reaction of sulfur present in the sample, water and oxygen, usually 0
m = Mass of the sample taken (sample+piece used as pendant), g

2.3.4 Determination of Calorific and Calorimetric Values of Different Propellant Samples

In case of composite propellant samples, due to delay in ignition time and need of high ignition temperature, a double base propellant, i.e., cordite was used for ignition purpose. Cordite is not required for ignition in the case of double base propellant. The cal-val for different propellant samples were determined by the following equation:

$$H_c = \frac{W \times T - e_1 - e_2 - h_1 \times m_1}{m} \tag{3}$$

where,
H_c = Cal-val of the propellant piece, cal/g
W = Water equivalent of the bomb used, cal/°C
T = Temperature rise observed,°C
e_1 = Heat produced by heating wire or fuse correction, cal
e_2 = Heat produced due to the formation of sulfuric acid from the reaction of sulfur present in the sample, water and oxygen, usually 0
h_1 = Heat produced by unit mass of the cordite, cal/g
m_1 = Mass of the cordite, g
m = Mass of the sample taken, g

2.3.5 Determination of pH Value of the Bomb Washings

After each run the bomb was washed with approximately 60 ml of distilled water. Washing was taken in a titrating beaker and pH was determined using Mettler Toledo Auto titrator DL-50.

3. RESULTS AND DISCUSSION

During the determination of cal-val of the propellant samples having burning rates in the range of 5 mm/s − 30 mm/s at different pressures, initially the bomb calorimeter was standardized as per standard methods for water equivalent, followed by determination of calorific/calorimetric values of cordite along with certain basic correction factors such as acid, ignition wire and pH. The standard propellant samples, used for this study, based on HTPB/AP/Al, are presented in Table 1. The steps involved in this study are as follows.

Table 1. Burning rate range of composite solid propellants used for cal-val determination

Serial No.	Types of propellants (HTPB/AP/Al)	Burning rate (mm/s @ 70 ksc)
I	Composite propellant	5−7
II	Composite propellant	25−30
III	Composite propellant	19−20
IV	Composite propellant	13−14
V	Composite propellant	6−8
VI	Composite propellant	18−23
VII	Composite propellant	11−12
VIII	Cordite	-

3.1 Determination of Water Equivalent

Initially, the water equivalent of bomb calorimeter was determined by taking benzoic acid (1 g pellet) and 10 cm long nichrome wire having specific heat of 2.3 cal/cm in the presence of oxygen at 30 atmospheric pressure for about 10 experiments. The average value of 10 experiments is presented in Table 2.

It is clear from the Table 2 that the value of water equivalent is very close to standard value of 2370 ± 30 cal/˚C after the acid correction and ignition wire or fuse wire correction. The fuse wire correction depends upon the un-utilized length of wire multiplied by the heat capacity, i.e., 2.3 cal/cm. Also, acid correction during the determination of water equivalent was found to be 2.63 cal to 3.28 cal. After putting these values in the Eqn. (1), the water equivalent of bomb calorimeter was increased by 2 cal/˚C. Therefore, this value was kept constant for further standardizations and is taken as standard for acid corrections. Also, pH of the bomb washing was determined by following standard method. The value of pH during the determination of water equivalent was observed in the range of 2.2−2.4 (Table 2) clearly confirms that during combustion of benzoic acid, CO_2 reacts with H_2O and forms weak carbonic acid which is responsible for the acidity of bomb washings.

3.2 Effect of Different Environments on Cal-Val of Cordite

After standardization of water equivalent of bomb calorimeter, the cal-val of cordite was determined in different environments such as air, industrial nitrogen, UHP-O_2, UHP-N_2, UHP-Ar at 30 atmospheric pressure except air and results obtained are presented in Table 3.

It is clear from the Table 3 that environment of oxygen gives maximum value, i.e., 2208 cal/g which is utmost calorific value of the cordite as complete combustion of H, C, N, O, took place. However, in the case of air, the value of cal-val is found to be 1394 cal/g where as in industrial nitrogen it is

Table2. Data on pH, fuse and acid corrections during determination of water equivalent

No. of Runs	Weight taken (g)	Fuse correction (cal)	pH	Temp rise (°C)	EE values (cal/°C)	KOH consumed (ml)	Acid correction (cal)	Corrected EE (cal/°C)
I	1.012	11	2.24	2.7054	2371	3.30	3.28	2373
II	0.996	17	2.22	2.6603	2373	3.20	3.18	2375
III	0.999	19	2.24	2.6669	2374	2.45	2.43	2376
IV	1.011	13	2.32	2.6978	2375	2.65	2.63	2377
V	1.013	12	2.25	2.6900	2379	3.30	3.28	2382
VI	1.010	17	2.23	2.6778	2383	3.18	3.00	2386
VII	1.000	16	2.20	2.6557	2379	2.85	2.83	2381
VIII	0.999	15	2.25	2.6609	2372	2.65	2.65	2374
IX	1.018	16	2.32	2.7138	2370	2.50	2.50	2372
X	1.012	15	2.20	2.6961	2372	2.54	2.54	2374

Table 3. Data on calorific/calorimetric and pH values of cordite in different environments

Environment employed	Air (r.t.p)	UHP-O_2 (30 atm)	Ind-N_2 (30 atm)	UHP-N_2 (30 atm)	UHP-Ar (30 atm)
Calorific/calorimetric values	1394	2208	1330	1198	1204
pH	7.655	1.922	7.535	7.292	7.775

1330 cal/g. The cal-val in UHP-N_2 and UHP-Ar are very close to each other and meets the standard value of cordite. The data further confirms that air contains 20.9 % oxygen while industrial nitrogen contains traces of oxygen which helps in oxidation of cordite. The presence of oxygen in air and industrial nitrogen always produce higher cal-val. Therefore, to have authentic cal-val, UHP-N_2 and UHP-Ar environment were chosen to study further as these gases do not contain even traces of oxygen.

3.3 Effect of Different Environments on Cal-Val of Propellant Samples

Based on the cal-val of cordite samples in different environments, the propellant samples having burning rate in the range of 5–30 mm/s at different pressures were also studied using bomb calorimeter in the mentioned environments and data obtained are presented in Table 4.

It is seen from the Table 4 that same trend in cal-val was observed as in case of cordite where oxygen always gives maximum value, i.e., calorific value not calorimetric value. However, in case of air and industrial nitrogen, the cal-val is on higher side in comparison to UHP-N_2 and UHP-Ar. The data further reveal that to have authentic cal-val, it should always be determined in absence of air. Also, the environment used for the same should not have even traces of oxygen.

3.4 Effect of Environment Pressure on Cal-Val of Propellant Samples

The effect of environment pressure in bomb calorimeter was studied using propellant samples in the range of 5–30 atm using industrial nitrogen, UHP-N_2 and UHP-Ar and results obtained are presented in Table 5.

Table 4. Data on cal-val of different composite propellants in different environments at 30 atmospheric pressure

Serial No.	Calorific/ Calorimetric values (cal/g)				
	Air	UHP-O_2	Ind-N_2	UHP-N_2	UHP-Ar
I	1832	3405	1535	1512	1511
II	1433	3181	1129	1081	1085
III	1815	3719	1463	1470	1474
IV	1874	3525	1560	1510	1498
V	1630	2543	1364	1314	1311
VI	1749	3364	1513	1479	1467
VII	2045	3091	1781	1733	1731

Table 5. Effect of pressure on calorimetric values of composite propellant (sample-I)

Pressure	5-atm	10-atm	15-atm	20-atm	30-atm
Industrial-N_2	1515	1515	1520	1528	1535
UHP-N_2	1512	1510	1510	1510	1512
UHP-Ar	1510	1510	1510	1512	1511

It is evident from the Table 5 that at 5 atm and 10 atm pressure of industrial N_2 the value of cal-val remains constant, while, beyond 10 atm pressure enhancement in cal-val was observed. The enhancement in cal-val clearly indicates that as pressure increases the amount of traces of oxygen also increases accordingly, which is responsible for the enhancement in cal-val. However, no change in cal-val was observed in case of UHP-N_2 and UHP-Ar from 5 atm to 30 atm pressure. Further, beyond 30 atmospheric pressure, the instrument cannot be operated due to safety related hazards.

The prime interest to study the cal-val using different environment was to have authentic and reproducible value for propellants, explosives and pyrotechnic compositions which do not take oxygen from the atmosphere during combustion, detonation and burning. Also, the cal-val reported in air and industrial nitrogen are always on higher side and not correct, therefore, a successful attempt has been carried out to choose a correct environment for reporting the true cal-val of any composition and based on the number of experiments the use of suitable environment was established successfully and implemented too.

4. CONCLUSION

A successful attempt has been carried out to rule out inaccuracy during the determination of cal-val of propellants, explosives and pyrotechnic compositions in air, industrial nitrogen, UHP-O_2, UHP-N_2, and UHP-Ar. The data indicate that air and industrial nitrogen always give higher cal-val while UHP-N_2 and UHP-Ar produce correct and authentic cal-val. The use of oxygen always produces calorific value due to complete combustion of the sample. Based on the findings, it is revealed that for authentic and correct cal-val data, only UHP-N_2/UHP-Ar environment should be used as this provide reproducible results. Also, for cost effectiveness, UHP-N_2 is preferred over UHP-Ar, as latter is costly to former.

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CONTRIBUTORS

Mrs Lalita S. Jawale received her M. Sc. in Organic Chemistry from University of Pune in 1995. She is actively involved in determination of calorific and calorimetric values of propellants and explosives samples as well as burning rate of composite propellants. She has published two research papers in international journal.

Mrs Chandrani Dey obtained her M. Sc. in Chemistry from I.I.T. Kanpur in 2006. She joined High Energy Materials research Laboratory in the year of 2009 as Scientist 'B'. Her area of specialization is analysis of raw materials of composite propellant ingredients and finished products.

Dr Mehilal received his PhD in Chemistry from Allahabad University in 1985. Presently working as a Joint Director at HEMRL, Pune. He made significant contributions in the field of plastic- bonded explosives. Presently he is working in the field of solid rocket propellants. He has published more than 100 research papers in national/international journals and filed 8 patents.

Dr Manoj Gupta obtained his MSc (Chemistry) from Garhwal University, in 1982 and PhD (Chemistry) from university of Pune, in 2001. Presently he is working as Associate Director at High Energy Materials Research Laboratory. His area of specialization is development of composite propellant for different tactical/strategical missiles. He has received many awards such as, *DRDO Scientist of the Year Award* in 2010. He is the fellow of many societies and has published 9 papers and 14 patents to his credit.

Mr B. Bhattacharya obtained his MTech (Chemical Engg.) from Banaras Hindu University, Varanasi. Presently working as an Outstanding Scientist and Director, High Energy Materials Research Laboratory, Pune. His area of research includes: Processing of composite propellants.