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LLNL-TR-527491

Integrated Data Collection Analysis (IDCA) Program--IDCA Quarterly Program Review, September 14 and 15, 2010

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February 7, 2012

Disclaimer

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

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Keywords: Small-scale safety testing, proficiency test, round-robin test, safety testing protocols, Program Review.

IDCA Quarterly Program Review, September 14 and 15, 2010

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Executive Summary

The IDCA conducted a program review at Los Alamos National Laboratory, September 14 and 15, 2010. The review was divided into three parts: 1) an update on the current status of the program, 2) an information exchange and discussion on technical details for current issues and future planning, and 3) a tour of the SSST testing facilities at LANL.

The meeting started with an update from DHS by Laura Parker and a restating of some of the objectives of the Proficiency Test of which the IDCA is currently engaged. This update was followed by a discussion of some high level programmatic issues particularly about ways of communicating the overall goals of the IDCA to non-technical representatives. The final topic focused on the difficulty of releasing information, including the DHS approval process, ITAR, and open publication.

Next JGR presented a technical summary of accomplishments, schedule, milestones, and future directions. These key points made were: 1) about 1/3 of the materials have been tested, 2) some participants are behind others causing a lag in report writing, 3) method reports have been assigned to various participants to speed up the process of reporting, 4) the SSST Compendium needs reformatting and restructuring, and 5) the Compendium needs a web site to house with access control.

After the technical update, some of the Proficiency Test results were shown comparing data from the various laboratories. These results included comparisons of the RDX standard, KC/sugar mixtures (-100 mesh and as received), KC/dodecane, KP/Al, and KP/C. Impact, friction, ESD, and DSC results were the focus. All the participants were involved in these discussions.

Many of the results showed the participants were obtaining similar data sets when examining the same material. For example, differences in the DSC of RDX among the participants are almost imperceptible. However, the results that were different among the participants generated most of the discussions. These types of results generally generate a more scientifically based discussion as opposed to the phenomenological based discussion that is normal realized for SSST testing. These are examples of very interesting results: 1) KC dodecane drop hammer results different among participants, 2) KC/sugar and KC/dodecane are more sensitive at LANL than LLNL, 3) Warning: KP/Al is really spark sensitive, and 4) DSC of KC/dodecane shows pan differences. Many more comparisons are found in the presentations. Also in the information exchange, several issues were discussed including changing the testing schedule for some materials for efficiency purposes.

In the afternoon session, the focus of the meeting changed to exploring new ideas for SSST testing. Of particular interest is the thermal instability of some of the materials being studied in the Proficiency Test. Certain HP formulations have shown run away thermal excursions just upon sitting at room temperature, leading to unsafe handling conditions. DSC is the standard for thermal analysis in SSST testing, but the current method does not adequately describe some of the thermal behavior of these types of HMEs. All participants were asked to discuss additional thermal analysis methods that their respec-

tive laboratories use. ARC, APTAC, VaC Stab, CRT, TGA, modified DSC, ODTX, STBMS and others were discussed and explained. The overall idea is to use these thermal techniques to develop a quick screening method for thermal stability that could be adapted into a modified DSC method.

Other topics were also covered during this discussion period. 1) The Bruceton vs Neyer methods of data analysis were discussed because various participants have been considering purchasing the Neyer software. Mary and Geoff from LANL, arranged to have Daniel Preston to give a demonstration of the Neyer's software on some drop hammer experimental data. 2) A question that has been raised over the last six months if statistics can be used in the Proficiency Test. Geoff prepared a short briefing explaining the use of statistical methods and which ones could apply to the Proficiency Test. 3) Drying ammonium nitrate for the Proficiency Test has proven to be rather complicated based on all the structural forms. The activated form of AN should be tested, but it is rather tricky to make. Mary showed some TGA data to explain the behavior and proposed a potential drying method. 4) The Proficiency Test has highlighted issues in SSST testing that are no fully understood and warrant further investigation if funding is available. All present were asked to rank in order of priority future proposed work. Eleven research topics have been identified, with 2 already in progress and 1 TBD. The top ranked proposed work is involvement of the IDCA in the International Round Robin sponsored by TSWG. This involvement would include measuring SSST data on RDX and PLX, two materials designated as the standards for the Round Robin.

The final effort of the day was to consider a logo for IDCA. JGR presented several that came from web searches. Dan volunteered to add an artistic touch to whatever design was chosen.

The tour was conducted in groups on the second day. Drop hammer, friction, electrostatic discharge, differential scanning calorimetry, thermogravimetric analysis, vacuum stability, adiabatic reaction calorimetry were among the systems examined and discussed.

This report includes summary notes, presentations, and explanatory information.

Abbreviations

AFRL-Tyndall—Air Force Research Laboratory, Tyndall
Al—Aluminum
APTAC—Automatic Pressure Tracking Adiabatic Calorimeter
ARA—Applied Research Associates
ARC—Adiabatic Reaction Calorimetry
CRT—Chemical Reactivity Test
DHS—Department of Homeland Security
DSC—Differential Scanning Calorimetry
ESD—Electro Static Discharge
HP—Hydrogen Peroxide
IDCA—Integrated Data Collection Analysis
ITAR—International Traffic in Arms Regulations
KC—Potassium Chlorate
KP—Potassium Perchlorate
LANL—Los Alamos National Laboratory
LLNL—Lawrence Livermore National Laboratory
NSWC-IHD—Navel Surface Warfare Center, Indian Head Division
ODTX—One Dimensional Time to Explosion
PLX—Picatinny Liquid Explosive
RDX—1,3,5-Trinitroperhydro-1,3,5-triazine
SNL—Sandia National Laboratory
SSST—Small Scale Safety and Thermal
STMBMS—Simultaneous Thermogravimetric Modulated Beam Mass Spectrometer
TGA—Thermogravimetric Analysis
Vac Stab—Vacuum Stability thermal test

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Meeting Notes

IDCA Program Review LANL 9.14-15.10

Brief comments by Laura at the start of the meeting.

Objective of the Proficiency Test is to answer all theses questions below
1. Why are there differences in the test?
2. Why are there differences in the lab and community?
3. What are the differences and significance in experimental results within a lab and among the labs?
4. Why are there differences in these tests and are they significant for how we handle explosives?
5. What is the error there is within tests from a single lab and within the community.

Communicating the IDCA mission and importance
This is the second year of the project and we need to find a good way of explaining the activities on a non-technical basis. We need a way of communicating the program to outsiders; maybe a one-page diagram.

Release of information from IDCA
There are significant time delays for getting permission to release information through DHS. ITAR seems to be the current issue. ITAR export control covers military explosives. Quinton doesn't think our work will get rolled into ITAR, but that has to be clarified. Makes it hard to get external communications out. Formulation is the sensitive point. This is regulated by the Departments of State and of Commerce. DHS needs one-month notice for presentations.

IDCA should have pre-reviewed documents in place as publically released documents. This will allow us to respond to potentially useful meetings within a reasonable time frame. Geoff would have given a presentation at a meeting on IDCA results, but there was not enough time to get the abstract or presentation approved. JGR did not apply to the ISADE meeting in November because of ITAR issues not being resolved.

Compendium information release is also affected by this. Eventually the proficiency test will go towards sharing the SSST data with the international community. Data will go into a compendium. We will have to work on how data is released, presented and also populate the compendium. How to disseminate the data to the community? Web based, etc. Export control is an issue as well as is money to pay for database programming. Release of IDCA data—ITAR issues; access control data; where will the data go—IDD Server, HE Reference Guide, TSWG HME Web Site.

JGR gave an update on the IDCA

Reviewed current status of the project followed by an introduction of the group to the Compendium and what is needed for formatting and expanding the data in the Compendium.

Specific issues were also addressed, including the division of labor on report writing.

KC/dodecane drop hammer results different among labs.

Lab	T, °C	RH, %[2]	DH_{50}, cm^3	σ, log unit
LLNL	23.9	23	34.0 (31.0-37.3)	0.041
LLNL	23.9	22	45.4 (43.3-47.6)	0.020
LLNL	22.2	16	41.2 (33.1-51.2)	0.095
LANL	24.0	<10	12.6	0.048
LANL	23.3	<10	9.0	0.068
LANL	24.0	<10	12.1	0.040

LLNL used 120 grit sandpaper for impact data, LANL and IHD used 180 grit. At the time, we had not yet decided on all participants using the same size sandpaper. LLNL will redo this with 180 grit sandpaper. Also dodecane evaporates, so some standardization of procedure must be determined. KC/dodecane preparation to test time should be a maximum of 2 hours.

KC/sugar and KC/dodecane are more sensitive at LANL than LLNL

Lab	T, °C	RH, %	TIL, kg	TIL, kg	F_{50}, kg	σ, log unit
LLNL	22.2	18	0/10 @ 11.2	1/10 @ 12.0	13.2	0.050
LLNL	22.2	18	0/10 @ 8.0	1/10 @ 8.4	12.5	0.106
LLNL	22.2	18	0/10 @ 7.2	1/10 @ 8.0	11.2	0.082
PETN	na	na	na	1/10 @ 6.4	na	na
LANL	22.1, 21.8	15.1, 13.8	Too low	2/10 @ 2.4	4.7	0.180
LANL	22.7, 22.7	15.3, 15.3	Too low	3/10 @ 2.4	4.9	0.170
LANL	22.2, 22.2	12.0, 12.0	Too low	2/10 @ 2.4	4.3	0.070
PETN	20.0	12.0	na	na	9.2	1.6

Also, dodecane evaporates KC/sugar and KC/dodecane both more sensitive at LANL than at LLNL on friction. Could be due to differences in the plates and in the pins used. LeRoy will be doing the SEM and surface profilometry on the on 3 pins and 3 plates from each participant. Each participant needs to send samples to LeRoy.

LANL has consistent Bruceton vs Neyer. LLNL used 120 grit. New 180 grit is thinner paper. Note time between formulation and testing. LANL, IH and LLNLmixed and tested same day. Hard to get consistently shaped pile of powder when damp. IH uses conical piles, LLNL and LANL uses cylindrical piles. Peter will test again with 180 grit paper. Leroy will run the SEM the paper and other items for other tests. There were some comments about reaction with sandpaper, but nothing definitive.

For a Go/No Go, both LANL and LLNL use audible signals. Peter's microphone measures peak as opposed to RMS. Could be mixture of frequency dependent output of sample and freq dependent response of different microphones. LANL has a new microphone set up. It uses a different frequency than their old microphones. It also measures RMS as opposed to peak. RMS is considered more sensitive. The microphone sensors used by LANL are about 3 feet away from the test table.

Friction from LLNL is much different than LANL or IH. Pins and plates are one possibility. Running with lights off is another. LLNL also has instrument in box (?). Leroy can check surface finish of plates with profilometer. Everyone's plate striations are perpendicular to the sliding.

Report assimilation and writing assignments. Report progress - testing reports and methods reports. Have spreadsheets from a long time ago.

For Methods report, need a list to show how we started and where we ended up. Need to be able to tell what differences lead to different results. Mary needs each lab to go back and note what they have modified. She can send out the most recent version and people can modify that. Need to capture multiple changes as well. Mary and Kirstin are working on methods report

For the Drying report, Tim is responsible and Mary is helping. SC/sugar showed no moisture in LANL. We can humidify it and check for dryness and sensitivity. Old literature (John) says in 60's there was detonation testing at various forms of natural hydration.

Mary's talk—our AN is chemically pure. We can do several cycles to put in phase III and then check with DSC and then formulate Want to stay below 90°C. Need TGA data at 90°C to see sublimation rate. Maybe also rate after dosing with water. See TGA results in presentations. AN drying method is to be finalized by end of October 2010.

LLNL can proceed with HP/fuel mixtures before AN drying method is finalized. Cumin and flour are already dried at 60°C by Tyndall.

Use Bullseye as-received, i.e. no drying. It will be done before the AN. Move up to top of 2nd series. JGR must make changes in GANTT chart and deliverable schedule to reflect this.

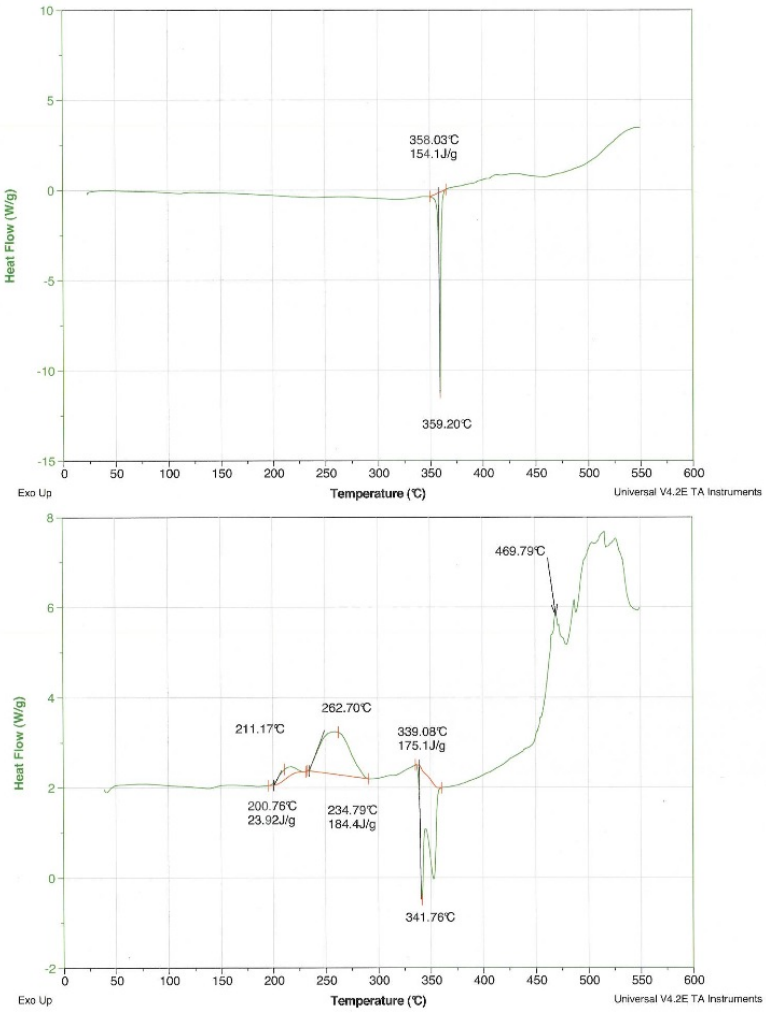
KC/Dodecane ESD data: Want to do Probit analysis with threshold data. Need data sheet that shows all of the runs including all No-Goes. Can use that to see if there is statistically significant difference among results.

Warning: KP/Al is really spark sensitive.

Lab	T, °C	RH, %[1]	TIL, Joule[2]	TIL, Joule[3]
LLNL	23.3	18	nd[5]	1/10 @ 0.49[5]
LLNL	22.2	23	0/10 @ 0.25[5]	2/3 @ 0.64[5]
LLNL	22.2	23	0/10 @ 0.25[5]	2/6 @ 0.64[5]
LANL	22.6	23.5	< 0.0625	< 0.0625
LANL	21.3	26.0	< 0.0625	< 0.0625
LANL	21.6	28.7	< 0.0625	< 0.0625

Even LLNL, with the 500 ohm resistor shows sensitivity. Watch out for this stuff.

DSC of KC/Dodecane shows pan differences



DSC of KC/dodecane show big differences between the LLNL hermetically sealed pans and the pin hole pan used as our standard method. Are the pressure pans stainless steel? LANL can run sealed pan DSC to see if can reproduce LLNL's data. LLNL might try Setaram DSC.

International round robin
From HME meeting. RDX and PLX (sensitized nitromethane) are the two materials to be run. This year collecting testing method information from all participants. (Canada has 3 labs that do it all differently.)

Prioritization of future topics of interest to the IDCA

1. Participation in the International Round Robin SSST testing
2. Developing a fast screening method by DSC for thermal analysis (relate to ARC, ODTX, APTAC, isothermal DSC)
3. Impact of aging of solid-solid, liquid-liquid and solid liquid mixtures on testing sensitivity.
4. Expansion of camera approach to SSST testing
5. Effects of impure source materials on testing

6. Effects of porosity of solid-solid and solid-liquid mixtures on sensitivity
7. Optimizing sandpaper for impact testing (design of experiments)
8. Developing methods so ABL vs. BAM data from different methods can be compared

In progress but could need support

1. Developing methods so Bruceton vs. Neyer data reduction methods can be compared
2. Recalibrating friction testing of solid mixtures

TBD

1. Additional HME threats that challenge SSST Testing

ACTION ITEMS

- Method Comparison Report—Mary and Kirstin
    - Initial method
    - Modification method
    - Presentation Format
- Revise Gantt Chart—JGR
- DSC work AN (cycling)—Mary and Geoff
- KC/Dodecane Mixture retest drop hammer—Peter
- KC/sugarb mixture retest at LLNL with LANL's pins and plates—Peter
- LLNL will send pins and plates to LeRoy—Peter
- SEM and profilometry of pins and plates—LeRoy
- Request additional support in SSST lab (3 threats behind)—Kirstin
- Reproduce KC/Dodecane in sealed pan—Mary and Geoff
- Compile all the thermal techniques and evaluate utility to HME program and include in future characterization—JGR
- Provide comments to team about calculations when using the spreadsheet—Dan Remmers
- Drying Techniques—Tim
- Statistics—Geoff, Peter and Tim
- Standardization of KC/dodecane formulation—not assigned yet

IDCA Quarterly Meeting Agenda

Los Alamos National Laboratory 9.14.10 to 9.15.10

Monday 9.13.10
Travel to LANL

Tuesday 9.14.10 Meeting commences

8:30 am Badge office for badging
9:00 am Welcome and Pastries
9:05 am LANL rules and regulations
9:10 am Overview from DHS
9:15 am IDCA progress to date overview
- Technical
- Financial

9:45 am DHS Comments on progress
10:00 am Break — All
10:15 am Specific report topics
- Testing reports progress and issues — JGR
- Methods report progress — Mary and Tim
- Drying Techniques report progress — Mary and Tim
- Statistics—how to deal with them — Geoff, Peter and Tim
- Thermal Analyses DSC — Mary

11:15 am Special issues at specific laboratories
11:30 am lunch LANL café.
1:00 pm
- The international round Robin — JGR
- Thermal analysis
  - Thermal analysis ARC — Kirstin
  - DTA bulk ignition test — Kirstin
  - Thermal Analysis ODTX — Peter
  - Thermal analysis STEX — Peter
  - Thermal Stability VacStab — Mary
  - Thermal analysis CRT — Peter
  - Thermal analysis DSC — Mary
  - STBMS — LeRoy

3:00 pm
- Proposals topics for next year — All
- Participation in the International Round Robin SSST testing
- Developing methods so data from different methods can be compared
  - ABL vs. BAM friction analysis
  - Bruceton vs. Neyer data reduction methods
- Modification of SSST testing for HMEs
  - Optimum grit size on sandpaper for impact testing
  - Recalibrating friction testing of solid mixtures
  - Effects of porosity of solid-solid and solid-liquid mixtures on sensitivity
  - Developing a fast screening method by DSC for thermal analysis (relate to ARC, ODTX, APTAC, isothermal DSC)

–Impact of aging of solid-solid, liquid-liquid and solid liquid mixtures on testing sensitivity.

Effects of impure source materials on testing

Decomposition mechanisms for impact and friction through molecular characterization

Additional HME threats that challenge SSST Testing

5:00 pm Wrap up and directions to dinner

Evening of 9.14.10 party at Gabriel Restaurant

Wednesday 9.15.10

8:00 am Welcome and Coffee
8:15 Any further discussion of IDCA topics (if needed)
8:30 Tour of SSST testing operations at LANL
11:30 am Lunch Café LANL?
1:00 pm Depart

Comparison of Bruceton and Neyer Methods

A material's sensitivity is best reported in terms of the probability of reaction as a function of input stimulus level. A detailed mapping of this reaction distribution requires many tests at many different stimulus levels, which can translate to large amounts of time, money, and sample material. More efficient methods to probe the distribution can be applied if it is known to be Gaussian or if the stimulus can be transformed so that the distribution becomes approximately Gaussian (e.g. using the logarithm of the stimulus). The mean (50% cumulative reaction probability) and the standard deviation are then the reported parameters describing the material. For small scale safety testing purposes we often have limited quantities of many different materials and so it is necessary to use efficient methods.

Two common methods used to probe the reaction distribution are the Bruceton method [1] and the Neyer method [2]. The Bruceton method (or Up-Down testing) has been used for over 60 years and is common in many laboratories today. The Neyer method (or D-optimal method) has been growing in popularity since its development in 1994 due to certain advantages described below. In the IDCA program we are examining both of these methods.

The Bruceton method was developed before 1943 at the Explosives Research Laboratory in Bruceton, Pennsylvania [1]. In this method, the distribution is probed by initially choosing a stimulus level near the anticipated 50% reaction point and then adjusting the stimulus level for each test based on the previous outcome – if the material reacts (Go), the stimulus is decreased one step and if the material does not react (No-Go), the stimulus is increased by one step. The mean and standard deviation (μ and σ) are then calculated from the number of Go's and No-Go's at each level using approximation formulas that assume a Gaussian distribution [3]. The advantages of this method are that it concentrates testing near the mean and that it can be carried out without the use of a computer. One disadvantage is that the formulas for μ and σ assume that the step size between stimulus levels is $> \frac{1}{2}\,\sigma$ and $< 2\,\sigma$. This may not be true if the operator has no estimate of σ before testing. A second disadvantage is that the step size must be constant. This can be a problem if a transformation is necessary since not all instruments provide arbitrarily adjustable stimulus levels. Another potential disadvantage is that the method can require a relatively large number of tests. The initial paper suggested 40 or 50 although in practice the mean can be estimated using fewer. For the IDCA program, 25 tests are used.

The Neyer method was described in 1994 [2] and is based on an algorithm that uses maximum likelihood estimation (MLE) of μ and σ to adjust the stimulus levels during testing so that the estimates of both parameters are optimized simultaneously. The testing proceeds in a manner similar to the Bruceton approach with the outcome of a given test determining the chosen stimulus level for the next test. As opposed to the Bruceton approach, the step sizes may change depending on the likelihood function. A commercial software package, available from the algorithm developer [4], computes the necessary stimulus level based on the MLE. Ultimately the step size approaches values between 1 σ and 2 σ by construction. The advantages of this method are that μ and σ are optimized together to better characterize the distribution. The adjustable step size also allows the distribution to be probed using typically fewer tests than the Bruceton method. A disadvantage of the method is that it requires a computer to carry out the analysis needed to compute σ and adjust the step sizes between tests.

A comparison of RDX Impact sensitivity using each of these methods is shown in Figure 1 below [5]. The top panels show an actual test series for each method. The bottom panels show the probability and cumulative distribution functions derived from the μ and σ values reported for each method.

The test progressions in the top panels illustrate the properties of each test method described above. The Bruceton method concentrates testing around the mean while the Neyer method adjusts the applied stimulus levels to between 1 σ and 2 σ. Once the Bruceton method finds a pair of levels that toggle between Go and No-Go behavior, the tests remain fairly constant. The Neyer method tracks in on the mean and keeps the stimulus levels at the distance from the mean to maximize confidence in both parameters.

From the bottom two panels we see the effect of these approaches. The narrower distribution obtained by the Bruceton method reflects the choice of step size prior to testing. The broader distribution from the Neyer method is due to adjustment of the stimulus step size during testing. Since the Neyer method chooses levels to minimize uncertainty of both μ and σ, it presumably gives a more accurate representation of the probability distribution function. In addition, the Bruceton σ (0.019) is less than half of the step size (0.05), suggesting that the results may not provide a reliable distribution width in this case. For SSST comparison purposes, however, the μ values obtained using either method are not significantly different for this small number of tests. Using formulas in [1] and the Neyer software [4], the 95% confidence intervals for μ from each method are: 25.6 cm to 27.4 cm for Bruceton with 25 tests and 20.2 cm to 27.3 cm for Neyer with 15 tests.

References

[1] W.J. Dixon and A.M. Mood (1948), *J. Am. Stat. Assoc.,* 43, 109-126.

[2] B.T. Neyer (1994), *Technometrics*, 36, 48-60.

[3] The Bruceton method also assumes that testing begins in the vicinity of the mean. Often this is not true and the initial testing to home in on the mean can skew the statistics. In practice, a "Modified" Bructeon method is used in which initial tests are used to bracket the mean before starting to count Go's and No-Go's. This is used by LANL in this work.

[4] "SenTest" from Neyer Software, 7275 Willowood Dr., Cincinnati, OH. www.neyersoftare.com

[5] Tests carried out by Daniel Preston, DE-1 MS C920, Los Alamos National Laboratory, 2010.

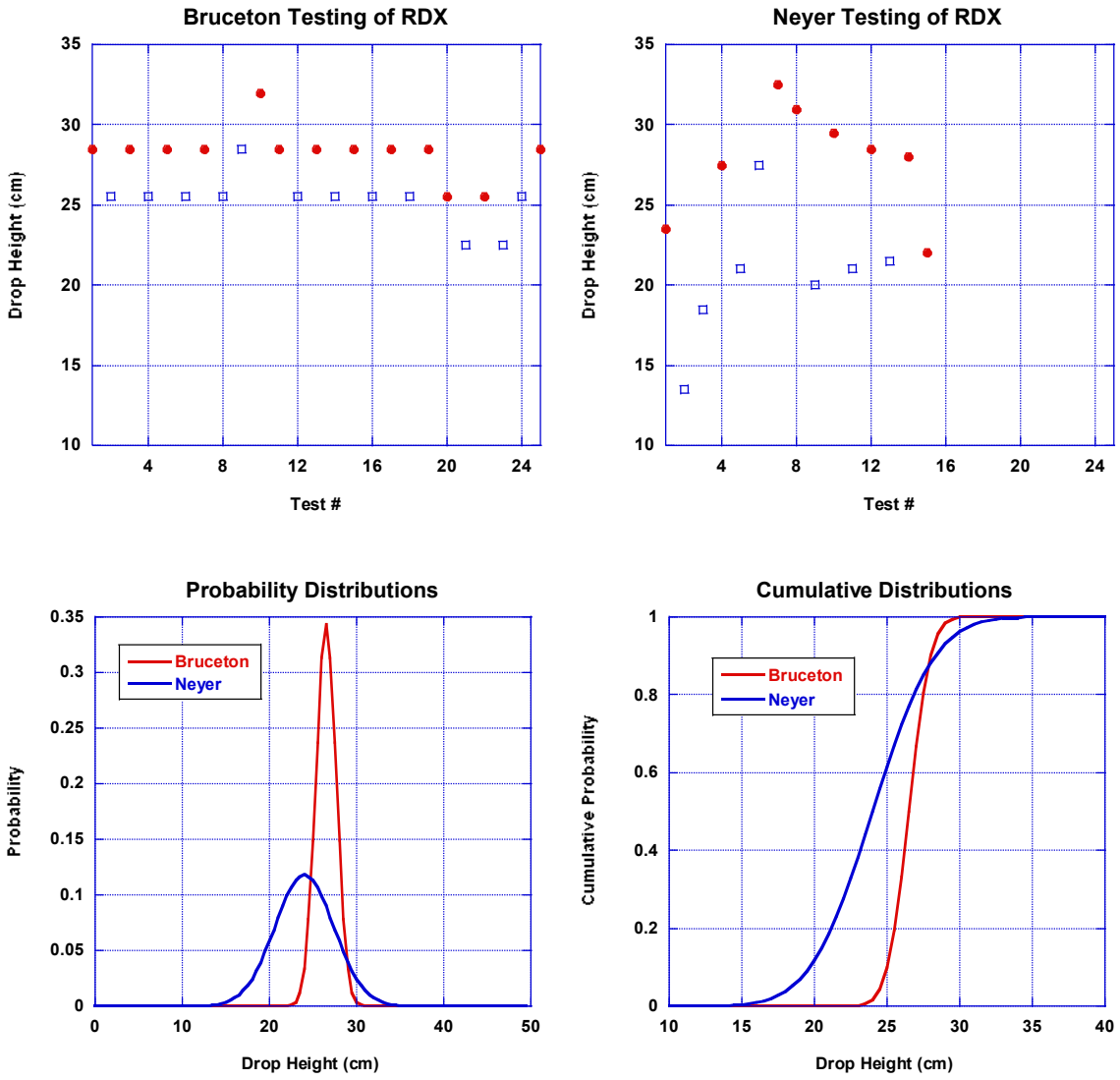


Figure 1. The top panels show RDX Impact sensitivity tests using the Bruceton method (left) and Neyer method (right). Red filled dots indicate a reaction while open blue squares indicate no reaction. The bottom left panel shows the probability distribution function for each method based on their reported μ and σ values. The bottom right panel shows the associated cumulative distribution function for each method.

Fast Thermal Analysis

Thoughts on thermal analysis—JGR 8.30.10. It is hoped that the presentations on various types of thermal analysis during our meeting will detail the information gained by these methods, but will also stimulate conversation on how to develop a new DSC method to accurately assess the "island of thermal stability" in a "sea of thermal instability."

Background. Recently, the FBI, NEXESS, DSTL and others have observed a thermal instability in selected formulations of home made explosives (HMEs). This instability was recently discussed at the International HME meeting where some dramatic examples were shown by the US and the UK highlighting the uncontrolled reactions and potential damage these reactions can cause. The community realizes that extreme caution must be taken when working with these formulations and significant thermal testing must be done to develop safe handling practices.

This type of extensive testing is not routinely done in developing safe handling practices. Standard SSST testing practices utilize DSC as a quick assessment of thermal stability. However, there is no quick equivalent for this extensive thermal testing required for these HME materials. The aim of this discussion is to lead toward developing a quick method. DSC would be the preferable analysis method because it is so wide spread in SSST testing laboratories.

Thermal issues. The thermal stability of these types of formulations is governed by two general chemical reactions occurring—catalytic decomposition of the oxidizer, and the stiochiometric oxidation of the fuel by the oxidizer.

The first reaction will most likely be due to trace contaminants. If there are such contaminants, they will most like be in the fuel as the oxidizer is purchased in very high purity, often with decomposition inhibitors. The second reaction commences as soon as the materials are mixed which is the oxidation of the fuel in the system, yielding liquid and gaseous products. At room temperature, this reaction is relatively slow, but at elevated temperature, can be very rapid. If the mixture is not in confinement that allows complete heat transfer, the reaction mixture will build up heat as the reaction proceeds. As the temperature increases, the rate increases, possibly leading to catastrophic events. Recent studies at room temperature for an example mixture to 4 days before reaction occur, but a similar system at an elevated temperature exhibited instability for the time period beginning within 1 hour. Control of the temperature is key to developing safe handling practices for these materials. However, it should be noted that this margin of safety has been developed from phenomenology and that no reaction mechanism(s) have bend determined. The behavior is unpredictable and cannot be extended to other mixtures.

The only path to develop account for this is to monitor thermal stability under the exact conditions under which the experimentation is to be done. This can be a vey time consuming process, potentially requiring handling large quantities. SSST testing was developed as a quick alternative to extensive full scale testing, so the challenge is how to do this for these thermally unstable reactive formulations.

Solution? An approach to solving this problem would be through understanding the reactions that cause the instability to at least the level where a quick measurement method can assess the stability, but preferably on the molecular level. For example, if a rate of a reaction that leads to catastrophic runaway could be determined, then activation energies of these reactions could be used to predict time a temperatures of safe and non-safe handling conditions.

The participants of the IDCA collectively have several thermal analysis methods as well as methods that determine whether mixtures are stable. All but DSC are not routine methods in most SSST Testing laboratories. The question is by using these methods, can the IDCA develop a quick screening method, preferably using DSC that can predict the stable window of opportunity.

DSC tells the thermal behavior when heating the material under a constant heating rate with perfect heat transfer. The mixtures in question exhibit a low temperature exothermic excursion, usually below 100°C at the 10°C/min heating rate. It also gives a rough enthalpy of this exothermic event. Assuming that the DSC has the capacity of multiple heating rates, it is conceivable that some activation energies can be derived for this exothermic event. What are those reactions leading to this and what do the activation energies refer to?

ODTX tells the thermal stability when a mixture in a closed vessel is exposed to a constant temperature. Multiple temperatures are chosen to find the temperature where stability is long term. The mixtures in question exhibit some of the lowest temperatures for instability. The technique can determine activation energies but a reactive model has to be developed. Does this model accurately reflect the reaction chemistry that causes thermal run away condition?

ARC tells of the thermal stability accelerating decomposition using a variable temperature profile. Can kinetics of reactions and activation energies be accurately determined?

STEX tells something?

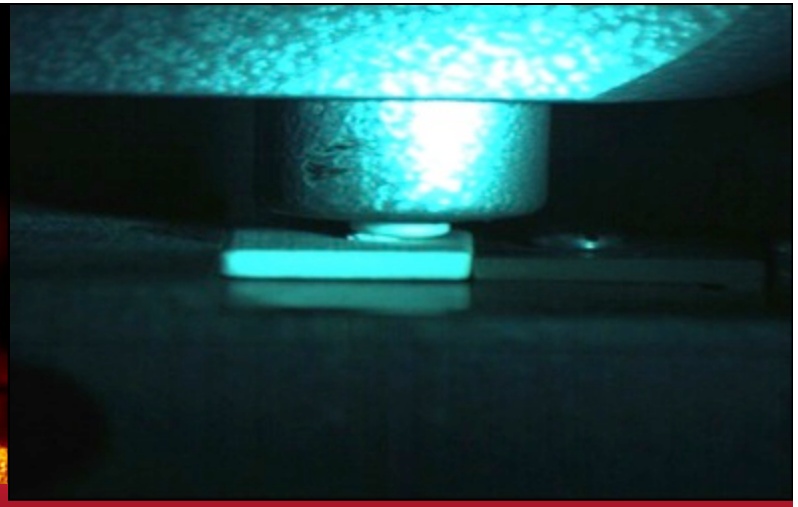
Other methods that may or may not apply—VacStab, CRT, TGA, Pyromat, others. VacStab and CRT give gas evolution at elevated temperatures. Can they be adapted to multiple temperatures and volatile liquids? TGA gives weight loss. Can it be adapted so that the weight loss is not through evaporation? Pyromat monitors light gas evolution as a function of temperature. Can it be adapted to handle liquids and can CO_2 be detected?

Homeland Security

IDCA Program Review

Quarterly Review Los Alamos National Laboratory

John G. Reynolds PhD, Lawrence Livermore National Laboratory (LLNL)
Mary M. Sandstrom, PhD, Los Alamos National Laboratory (LANL)
Timothy J. Shelley PhD, Tyndall Air Force Base (Tyndall)
Kirstin F. Warner PhD, Indian Head Division, Naval Surface Warfare Center (IHD, NSWC)
Leroy L. Whinnery PhD, Sandia National Laboratories (SNL)



August 14, 2010

LLNL-PRES-XXXXXX

The IDCA Gang

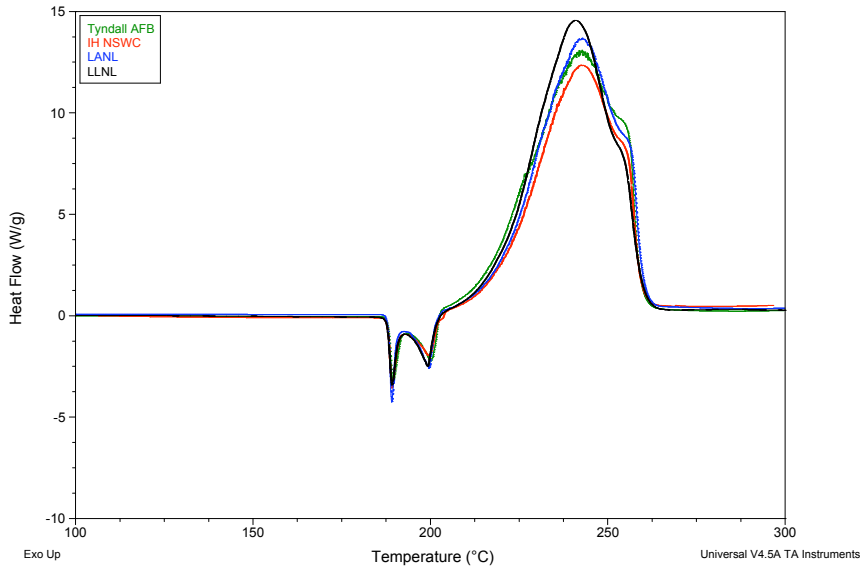
- Mary M. Sandstrom (LANL)
- Geoffrey W. Brown (LANL)
- Daniel Preston (LANL)
- Becky Olinger (LANL)
- Kirstin F. Warner (IHD, NSWC)
- Daniel N. Sorensen (IHD, NSWC)
- Daniel L. Remmers (IHD, NSWC)
- Jesse S. Moran (IHD, NSWC)
- Timothy J. Shelley (AFRL-Tyndall)
- Jose Reyes (AFRL-Tyndall)
- LeRoy L. Whinnery (SNL)
- Timothy J. Shepodd (SNL)
- Peter C. Hsu (LLNL)
- Richard E. Whipple (LLNL)
- Gary Hust (LLNL)
- Heidi Turner (LLNL)
- John G. Reynolds (LLNL)
- Doug Bauer (DHS)
- Laura Parker (DHS)
- Greg Struba (BAH)

Outline for 9.14.10

Topics:

- Status of Project
- Status of Proficiency Test
  - Test list
  - Report status
  - Deliverables
  - GANTT chart
- Really Exciting Results
  - RDX standard first round
  - Potassium chlorate/sugar
  - Potassium chlorate dodecane
  - Potassium perchlorate Al
- Summary for the future

DSC of RDX by IH, Tyndall, LANL and LLNL



IDCA Program

- Collect SSST test data of improvised explosives or HMEs
  - Small group of participants at first to set criteria for testing and methods to produce data acceptable for comparison
  - Broaden the group of participants to include the international community
  - Ultimately incorporate data obtained from sources outside the group of participants
- Determine if SSST test protocols need to be modified for handling HMEs vs. standard explosives
- Share and distribute SSST testing data that will help the community safely handle these materials
  - Proficiency test
  - Methodology reviews
  - HME SSST testing compendium

SSST Test Compendium

- Will be the definitive reference for small scale safety testing of home made explosives
- Data provided is from reputable sources that have been screened for
  - methodology
  - equipment
  - procedures
- Comparable data on standard reference explosives
- Detailed description of the testing equipment and procedures used for measuring the safety data
- Available for all who are legitimately working in HMEs (including International Partners)

Program Plan for Compendium

Three Parts

- Proficiency test—standardization of testing of materials and interpretation of results
- Collection of data—sources that are screened to assure high quality, properly obtained data
- Dissemination of information—web based, easily updated, access controlled

Homeland Security

Part 1—Proficiency test

- High fidelity testing data
  - Participants produce high quality data in a comparable format
  - Appropriate reference standards are measured
- Assured testing methods
  - Equipment is well documented
  - Measurement Methods are well documented
  - Analysis methods are well documented
- Understand SSST testing as applied to HMEs
  - Broad range of HMEs has been selected
  - Challenges in measurements are being compared
- Understand the significance of variability in measured values from each participant

Homeland Security

Part 2—Collection of Data for Compendium

- Current data sources—laboratories
  - LLNL, LANL, NSWC—IHD, AFRL—Tyndall
- Current data sources—programs
  - NEXESS, IDD, Proficiency test
- Potential future data sources
  - International Round Robin
  - URI, FBI(?), ARA(?)
  - Historical data
  - Other?

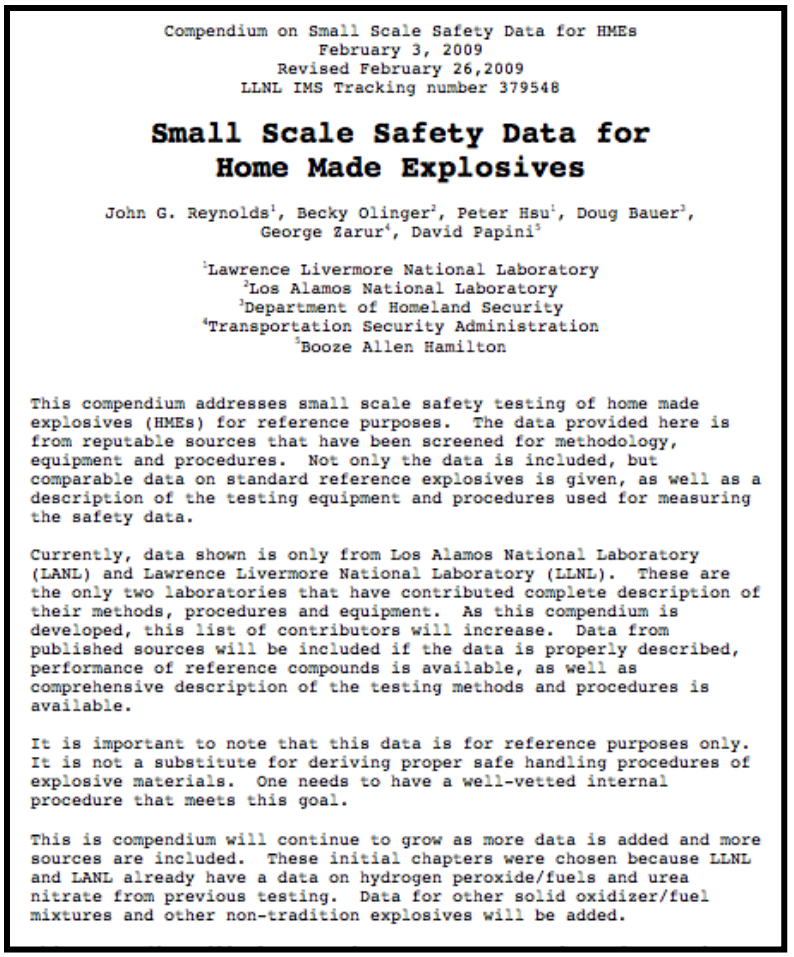
Homeland Security

Part 3—Access to the Compendium

- Web based access
  - IDD server
  - HE Reference Guide
  - TSWG HME Web site
  - DHS
- Access controlled
  - Foreign national access
  - No export controlled information
  - No ITAR information
- Uni- to multi-lateral agreements (?)
- Updates
  - Staff to enter in new data
  - Committee to review new data

Status of Compendium

- Beta copy delivered to Sponsor in 2009 as hard copy and e-file
- Format is being revised
- Data from LLNL and LANL only
- Includes impact, friction, ESD, DSC and limited other thermal tests
- Methods and procedures will be added
- Data on selected HP/fuels and UN/fuels
- Additional reference materials will be completed
- Additional data from LLNL, LANL, IH and Tyndall ready to be added



Compendium on Small Scale Safety Data for HMEs
February 3, 2009
Revised February 26,2009
LLNL IMS Tracking number 379548

Small Scale Safety Data for Home Made Explosives

John G. Reynolds[1], Becky Olinger[2], Peter Hsu[1], Doug Bauer[3], George Zarur[4], David Papini[5]

[1]Lawrence Livermore National Laboratory
[2]Los Alamos National Laboratory
[3]Department of Homeland Security
[4]Transportation Security Administration
[5]Booze Allen Hamilton

This compendium addresses small scale safety testing of home made explosives (HMEs) for reference purposes. The data provided here is from reputable sources that have been screened for methodology, equipment and procedures. Not only the data is included, but comparable data on standard reference explosives is given, as well as a description of the testing equipment and procedures used for measuring the safety data.

Currently, data shown is only from Los Alamos National Laboratory (LANL) and Lawrence Livermore National Laboratory (LLNL). These are the only two laboratories that have contributed complete description of their methods, procedures and equipment. As this compendium is developed, this list of contributors will increase. Data from published sources will be included if the data is properly described, performance of reference compounds is available, as well as comprehensive description of the testing methods and procedures is available.

It is important to note that this data is for reference purposes only. It is not a substitute for deriving proper safe handling procedures of explosive materials. One needs to have a well-vetted internal procedure that meets this goal.

This is compendium will continue to grow as more data is added and more sources are included. These initial chapters were chosen because LLNL and LANL already have a data on hydrogen peroxide/fuels and urea nitrate from previous testing. Data for other solid oxidizer/fuel mixtures and other non-tradition explosives will be added.

Homeland Security

Compendium Chapter Information

- Impact Sensitivity
- Friction Sensitivity
- Electrostatic Discharge
- Thermal Safety Tests
  - Differential Scanning Calorimetry (DSC) primary
  - One Dimensional Time to Explosion (ODTX), Vacuum Thermal Stability (VTS), Chemical Reactivity Test (CRT), Accelerated Rate Calorimetry (ARC) supplementary
- Aging Studies
- Additional Information on Hazards
- Nomenclature
- X-Ray Z-Effective and Mu

Impact SSST Compendium Example

Table 3.1.1. Impact Sensitivities (DH_{50}, cm) LLNL data (1.0 Kg striker)	
90% H_2O_2, 90% concentration (10% H_2O)	>177
90% H_2O_2/isopropanol, 80%/20% mix by weight (8% H_2O)	31
90% H_2O_2/black pepper, 70%/30% mix by weight (7% H_2O)	61
90% H_2O_2/cumin, 80%/20% mix by weight (8% H_2O)	41
90% H_2O_2/flour, 70%/30% mix by weight (7% H_2O)	70
90% H_2O_2/glycerol, 75%/25% mix by weight (7.5% H_2O)	82
90% H_2O_2/nitromethane, 48.1%/51.9% mix by weight (4.8% H_2O)	30
90% H_2O_2/sucrose, 65%/35% mix by weight (6.5% H_2O)	84
90% H_2O_2/fructose, 65%/35% mix by weight (6.5% H_2O)	63
90% H_2O_2/tang, 65%/35% mix by weight, (6.5% H_2O)	56
TMETN (note 1.0 Kg striker)	14
FEFO (note 1.0 Kg striker)	32
PETN (note 1.0 Kg striker)	10
HMX (note 1.0 Kg striker)	23
PETN (note 2.5 Kg striker)	15
HMX (note 2.5 Kg striker)	32
TATP (note 2.5 Kg striker)	11
HMTD (note 2.5 Kg striker)	10

Compendium Path Forward

- Next FY will populate compendium with more data
  - Solid Oxidizer/Fuel mixtures, additional HP/fuels...
  - Proficiency test results
- Find volunteers to help with the following elements of the data compendium and overall small scale testing of HME
  - Peer Reviewers of Documentation
  - Contributors to Compendium
  - Method development to incorporate data that is incomplete or collected by other means
    - Different Procedures, Equipment, etc . . .
    - Data from International Sources

Status of Proficiency Test

Participants

- Los Alamos National Laboratory
- Lawrence Livermore National Laboratory
- Indian Head Division, NSWC
- AFRL Tyndall Air Force Base
- Sandia National Laboratories

Drop Hammer

Threats:

- 20 threats selected for testing

Testing Methods

- Impact (Drop Hammer)
- Friction
- Electrostatic Discharge
- Thermal (Differential Scanning Calorimetry: DSC)

Homeland Security

Update of project since last review

- International HME meeting in May 2010
  - Presented annual update
  - Connected with the International Round Robin
- US-France Security meeting June 2010
  - Presented Proficiency test
  - Temporary ban on communications because of ITAR
- DHS internal review July 2010
- NEXESS Tri Annual briefing in DC 8.24-25.10
  - Described IDCA (not many actually know)
    - Definition
    - Aim for HME SSST data
    - Future participation with the international community
  - Described Proficiency Test
  - Described compendium
  - Set path forward
- Some still banned from NSWC IH

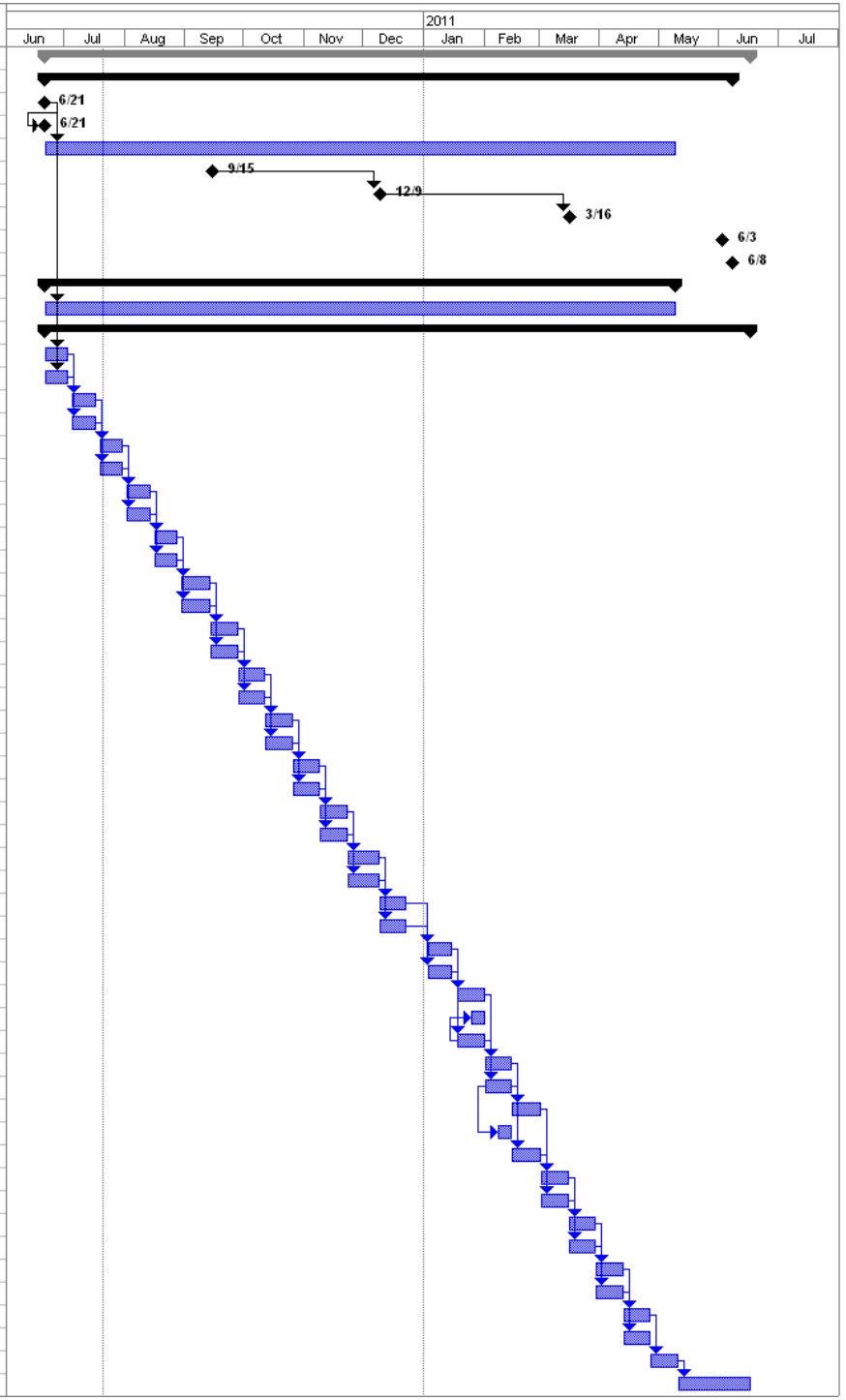
Material[1,5]	IH	AFRL	LANL	LLNL	Task Complete[4]
RDX Class 5[2]	X	X	X	X	06.21.10
KC/Sugar		X	X	X	06.21.10
KC (-100)/Sugar	X		X	X	06.21.10
KC/Dodecane			X	X	07.16.10
KP/Al			X	X	07.30.10
KP/Charcoal			X	X	08.13.10
KP/Dodecane				X	08.27.10
SC/Sugar					09.13.10
RDX Class 5					10.11.10
AN					09.27.10
AN/Gunpowder					10.25.10
HP 70%/Cumin					11.08.10
HP 70%/Flour					11.22.10
HP 70%/Glycerine					12.08.10
Gunpowder					12.22.10
RDX Class 5					01.11.11
PETN Class 4					01.31.11
HP 90%/NM					02.14.11
MEKP					03.01.11
Methyl nitrate					03.15.11
UNi/Al					03.29.11
UNi/Al/S					04.12.11
HMX					04.26.11
RDX Class 5					05.10.11
Final Summary Report					06.11.11

1. each material will be run in triplicate. 2. RDX standard will be run in triplicate 3 times. 3. KC = potassium chlorate, KP = potassium perchlorate, SC = sodium chlorate, AN = ammonium nitrate, HP = hydrogen peroxide, NM = nitromethane, UNi = urea nitrate, MEKP = methyl ethyl ketone peroxide. 4. Due date for task completion is met by the issue of the analysis report on the material. 5. X = SSST testing data taken compiled into data report and submitted for the analysis report

Reports

- Integrated Data Collection Analysis (IDCA) Program Phase I—Proficiency Study for Small Scale Safety Testing of Homemade Explosives, B. D. Olinger, M. M. Sandstrom, K. F. Warner, D. N. Sorensen, D. L. Remmers, J. S. Moran, T. J. Shelley, L. L. Whinnery, P. C. Hsu, R. E. Whipple, M. Kashgarian, and J. G. Reynolds, IDCA NEXESS Report 0001 (OUO), September, 2009
- Integrated Data Collection Analysis (IDCA) Program Phase II— Mixing Procedures and Materials Compatibility, B. D. Olinger, M. M. Sandstrom, K. F. Warner, D. N. Sorensen, D. L. Remmers, J. S. Moran, T. J. Shelley, L. L. Whinnery, P. C. Hsu, R. E. Whipple, M. Kashgarian, and J. G. Reynolds, IDCA NEXESS Report 0002 (OUO), December 2009
- Integrated Data Collection Analysis (IDCA) Program Phase III— Methyl Ethyl Ketone Peroxide-Monomer (MEKP-Monomer) Synthesis, L. L. Whinnery, IDCA NEXESS Report 0003 (OUO), May 2010.
- Integrated Data Collection Analysis (IDCA) Program Phase IV— Drying Procedures, B. D. Olinger, M. M. Sandstrom, K. F. Warner, D. N. Sorensen, D. L. Remmers, J. S. Moran, T. J. Shelley, L. L. Whinnery, P. C. Hsu, R. E. Whipple, M. Kashgarian, and J. G. Reynolds, IDCA NEXESS Report 0004 (OUO), in process, September 2010.
- Integrated Data Collection Analysis (IDCA) Program Phase V—RDX Standard Test Number 1, M. M. Sandstrom, K. F. Warner, D. N. Sorensen, D. L. Remmers, J. S. Moran, T. J. Shelley, J. A. Reyes, P. C. Hsu, R. E. Whipple, and J. G. Reynolds, IDCA NEXESS Report 0005 (OUO),final review.

ID	Task Name	Duration	Start	Finish	Predecessors
0	**LLNL IDCA FY10 U1!**	**247 days**	**6/21/10**	**6/16/11**	
1	**Task 1: Project Management**	**240 days**	**6/21/10**	**6/8/11**	
2	Funding received	0 days	6/21/10	6/21/10	
3	Project start	0 days	6/21/10	6/21/10	2
4	Monthly Status Reports	219 days	6/21/10	5/9/11	2
5	Quarterly Meeting	0 days	9/15/10	9/15/10	
6	Quarterly Meeting	0 days	12/9/10	12/9/10	5FS+60 days
7	Quarterly meeting	0 days	3/16/11	3/16/11	6FS+60 days
8	Final proficiency reports complete	0 days	6/3/11	6/3/11	
9	Sponsor briefing	0 days	6/8/11	6/8/11	
10	**Task 2: Risk Assessments**	**219 days**	**6/21/10**	**5/9/11**	
11	Test procedure and method Review (See task 3	219 days	6/21/10	5/9/11	2
12	**Task 3: Proficiency Test**	**247 days**	**6/21/10**	**6/16/11**	
13	KC(100 mesh) /sugar SSST/DSC report complete	10 days	6/21/10	7/2/10	2
14	KC/dodecane	10 days	6/21/10	7/2/10	2
15	KC dodecane SSST/DSC report completed	10 days	7/5/10	7/16/10	13
16	KP/Al	10 days	7/5/10	7/16/10	14
17	KP/Al SSST/DSC report completed	10 days	7/19/10	7/30/10	15
18	KP/Charcoal	10 days	7/19/10	7/30/10	16
19	KP/Charcoal SSST/DSC report completed	10 days	8/2/10	8/13/10	17
20	KP/dodecane	10 days	8/2/10	8/13/10	18
21	KP/dodecane SSST/DSC report completed	10 days	8/16/10	8/27/10	19
22	SC/sugar	10 days	8/16/10	8/27/10	20
23	SC/Sugar SSST/DSC report completed	10 days	8/30/10	9/13/10	21
24	RDX Standard #2	10 days	8/30/10	9/13/10	22
25	AN	10 days	9/14/10	9/27/10	24
26	AN SSST/DSC report	10 days	9/14/10	9/27/10	23
27	RDX#2 SSST/DSC report	10 days	9/28/10	10/11/10	26
28	AN/Gunpowder	10 days	9/28/10	10/11/10	25
29	AN/Gunpowder SSST/DSC report completed	10 days	10/12/10	10/25/10	27
30	HP/cumin	10 days	10/12/10	10/25/10	28
31	HP/cumin SSST/DSC report completed	10 days	10/26/10	11/8/10	29
32	HP/flour	10 days	10/26/10	11/8/10	30
33	HP/flour SSST/DSC report completed	10 days	11/9/10	11/22/10	31
34	HP/glycerin	10 days	11/9/10	11/22/10	32
35	HP/glycerine SSST/DSC report completed	10 days	11/23/10	12/8/10	33
36	Bullseye gunpowder	10 days	11/23/10	12/8/10	34
37	Bullseye gunpowder SSST/DSC report completec	10 days	12/9/10	12/22/10	35
38	RDX standard #3	10 days	12/9/10	12/22/10	36
39	PETN Class #4	10 days	1/3/11	1/14/11	38
40	RDX #3/PETN SSST/DSC report completed	10 days	1/3/11	1/14/11	37
41	PETN CLASS #4 Report	10 days	1/18/11	1/31/11	40
42	MEKP Synthesis	5 days	1/25/11	1/31/11	43SS+5 days
43	HP/NM	10 days	1/18/11	1/31/11	39
44	HP/NM SSST/DSC report completed	10 days	2/1/11	2/14/11	41
45	MEKP	10 days	2/1/11	2/14/11	43
46	MEKP SSST/DSC report completed	10 days	2/15/11	3/1/11	44
47	MN synthesis	5 days	2/8/11	2/14/11	45SS+5 days
48	MN	10 days	2/15/11	3/1/11	45
49	MN SSST/DSC report	10 days	3/2/11	3/15/11	46
50	UN/Al	10 days	3/2/11	3/15/11	48
51	UN/AL SSST/DSC report completed	10 days	3/16/11	3/29/11	49
52	UN/Al/S	10 days	3/16/11	3/29/11	50
53	UN/AL/S SSST/DSC report completed	10 days	3/30/11	4/12/11	51
54	HMX	10 days	3/30/11	4/12/11	52
55	HMX SSST/DSC report completed	10 days	4/13/11	4/26/11	53
56	RDX standard #4	10 days	4/13/11	4/26/11	54
57	RDX standard #4 SSST/DSC report completed	10 days	4/27/11	5/10/11	55
58	Draft final reports	27 days	5/11/11	6/16/11	57



FY 10 Deliverables

Deliverable	Due Date
KC (100 mesh)/Sugar Analysis Report	07.02.10
KC/Dodecane Analysis Report	07.16.10
KP/Al Analysis Report	07.30.10
KP/Charcoal Analysis Report	08.13.10
KP/Dodecane Analysis Report	08.27.10
SC/Sugar Analysis Report	09.13.10
AN Analysis Report	09.27.10
RDX Standard Run #2 Report	10.11.10
AN/Gunpowder Analysis Report	10.25.10
HP/Cumin Analysis Report	11.08.10
HP/Flour Analysis Report	11.22.10
HP/Glycerin Analysis Report	12.08.10
Gunpowder Analysis Report	12.22.10
RDX Standard Run #3 Report	01.14.11
PETN Analysis Report	01.31.11
HP/Nitromethane Analysis Report	02.14.11
MN Synthesis Method Report	03.01.11
MEKP Analysis Report	03.01.11
MN Analysis Report	03.15.11
UNi/Al Analysis Report	03.29.11
UNi/Al/S Analysis Report	04.12.11
HMX Analysis Report	04.26.11
RDX Standard Run #4	05.10.11
Final Analysis of Proficiency Test Report	06.16.11

Future needs (in no particular order)

- 1. Participation in the International Round Robin SSST testing
- Developing methods so data from different methods can be compared
  - 99. of ABL vs BAM friction analysis,
  - Bruceton vs Neyer data reduction methods (in progress)
- Modification of SSST testing for HMEs
  - 50. Optimizing sandpaper for impact testing (design of experiments)
  - Recalibrating friction testing of solid mixtures (in progress)
  - 10. Effects of porosity of solid-solid and solid-liquid mixtures on sensitivity
  - 2. Developing a fast screening method by DSC for thermal analysis (relate to ARC, ODTX, APTAC, isothermal DSC)
  - 3. Impact of aging of solid-solid, liquid-liquid and solid liquid mixtures on testing sensitivity.
  - 4. Expansion of camera approach to SSST testing
- 5. Effects of impure source materials on testing
- 45. Decomposition mechanisms for impact and friction through molecular characterization
- TBD. Additional HME threats that challenge SSST Testing

Future needs (in no particular order)

- Participation in the International Round Robin SSST testing
- Developing methods so data from different methods can be compared
  - of ABL vs BAM friction analysis,
  - Bruceton vs Neyer data reduction methods
- Modification of SSST testing for HMEs
  - Optimum grit size on sandpaper for impact testing
  - Recalibrating friction testing of solid mixtures
  - Effects of porosity of solid-solid and solid-liquid mixtures on sensitivity
  - Developing a fast screening method by DSC for thermal analysis (relate to ARC, ODTX, APTAC, isothermal DSC)
  - Impact of aging of solid-solid, liquid-liquid and solid liquid mixtures on testing sensitivity.
- Effects of impure source materials on testing
- Decomposition mechanisms for impact and friction through molecular characterization
- Additional HME threats that challenge SSST Testing

Summary

- Roughly one fourth the way through testing
  - $KClO_3$ mixtures are almost done
  - $KClO_4$ mixtures are in progress
- Modified testing procedures for IDCA
  - Sand paper for impact 180 grit
  - 35 mg powder samples for solids
  - Modified Bruceton, modified TIL and Neyer's analysis methods adapted
  - DSC is still in discussion
- Testing schedule modified for some participants
  - Funding
  - Experience

Results!

74% $KClO_3$ (-100 mesh)/26% Icing Sugar

Impact Data, modified Bruceton Method

Lab	T, °C	RH, %	DH_{50}, cm	σ, log unit
LLNL	23.3	21	16.3	0.065
LLNL	22.8	28	12.5	0.022
LLNL	22.8	28	14.4	0.020
LANL	21.2	13.5	15.0	0.076
LANL	21.1	14.2	17.7	0.044
LANL	21.8	13.5	18.8	0.035
IH	26	40	14	0.07
IH	27	40	15	0.18
IH	27	40	14	0.14

LANL: PETN DH_{50} = 14.7 cm; RDX DH_{50} = 25 cm; LLNL: PETN DH_{50} = 15 cm

All participants have about the same values

Homeland Security

KC/Sugar as received vs -100 mesh

Impact data (AR = as received, -100 = sieved through 100 mesh)

Lab	Sample	T, °C	RH, %	DH_{50}, cm	σ, log unit
LLNL	AR	22.7	18	16.8	0.025
LLNL	AR	23.3	18	13.3	0.029
LLNL	AR	23.3	18	15.2	0.082
LLNL	-100	23.3	21	16.3	0.065
LLNL	-100	22.8	28	12.5	0.022
LLNL	-100	22.8	28	14.4	0.020
LANL	AR	22.1	15.1	15.3	0.131
LANL	AR	22.3	16.0	13.8	0.049
LANL	AR	21.8	12.2	16.3	0.049
LANL	-100	21.2	13.5	15.0	0.076
LANL	-100	21.1	14.2	17.7	0.044
LANL	-100	21.8	13.5	18.8	0.035

LANL: PETN DH_{50} = 14.7 cm; RDX DH_{50} = 25 cm; LLNL: PETN DH_{50} = 15 cm

Homeland Security

Little difference between 100 mesh and as received

KC/Dodecane—Impact

Lab	T, °C	RH, %[2]	DH_{50}, cm^3	σ, log unit
LLNL	23.9	23	34.0 (31.0-37.3)	0.041
LLNL	23.9	22	45.4 (43.3-47.6)	0.020
LLNL	22.2	16	41.2 (33.1-51.2)	0.095
LANL	24.0	<10	12.6	0.048
LANL	23.3	<10	9.0	0.068
LANL	24.0	<10	12.1	0.040

Difference caused by evaporation, sand paper ?

Homeland Security

KC/Sugar (as received) Bruceton vs Neyer's methods

Impact data

Lab	method	T, °C	RH, %	DH_{50}, cm	σ, log unit
LANL	Bruceton	22.1	15.1	15.3	0.030
LANL	Bruceton	22.3	16.0	13.8	0.050
LANL	Bruceton	21.8	12.2	16.3	0.020
LANL	Neyer's	21.7	16.3	15.3	0.9
LANL	Neyer's	22.2	16.5	14.1	1.5
LANL	Neyer's	21.0	16.0	15.3	0.6

LANL: PETN $DH_{50\ (Bruceton)} = 14.7$ cm, $DH_{50\ (Neyer's)} = 13.5$ cm
RDX $DH_{50\ (Bruceton)} = 25$ cm, $DH_{50\ (Neyer's)} = 24$ cm

Little difference between Neyer's and Bruceton methods for impact

KC/Dodecane Bruceton vs Neyer's methods

Impact data

Lab	method	T, °C	RH, %	DH_{50}, cm	σ, log unit
LANL	Bruceton	24.0	< 10	12.6	0.048
LANL	Bruceton	23.3	< 10	9.0	0.068
LANL	Bruceton	24.0	< 10	12.1	0.040
LANL	Neyer's	24.0	< 10	12.3	0.082
LANL	Neyer's	24.0	< 10	10.2	0.175
LANL	Neyer's	23.0	< 10	13.6	0.111

LANL: PETN $DH_{50\ (Bruceton)} = 14.7$ cm, $DH_{50\ (Neyer's)} = 13.5$ cm
RDX $DH_{50\ (Bruceton)} = 25$ cm, $DH_{50\ (Neyer's)} = 24$ cm

Little difference between Neyer's and Bruceton methods for impact

KC/Sugar (as received) Friction

BAM friction method, Yellow font with blue background = PETN

Lab	T, °C	RH, %	TIL, kg	TIL, kg	F_{50}, kg	σ, log unit
LLNL	22.2	18	0/10 @ 11.2	1/10 @ 12.0	13.2	0.050
LLNL	22.2	18	0/10 @ 8.0	1/10 @ 8.4	12.5	0.106
LLNL	22.2	18	0/10 @ 7.2	1/10 @ 8.0	11.2	0.082
LLNL	na	na	na	1/10 @ 6.4	na	na
LANL	22.1, 21.8	15.1, 13.8	Too low	2/10 @ 2.4	4.7	0.180
LANL	22.7, 22.7	15.3, 15.3	Too low	3/10 @ 2.4	4.9	0.170
LANL	22.2, 22.2	12.0, 12.0	Too low	2/10 @ 2.4	4.3	0.070
LANL	20.0	12.0	na	na	9.2	1.6

LLNL data shows KC/Sugar as received less sensitive than PETN
LANL data shows KC/Sugar as received more sensitive than PETN

KC/Dodecane—BAM Friction

Lab	T, °C	RH, %[1]	TIL, kg[2]	TIL, kg[3]	F_{50}, kg[4]	σ, log unit
LLNL	23.9	19	0/10 @ 11.2	1/10 @ 12.0	32.6	0.026
LLNL	22.2	18	0/10 @ 12.8	1/10 @ 14.4	24.8	0.284
LLNL	23.9	19	0/10 @ 12.8	1/10 @ 13.6	30.3	0.081
LANL	24.0	<10	na[6]	na[6]	20.2	6.8
LANL	24.0	<10	na[6]	na[6]	20.4	3.0
LANL	22.7	<10	na[6]	na[6]	19.1	5.3
LANL	23.6	<10	0/10 @ 7.2	1/3 @ 9.6	na[5]	na[5]
LANL	24.0	<10	0/10 @ 7.2	1/6 @ 9.6	na[5]	na[5]
LANL	23.0	<10	0/10 @ 7.2	1/2 @ 9.6	na[5]	na[5]

KP/Al BAM Friction

Lab	T, °C	RH, %[1]	TIL, kg[2]	TIL, kg[3]	F_{50}, kg[4]	σ, log unit
LLNL	23.3	18	0/10 @ 9.6	1/10 @ 10.2	12.2	0.042
LLNL	22.8	24	0/10 @ 10.8	2/10 @ 11.2	20.3	0.100
LLNL	23.3	21	0/10 @ 8.4	1/10 @ 9.6	21.2	0.167
LANL	22.1	26.5	na[6]	na[6]	14.1	9.4
LANL	21.8	21.5	na[6]	na[6]	15.6	4.0
LANL	21.2	27.4	na[6]	na[6]	15.8	3.6
LANL	23.5	22.6	0/10 @ 7.2	1/3 @ 9.6	na[5]	na[5]
LANL	21.7	21.4	0/10 @ 7.2	1/3 @ 9.6	na[5]	na[5]
LANL	21.5	25.8	0/10 @ 7.2	1/4 @ 9.6	na[5]	na[5]

KP/Al ESD

Lab	T, °C	RH, %[1]	TIL, Joule[2]	TIL, Joule[3]
LLNL	23.3	18	nd[5]	1/10 @ 0.49[5]
LLNL	22.2	23	0/10 @ 0.25[5]	2/3 @ 0.64[5]
LLNL	22.2	23	0/10 @ 0.25[5]	2/6 @ 0.64[5]
LANL	22.6	23.5	< 0.0625	< 0.0625
LANL	21.3	26.0	< 0.0625	< 0.0625
LANL	21.6	28.7	< 0.0625	< 0.0625

Very spark sensitive

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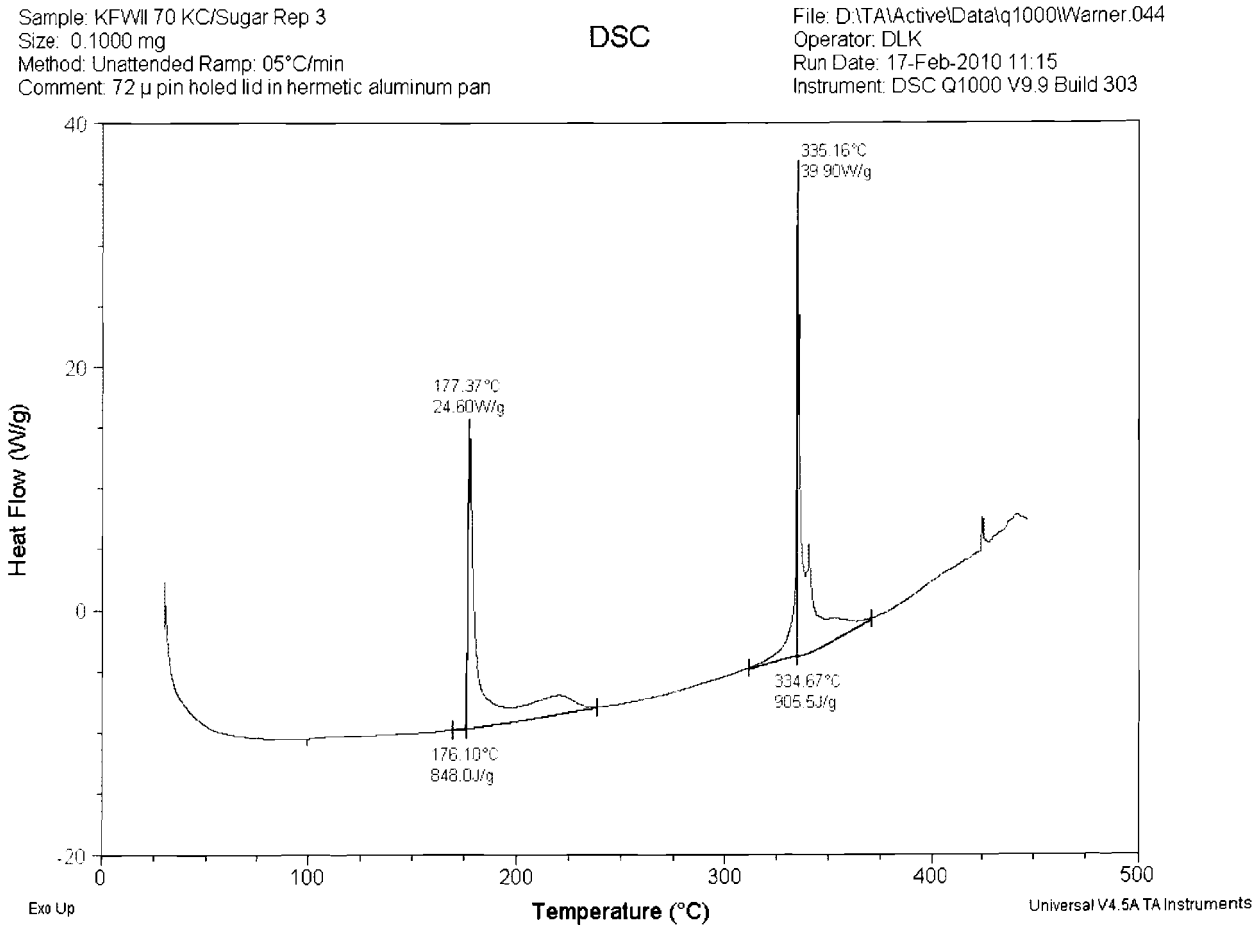
74% $KClO_3$ (-100 mesh)/26% Icing Sugar

DSC at 10°C/min ramp rate, Indian Head Data



IH and LANL show two exothermic excursions in most cases

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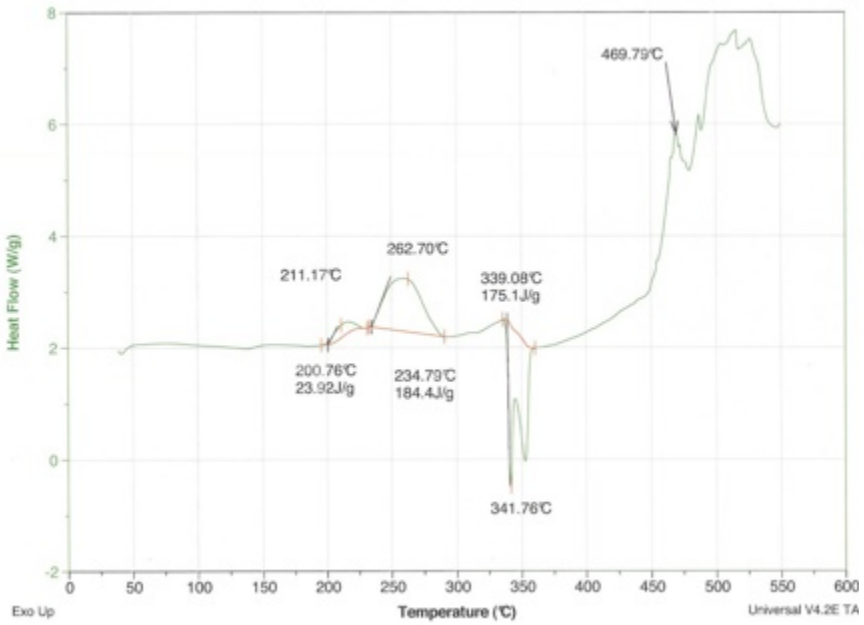
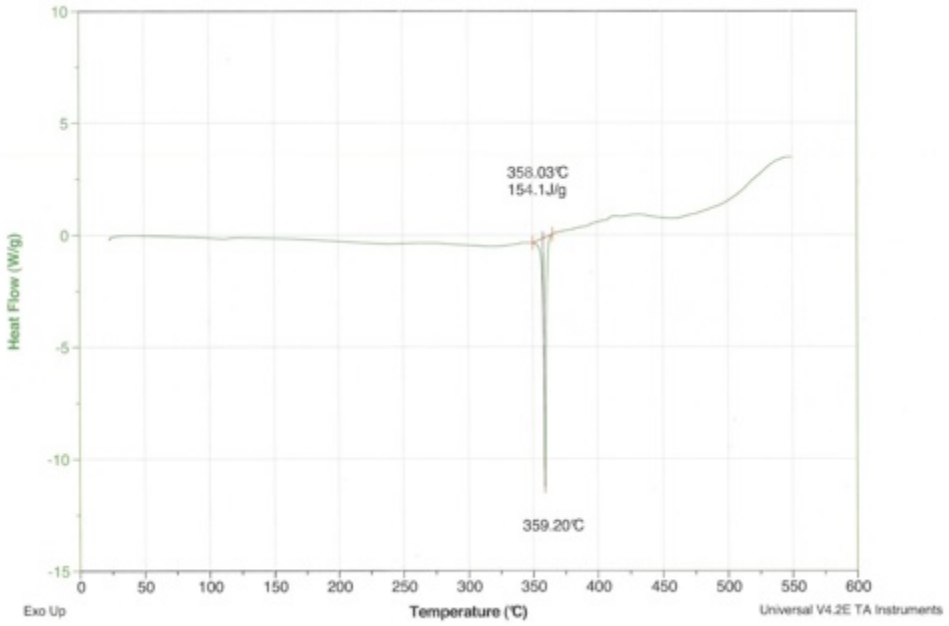
KC/Dodecane DSC



Hermetically sealed pan

Pin hole pan



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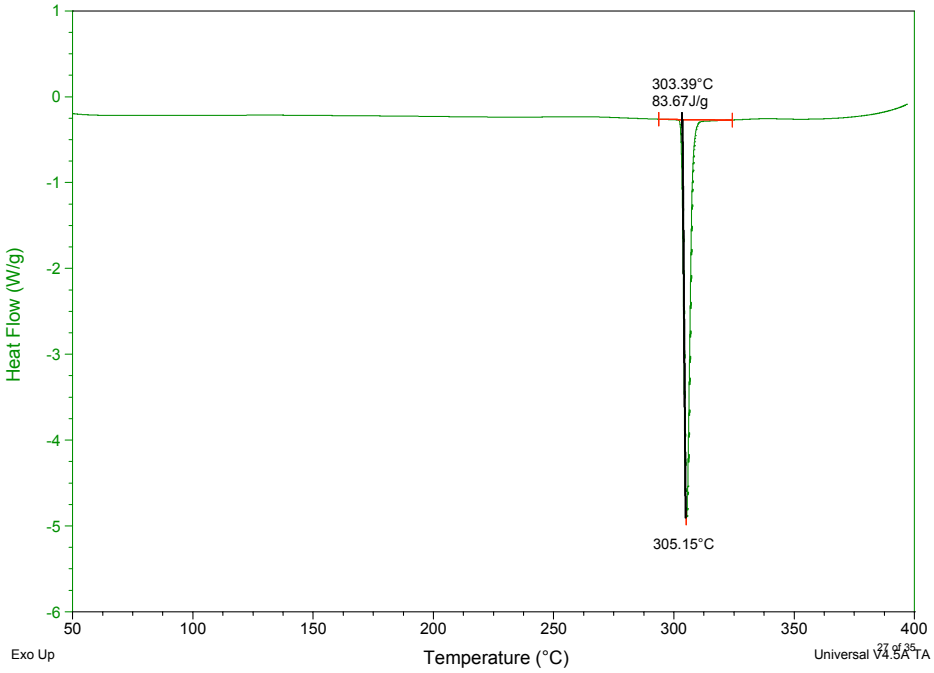
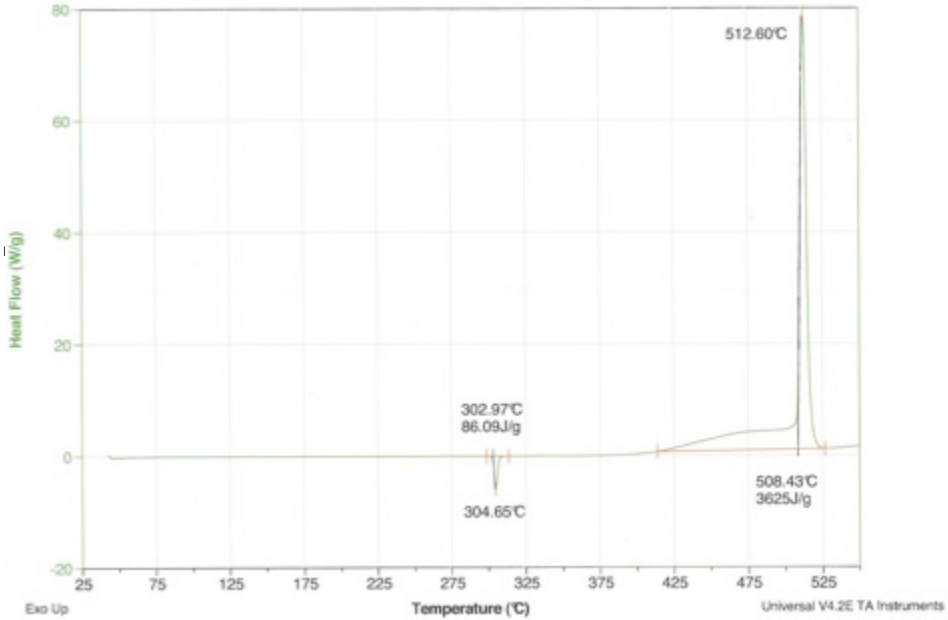
KP/C DSC


303.39°C
83.67J/g
305.15°C
Heat Flow (W/g)
Temperature (°C)
Exo Up
Universal V4.5A TA
27 of 35


512.60°C
302.97°C
86.09J/g
304.65°C
508.43°C
3625J/g
Heat Flow (W/g)
Temperature (°C)
Exo Up
Universal V4.2E TA Instruments

Acknowledgments

This work is funded by Department of Homeland Security Science and Technology's Explosives Division

- Jim Tuttle, DHS Explosives S&T
- Doug Bauer, DHS Explosives S&T
- Quinton Krueger, DHS Explosives S&T
- Laura Parker, DHS Explosives S&T
- Greg Struba, SETA support DHS Explosives S&T

The work was performed by the National Explosives Engineering Science Security (NEXESS) Center, a tri-lab effort supported by Sandia National Laboratories, Los Alamos National Laboratory, and Lawrence Livermore National Laboratory under sponsorship of the US Department of Homeland Security, Office of Science and Technology, Explosives Division, and the Transportation Security Administration. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000. Los Alamos National Laboratory is operated by Los Alamos National Security, LLC, for the United States Department of Energy under contract DE-AC52-06NA25396. This work was performed under the auspices of the U. S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. The Air Force Research Laboratory (AFRL/RXQF) and The Indian Head Division, Naval Surface Warfare Center (IHD, NSWC) also performed work in support of this effort. The work performed by AFRL/RXQF and IHD, NSWC is under sponsorship of the US Department of Homeland Security, Office of Science and Technology, Explosives Division.

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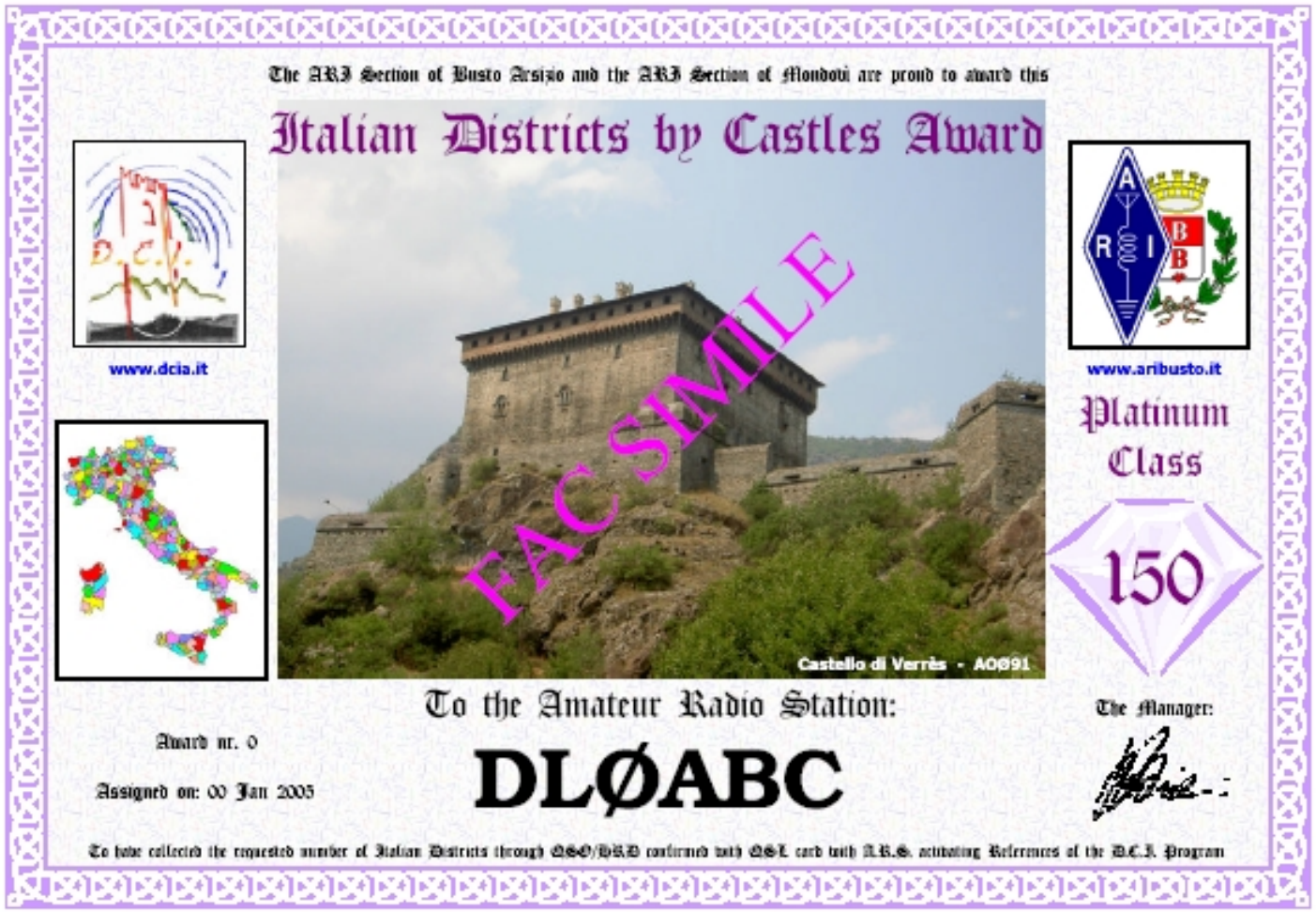
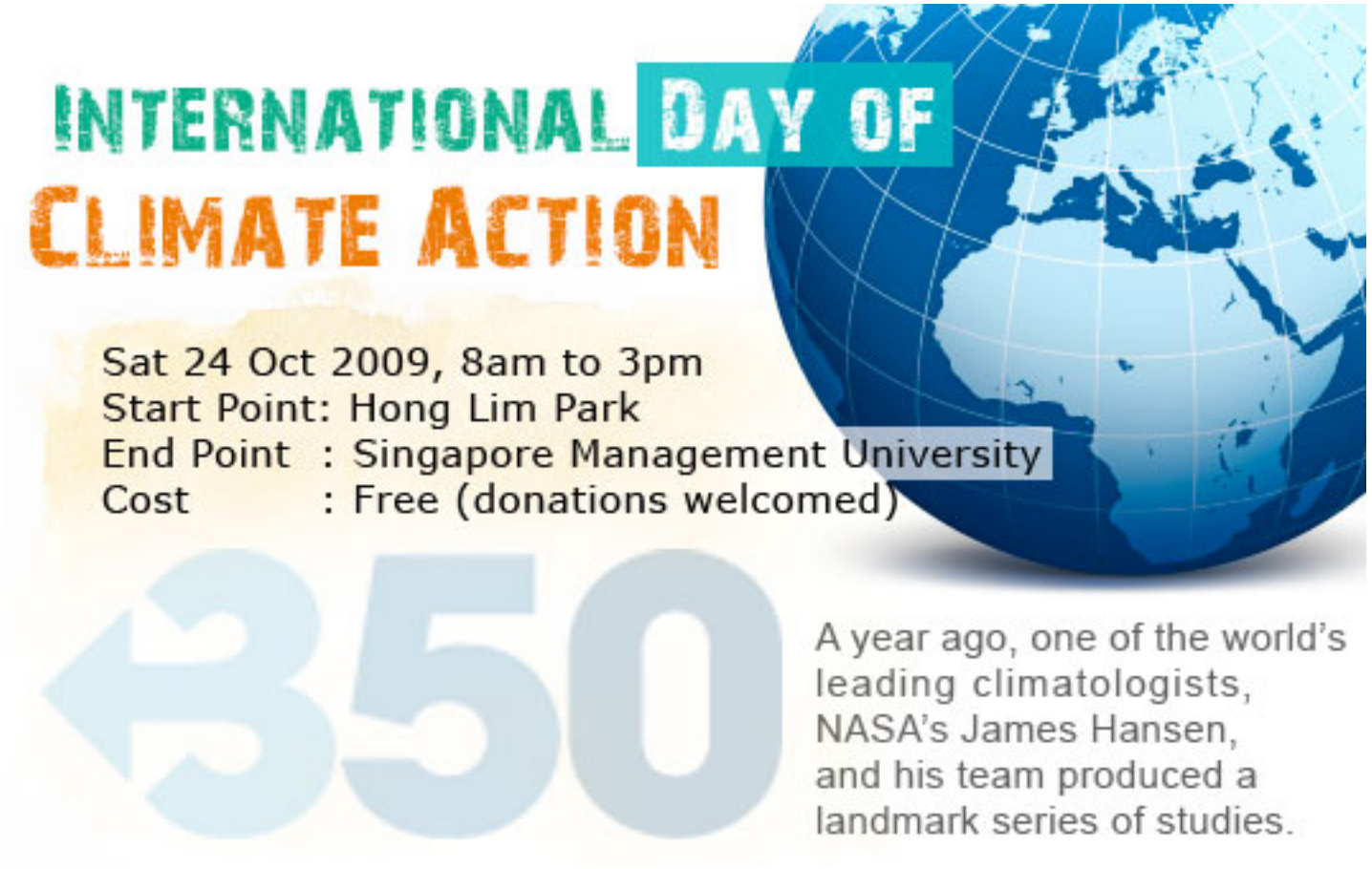
IDCA needs a logo

International Diamond Certifiers of America

Italian District Castle Awards



International Day of Climate Action



Internet Data Centers Asia

Sept 2007

- **Webvisions at Internet Data Centers Asia (IDCA) 2007**

  Internet Data Centres Asia (IDCA) 2007 - 28-29 Sep 2007. Pan Pacific Hotel, Pacific 3 Following the third successful year of the regional event, Data Centres Europe, IDCA 2007 is the first of its kind in Asia Pacific. The exhibition cum conference will bring together leading data centres and businesses engaged in the sector across the region to engage in robust debate, providing insight and content, and also facilitate top level networking opportunities. Visit Webvisions at booth M and attend "CXO Roundtable: Responding to the Data Centre Challenge" on 27th Sep, 920 am which will be represented by Mr Roger Lim, CEO of Webvisions.

Independent Diagnostic Clinics Association

Independent
Diagnostic Clinics
Association

2075 Hadwen Road
Mississauga, Ontario
L5K 2L3

Telephone: (905) 855-0739
Fax: (905) 855-1863

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Irish Dramatic Combat Academy

IDCA—Yes, it is a washing machine!

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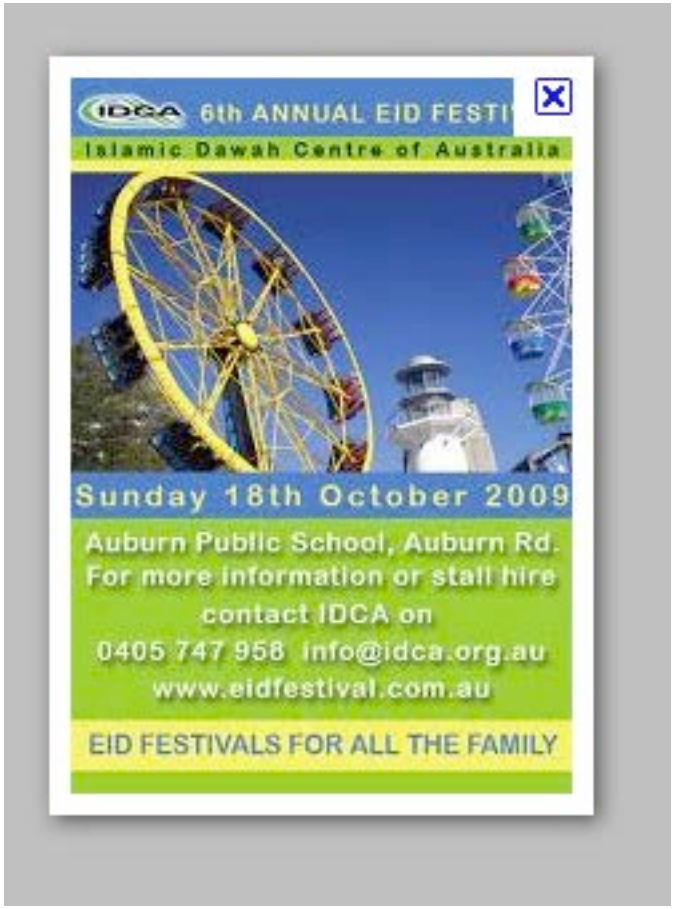
Islamic Dawah Centre of Australia



IDCA

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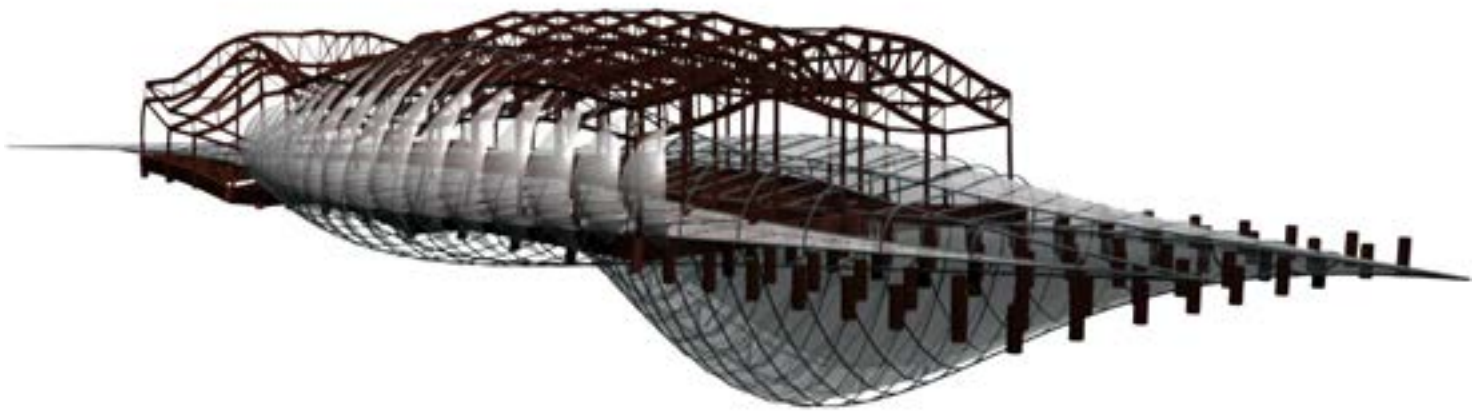
International Digitizing Centre ACCRE

IDCA Satellite Symposium—Amphibious Architecture



Homeland Security

Industrial Canada

Homeland Security

IDCA Update

IHD IDCA Team: Daniel N. Sorenson, Daniel L. Remmers, Jesse S. Moran and Kirstin F. Warner

Sept. 14 2010

Financials

Title of Effort: IDCA Support
PR: HSHQDC-10-X-00414
Total Funding: $431,078
Billed to date: $37,432.82
Expiration Date: 5/16/2011

Task #	Task Title	Funds Allocated	Billed
2.0	IDCA/Round Robin Support	$431,078	$21,904.79
	Program Management Task 2		$12,225.84
	Technical Meeting Technical Reports Monthly Status Reports		
	Non-Labor (Shipping RDX to Sandia)		$3302.19
Totals			$37,432.82

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Status

Sample ID	Status
RDX Report	Completed
KC/Icing Sugar (100 mesh) Report	Completed
KC/Icing Sugar (as received) Report	Completed
KC/Dodecane Report	Completed
KP/Al Report	30 Sept

Spread Sheet Discussion

- Dan Remmers would like discuss Peter's spreadsheet
- IHD data

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Thermal Techniques

Techniques	POC
Accelerated Rate Calorimetry (ARC)	Lawrence/Knott
Differential Thermal Analysis (2g-DTA)	Sorensen
Differential Scanning Calorimetry (DSC)	Sorensen
Rapid Screen Device (RSD)	Bryant/Mackey
Heat Flow Calorimetry	Bryant
Micro-reaction Calorimeter	Would like to purchase (Warner)
* Small Scale Cap Sensitivity	Granholm

**Not a thermal technique but useful information (nitrate ester dilution studies)*

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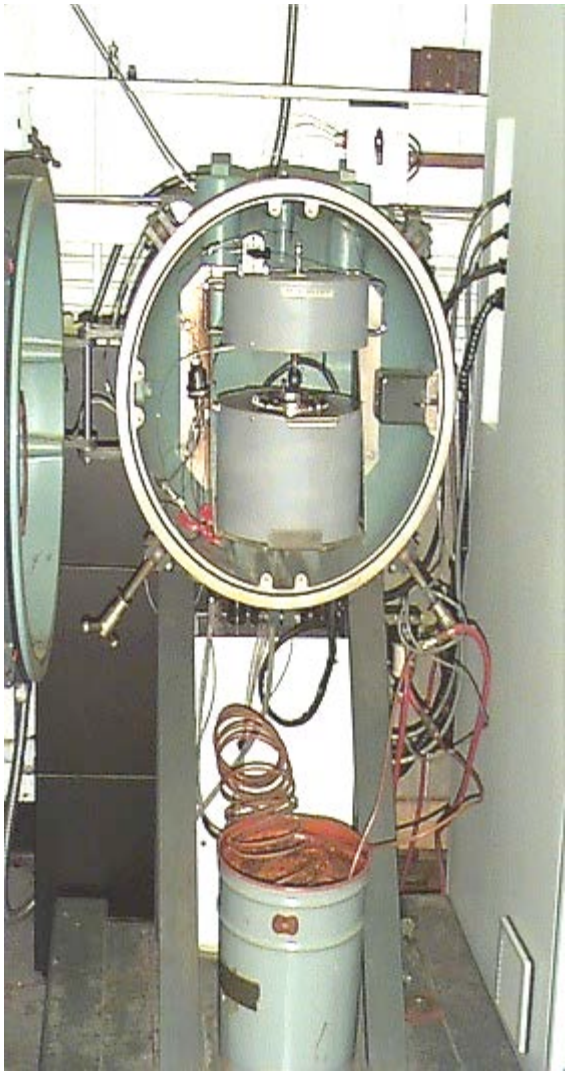
ARC



- An exotherm is considered to have occurred when a self-heat rate is detected above 0.02°C/min. If no exotherm is detected, the instrument increases the temperature to a 5°C increment and allows to equilibrate again.
- This heat-wait-search cycle is repeated until either an exotherm is detected or the upper temperature limit (400°C) is reached.
- If an exotherm is detected, the surroundings are kept at the same temperature as the reaction bomb/ container, allowing the system to be maintained without heat loss as the temperature of the system increases due to the heat evolved during the exotherm.

ARC

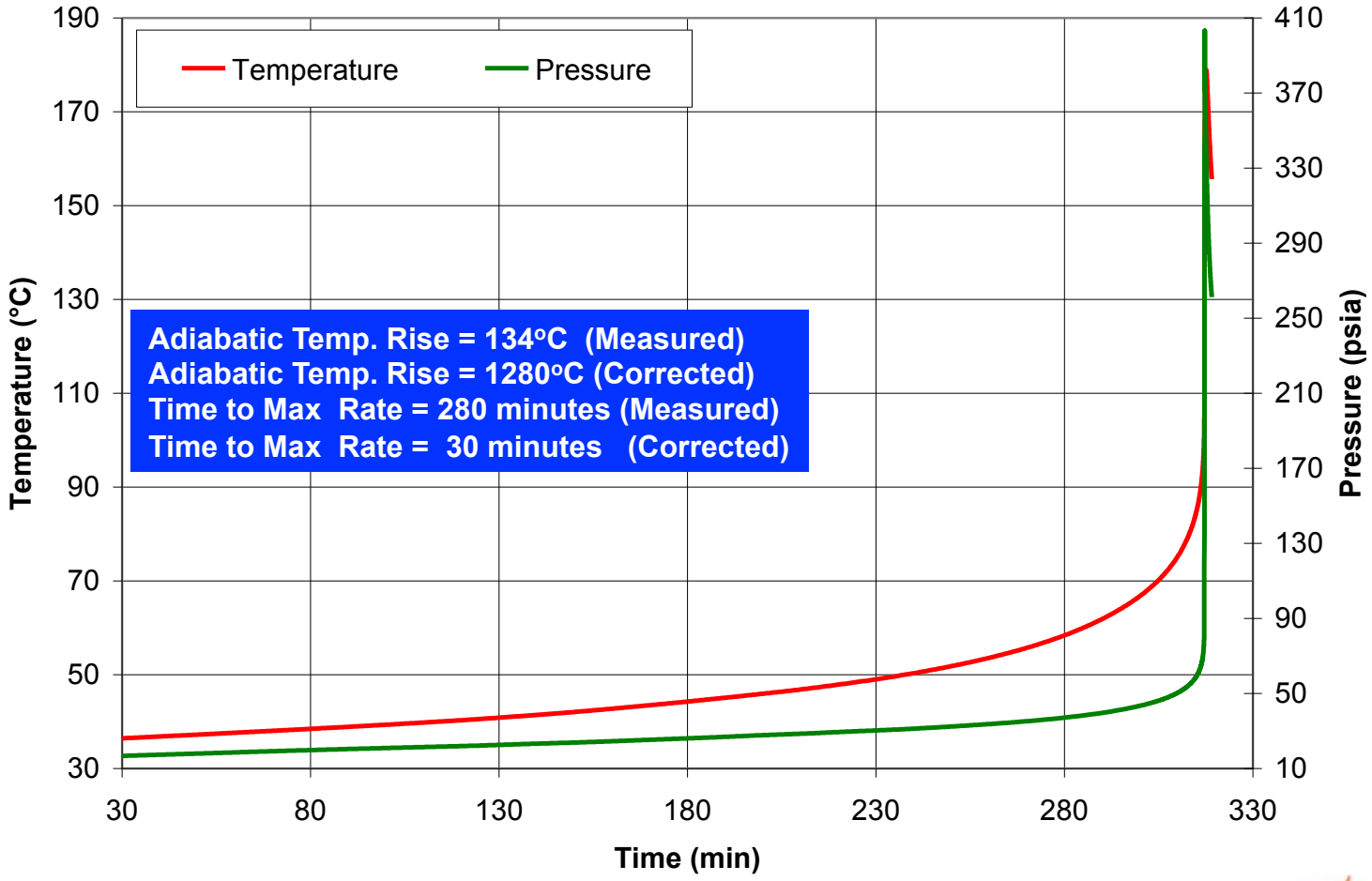
- ARC is an important method for studying the thermal behavior of materials under adiabatic conditions. The instrument will hold the sample in an adiabatic state, looking for heat generated by the sample.

- If no heat generation is detected, the instrument increases the temperature and looks for a self-heating. The bomb is heated to 35°C and allowed to come to equilibrium, a search for evidence of an exothermic reaction is undertaken.

ARC

- Thermal and pressure hazard parameters related to ARC data include:
  - onset temperature
  - adiabatic temperature rise
  - pressure developing rate (PDR)
  - self heating rate (SHR)
  - time to maximum rate (TMR)
  - evaluate worst-case energy release
  - probability of the occurrence of an incident, or the occurrence of a thermal runaway reaction

HME Mixture



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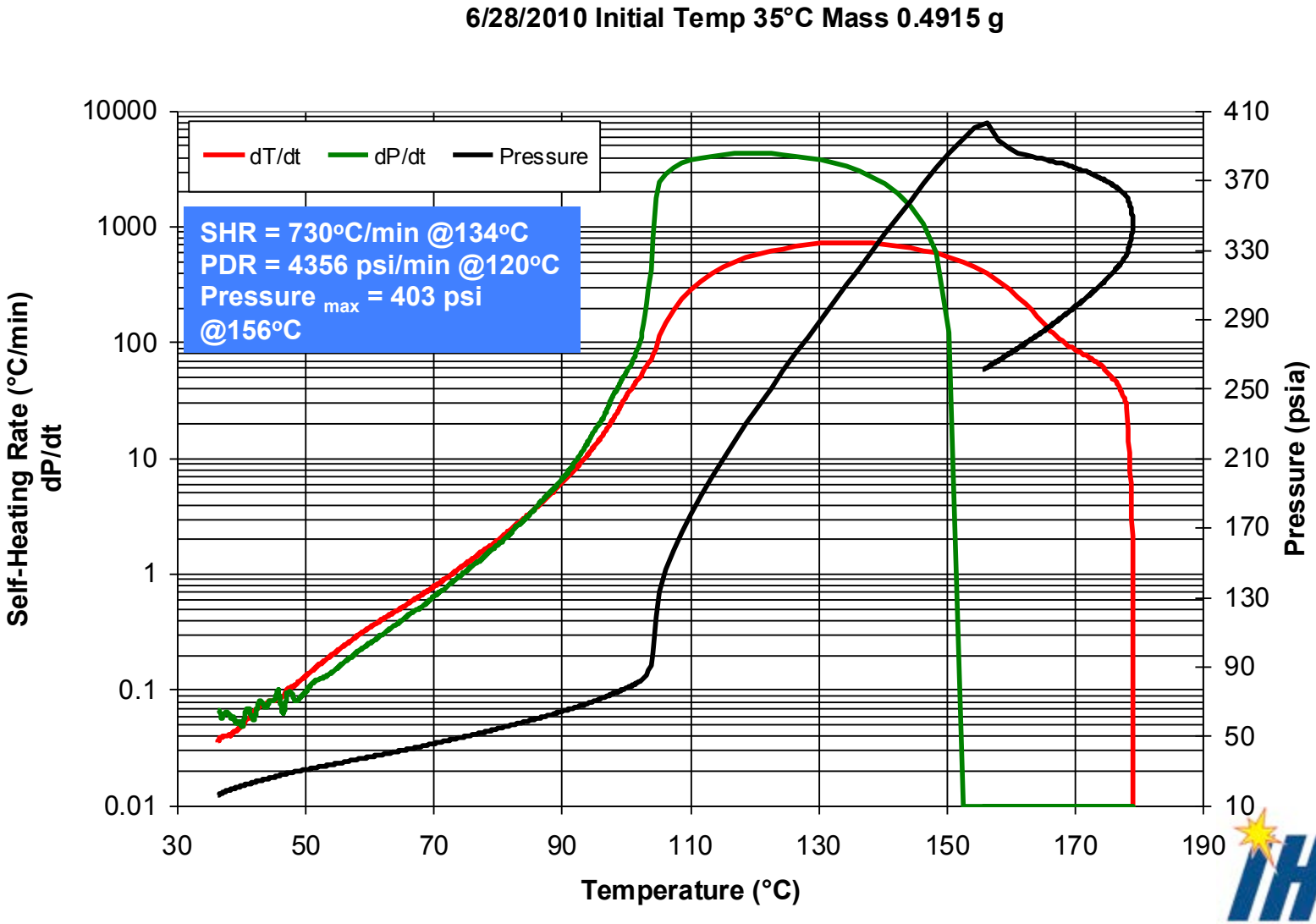
HME Mixture



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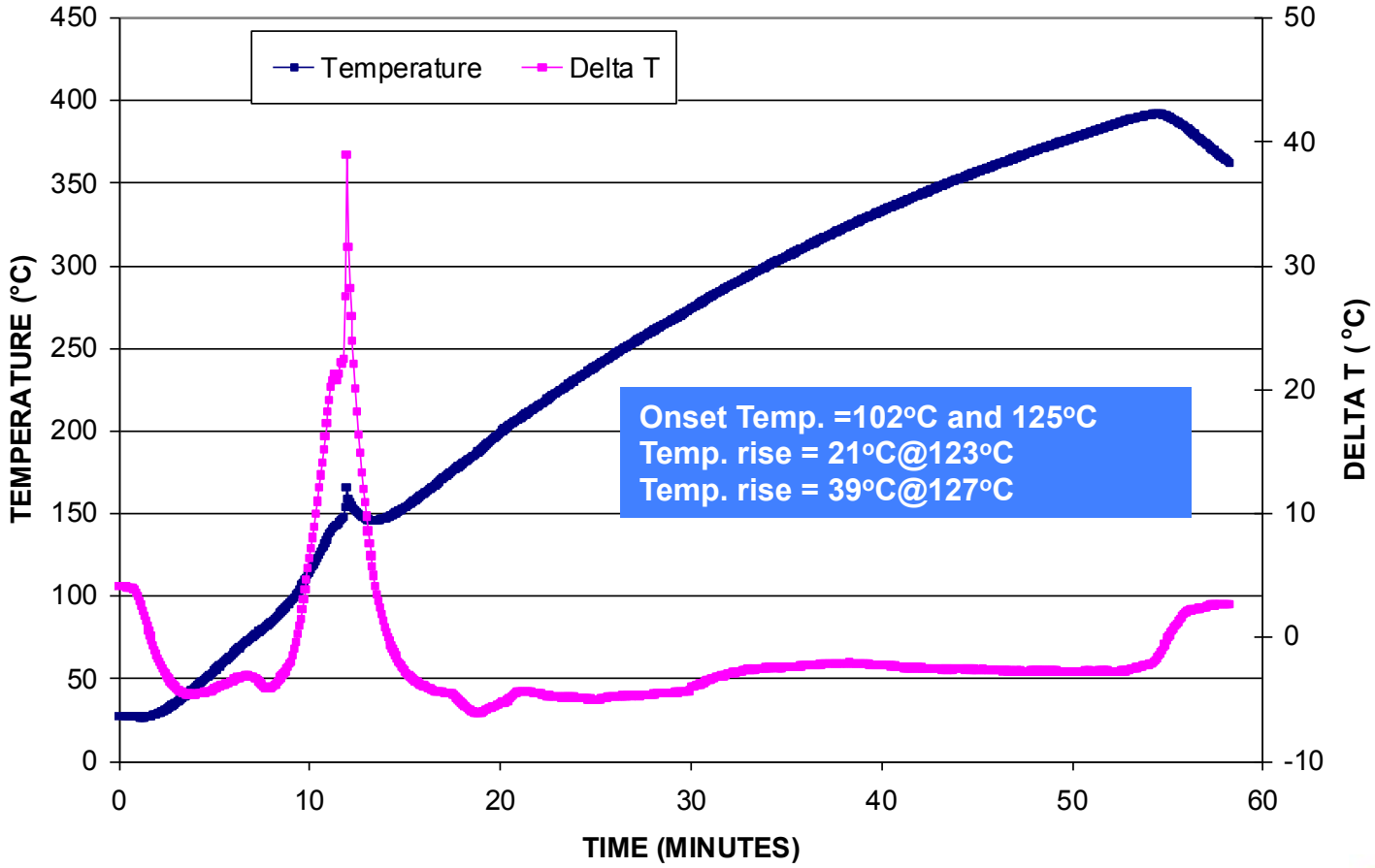
HME Mixture



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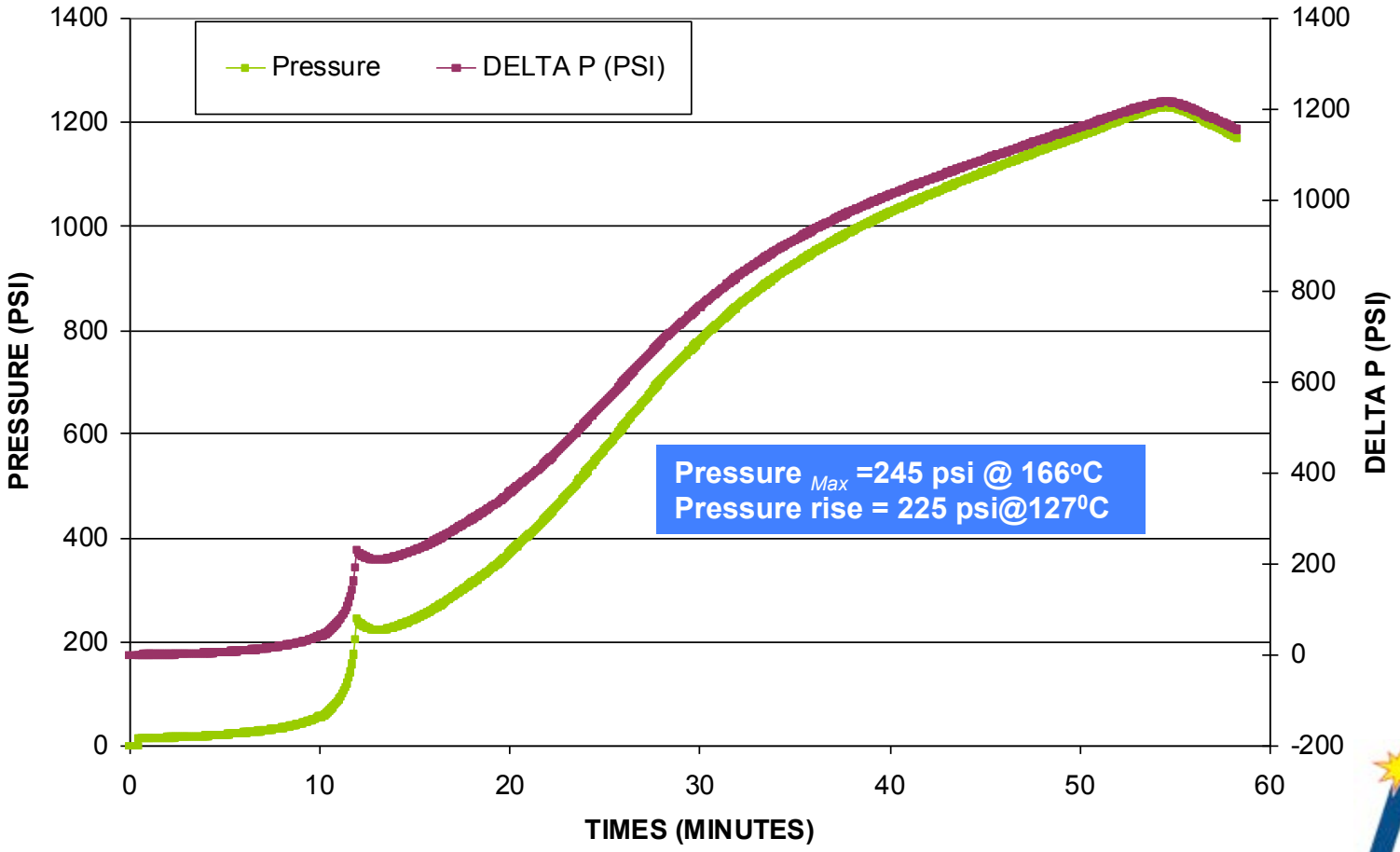
HME Mixture



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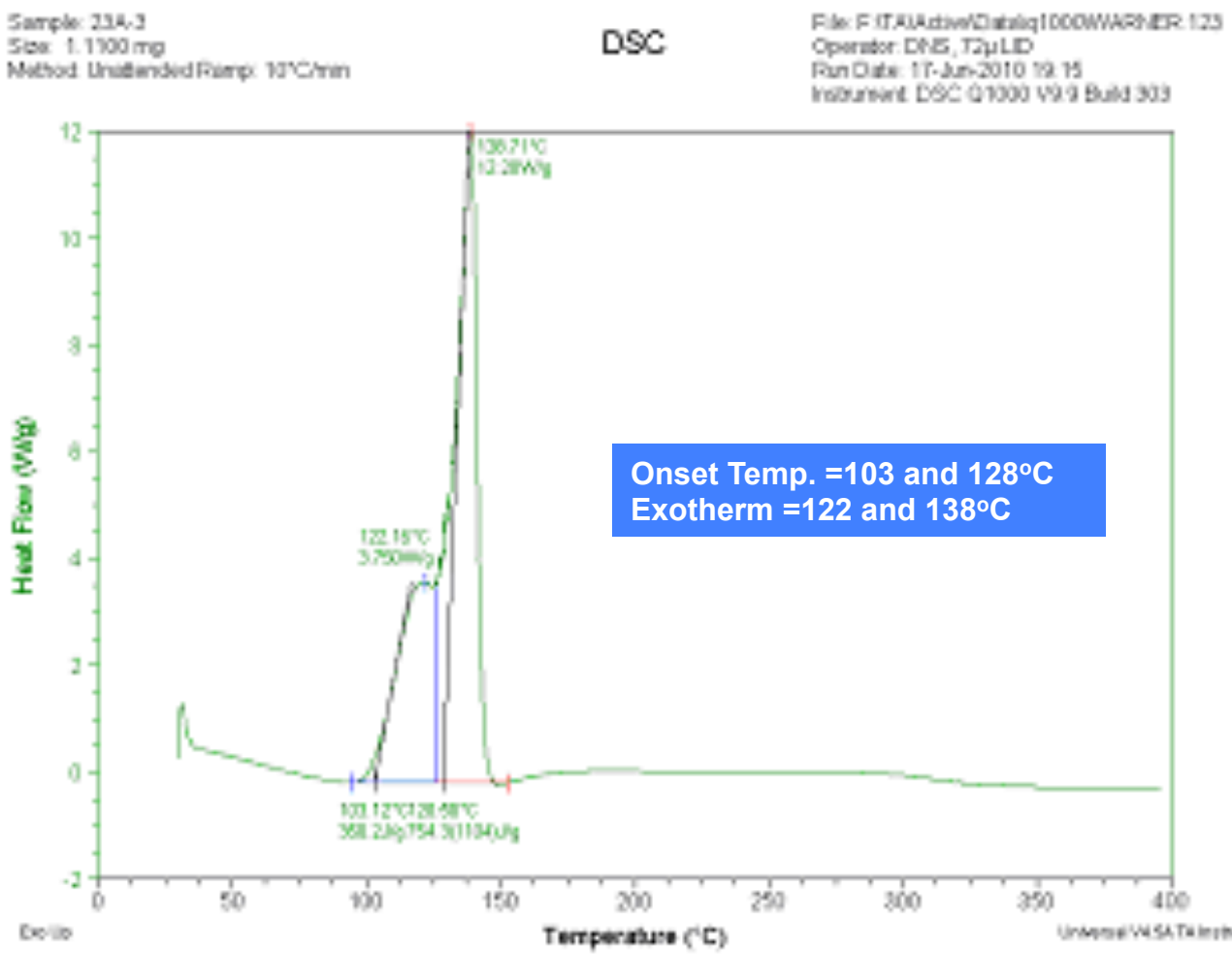
HME Mixture



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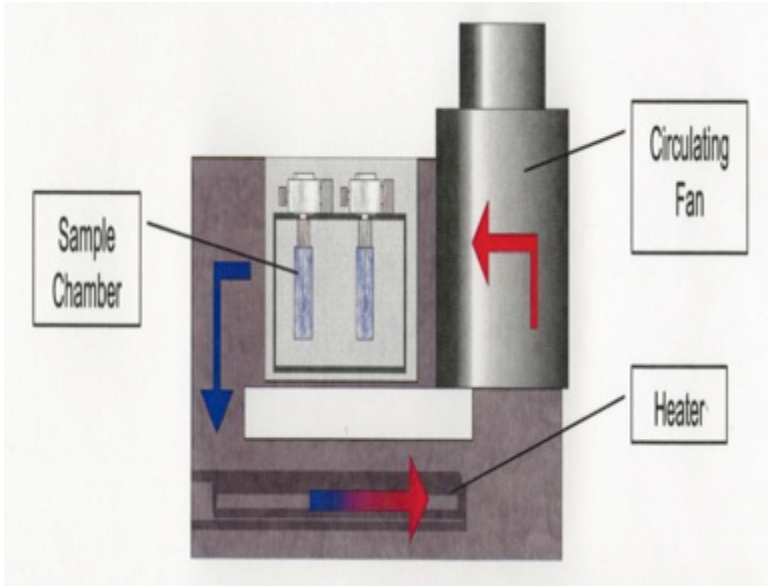
Summary

- **ARC**
  - SHR > 15°C/min 96-150°C
  - SHR_{max} = 730°C/min @134°C
  - PDR_{max} = 4356 psi/min @120°C
  - $Pressure_{max}$ = 403 psi @156°C
  - TMR = 30 minutes (corrected)
  - Sample Mass Loss 39%
- **Maximum exothermic behavior 96-150°C**
- **RSD**
  - Onset Temp. 102°C and 125°C
  - Temp. Rise 21°C @23°C and 39°C@127°C
  - $Pressure_{max}$ =245 psi
- **Maximum exothermic behavior 102-147°C**
- **DSC**
  - Onset Temp. 103°C and 128°C
  - Exotherm Temp.122°C and 138°C
- **Maximum exothermic behavior 103-138°C**

What is the RSD (Rapid Screening Device)?



Calorimeter designed to study exothermic (endothermic) reactions

- quantifies heat of reaction (measures accumulated heat)
- kinetics of reaction (measures heat transfer rates)
- operates isothermally or dynamically (up to 400°C; 10°C/ min)
- determine onset of reaction
- pressure measurements (up to 2400 psi)
- compatibility studies
- measure heat capacities
- sample sizes (~ 100 mg – 50 g)
- < 10J/g sensitivity
- six sample capacity
- manual or automated rapid quench/cool

DTA

- The DTA system is a predrilled aluminum-heating block with four sample holes and a block thermocouple control hole.
- DTA samples were prepared by adding 1-2g of the sample to fit inside a 15mm OD test tube. After the sample was in the tube, a 1.5-1.8 x 90mm glass melting point capillary tube was inserted into the sample.
- Two pierced Fiberfrax Duraboard plugs were used to hold the capillary in the center of the test tube. The plugs were punched out with a cork borer and drill bit kept for this purpose.
- After the capillary and first plug was in place, alumina was used as an inert filler to minimize thermal lag due to air gaps in the sample to be tested. Glass wool was added for additional insulation and then topped with a second plug.
- The test system was completed once an Omega Type T thermocouple was completely inserted down the capillary tube. This setup provided thermal contact with the sample while providing some protection against any corrosive gases which could occur during decomposition. A reference tube of alumina was also prepared.

DTA

- Heating two grams of energetic in the 2g-DTA system has one of three outcomes for the thermocouple.
  - First, the energetic decomposes under relatively mild conditions and the resultant 2g-DTA curve appears similar to conventional DSC curves.
  - Second, a more frequent occurrence, particularly when decomposing propellants.
    - The test tube acts like the end of a gun barrel and the decomposition expels the thermocouple housing.
    - A peak temperature is observed in the difference curve prior to rapidly going to negative as the sample thermocouple returns to ambient.
  - Third, the thermocouple may be destroyed and the sample thermocouple reading goes to an open circuit value for the duration of the test.
    - For purposes of scaling on thermal curves, the open circuit values are converted to an arbitrary value of 500 for both the sample and delta temperature whenever they are observed.

DTA

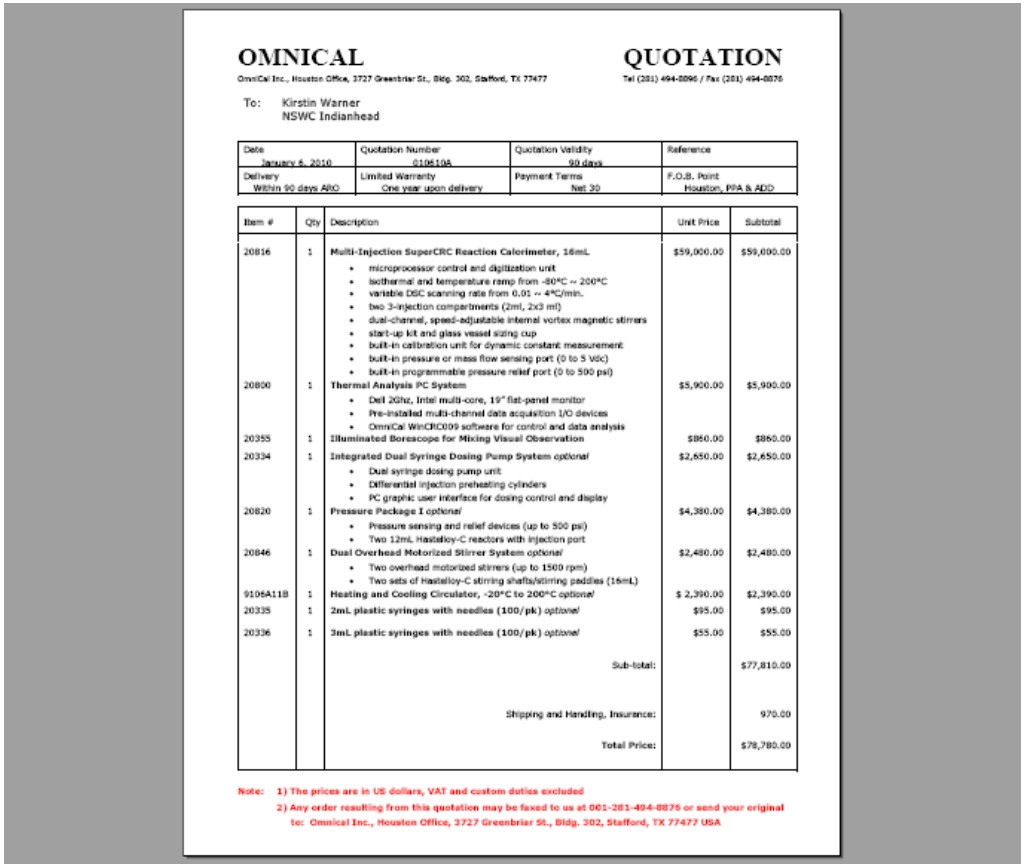
- The aluminum heating block was attached to an Omega heater/controller to produce a heating rate of 1°C/min.
- Once the individual test tubes were in place in the heating block, the thermocouple leads were fed through a hole in the bay to a simple RS-232 port attached to a computer running Labview software.
- Testing collected the reference temperature, the sample temperature, the difference between the two and the time every second during the course of the test as an ASCII file.
- On completion of the experiment, the data was converted through Microsoft Excel macros into a file readable by the TA Instruments Universal Analysis (UA) software.
- This last step was performed as a matter of preference to use features of UA not found in Microsoft Excel.

Micro-Reaction Calorimeter

Reaction Hazards

- This reaction microcalorimeter provides scalable heat flow data
- Total heat released and maximum release rate
- Reaction kinetics and Thermodynamics
- Heat capacity and Thermochemical conversion
- This unique calorimetric platform combines three calorimetric operations in one instrument: reaction calorimetry, pressure-tracking macro-DSC and conventional microcalorimetry
- Deliver simple heats of mixing in as short as 60 minutes.

Quote



OMNICAL **QUOTATION**

OmniCal Inc., Houston Office, 3727 Greenbriar St., Bldg. 302, Stafford, TX 77477 Tel (281) 494-8896 / Fax (281) 494-8876

To: Kirstin Warner
NSWC Indianhead

Date	Quotation Number	Quotation Validity	Reference
January 6, 2010	0106108A	90 days	
Delivery	Limited Warranty	Payment Terms	F.O.B. Point
Within 90 days ARO	One year upon delivery	Net 30	Houston, PPA & ADD

Item #	Qty	Description	Unit Price	Subtotal
20816	1	**Multi-Injection SuperCRC Reaction Calorimeter, 16mL** • microprocessor control and digitization unit • isothermal and temperature ramp from -80°C ~ 200°C • variable DSC scanning rate from 0.01 ~ 4°C/min. • two 3-injection compartments (2ml, 2x3 ml) • dual-channel, speed-adjustable internal vortex magnetic stirrers • start-up kit and glass vessel sizing cup • built-in calibration unit for dynamic constant measurement • built-in pressure or mass flow sensing port (0 to 5 Vdc) • built-in programmable pressure relief port (0 to 500 psi)	$59,000.00	$59,000.00
20800	1	**Thermal Analysis PC System** • Dell 2Ghz, Intel multi-core, 19" flat-panel monitor • Pre-installed multi-channel data acquisition I/O devices • OmniCal WinCRC009 software for control and data analysis	$5,900.00	$5,900.00
20355	1	**Illuminated Borescope for Mixing Visual Observation**	$860.00	$860.00
20334	1	**Integrated Dual Syringe Dosing Pump System** *optional* • Dual syringe dosing pump unit • Differential injection preheating cylinders • PC graphic user interface for dosing control and display	$2,650.00	$2,650.00
20820	1	**Pressure Package I** *optional* • Pressure sensing and relief devices (up to 500 psi) • Two 12mL Hastelloy-C reactors with injection port	$4,380.00	$4,380.00
20846	1	**Dual Overhead Motorized Stirrer System** *optional* • Two overhead motorized stirrers (up to 1500 rpm) • Two sets of Hastelloy-C stirring shafts/stirring paddles (16mL)	$2,480.00	$2,480.00
9106A118	1	**Heating and Cooling Circulator, -20°C to 200°C** *optional*	$ 2,390.00	$2,390.00
20335	1	**2mL plastic syringes with needles (100/pk)** *optional*	$95.00	$95.00
20336	1	**3mL plastic syringes with needles (100/pk)** *optional*	$55.00	$55.00
		Sub-total:		$77,810.00
		Shipping and Handling, Insurance:		970.00
		Total Price:		$78,780.00

Note: 1) The prices are in US dollars, VAT and custom duties excluded
2) Any order resulting from this quotation may be faxed to us at 001-281-494-8875 or send your original to: Omnical Inc., Houston Office, 3727 Greenbriar St., Bldg. 302, Stafford, TX 77477 USA

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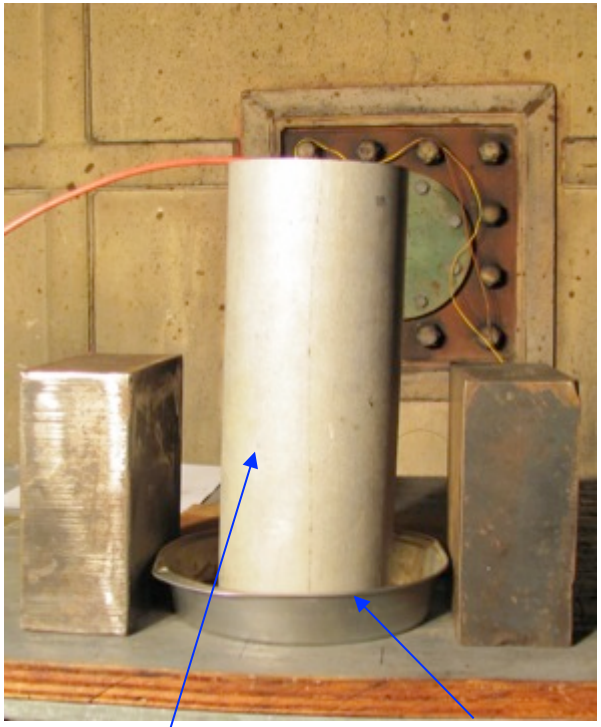
Small Scale Cap Sensitivity Test

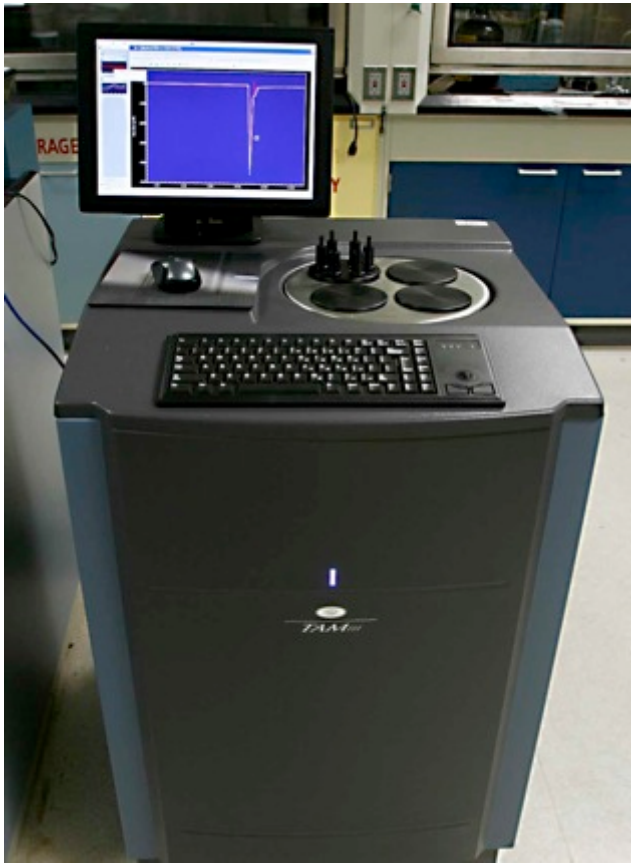
- Nine ml of liquid explosive solution is loaded into a 10-ml glass vial.
- The vial is then closed with a plastic cap pre-fitted with an RP-81 detonator, equivalent to a standard #8 blasting cap.
- The end of the detonator usually had glass microballoons adhering to a thin layer of RTV silicone rubber, to help ensure good ignition of the sample.
- The vial is glued to a ¼-inch aluminum witness plate with epoxy, completely filling the "dimple" in the base of the vial to eliminate shock-focusing effects.

Small Scale Cap Sensitivity Test



- The witness plate sits on a 1-inch thick polyethylene metal cylinder pad
- A metal cylinder surrounding the vial confines the detonator energy to burn unreacted liquid in case of a "No-Go"
- In that case, a steel pan helps contain any unburned residue

Heat Flow Calorimetry



- Heat flow microcalorimetry is a very sensitive method used for measuring heat flow, either exothermic or endothermic, on a microwatt scale, associated with chemical and physical processes.
- The basic setup consists of a large heat sink, usually and aluminum block, that is placed within a stable isothermal temperature bath.
- Thermoelectric sensors consisting of a series of thermocouples for detecting temperature differences allow for extreme sensitivity.
- Within the heat sink is a chamber in which the thermoelectric sensors are housed in close proximity to the sample, which is generally contained in a sealed glass or metal vial.

Heat Flow Calorimetry

- Most materials, particularly energetic materials such as propellants, undergo some degradation over time as a result of chemical reactions taking place within the material.

- Because to of the extreme sensitivity of the method, a heat flow rate, which is the sum of heat flow associated with all the measureable chemical processes taking place within the sample, is usually measurable within a few minutes or hours after the sample is introduced into the calorimeter; however, sometimes up to 24 hours may be necessary to reach equilibrium.

- The raw data are obtained as a table of heat flow rate as a function of time. The sensitivity of the method often allows measurements to be made at temperatures closer to ambient conditions than other thermal techniques.

Heat Flow Calorimetry

- Often the heat flow measured is a result of one predominant reaction and it proportional to the rate of that process. Measurement of the heat flow rate alone does not identify the process or mechanism responsible for the thermal activity and when complex materials are involved there may be multiple processes taking place simultaneously.

- Processes/mechanisms responsible for the thermal activity may be known from previous work, but if not, this determination has to be made by other methods which may be used in conjunction with heat flow data.

- A measure of the heat flow rate at a series of different temperatures can usually be fitted to the Arrhenius equation to obtain the activation energy associated with the process being measured.

- Once this activation energy is obtained, predictions regarding the safe-life or service-life of a material can be made if the processes being measured are those that limit either the safe-life or service-life, respectively. In order for predictions to have any validity, the rates for the life-limiting processes must be to ones being measured to determine the relevant activation energy.

Plans Forward
Ideas

- Possible select 1 HME and perform complete characterization to include synthesis vs. commerical material
  - UN
- Thermal Characterization (ARC) to support compendium

IHDIV
DoD ENERGETICS CENTER
Excellence for the Warfighter

IDCA Materials: Bruceton values vs. Neyer

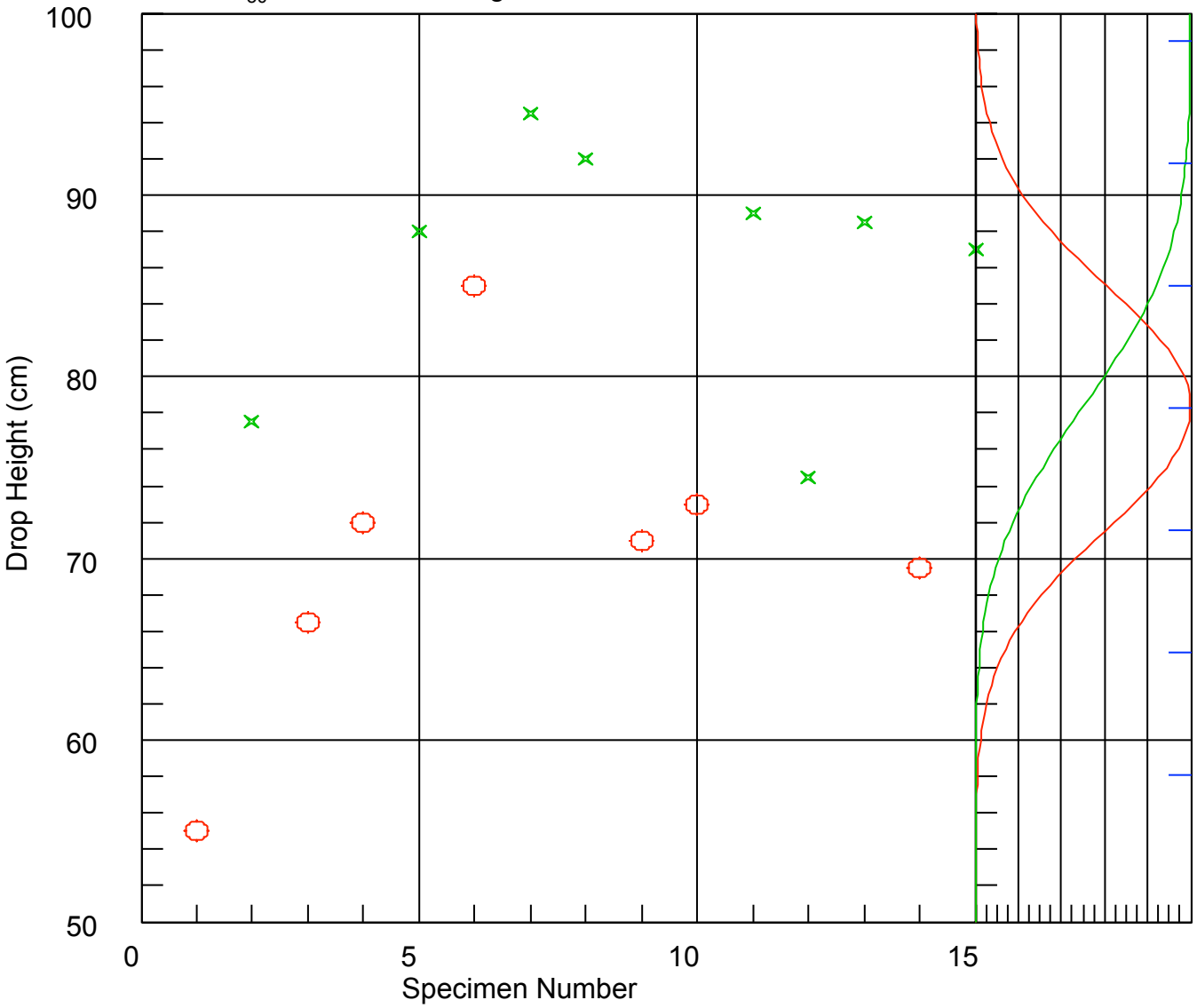
Material	Neyer H50	Neyer σ	Bruceton H50	Bruceton σ (log)
KC + sugar sieve 1	10.3	1.0	10.7	0.076
KC + sugar sieve 2	8.8	1.2	11.8	0.147
KC + sugar sieve 3	8.9	1.7	9.2	0.062
KC + sugar AR 1	11.5	1.7	11.0	0.139
KC + sugar AR 2	11.1	2.3	10.7	0.105
KC + sugar AR 3	8.9	1.6	9.5	0.043
KC + Dodecane 1	6.9	0.6	6.4	0.061
KC + Dodecane 2	7.6	0.5	7.6	0.027
KC + Dodecane 3	9.3	1.5	10.2	0.08
KP + Al 1	78.3	6.7	56.7	0.157
KP + Al 2	53.1	7.0	60.0	0.043
KP + Al 3	67.9	5.2	69.1	0.04

Standard material	Neyer H50	Neyer σ	Bruceton H50	Bruceton σ (log)
PETN 4/16/10	10.3	1.8	8.7	0.076
PETN 4/28/10	7.4	2.5	7.1	0.243
PETN 5/25/10	9.3	1.5	11.2	0.035

ERL Type 12 Impact Sensitivity: *Neyer D-Optimal Method*

Analytical Lab No.: 51088 E, LIMS#: 100414001, **Material:KClO4/Al 68/32**, Date: 04/16/2010

H_{50} = 78.3072 cm, Sigma = 6.72881 cm

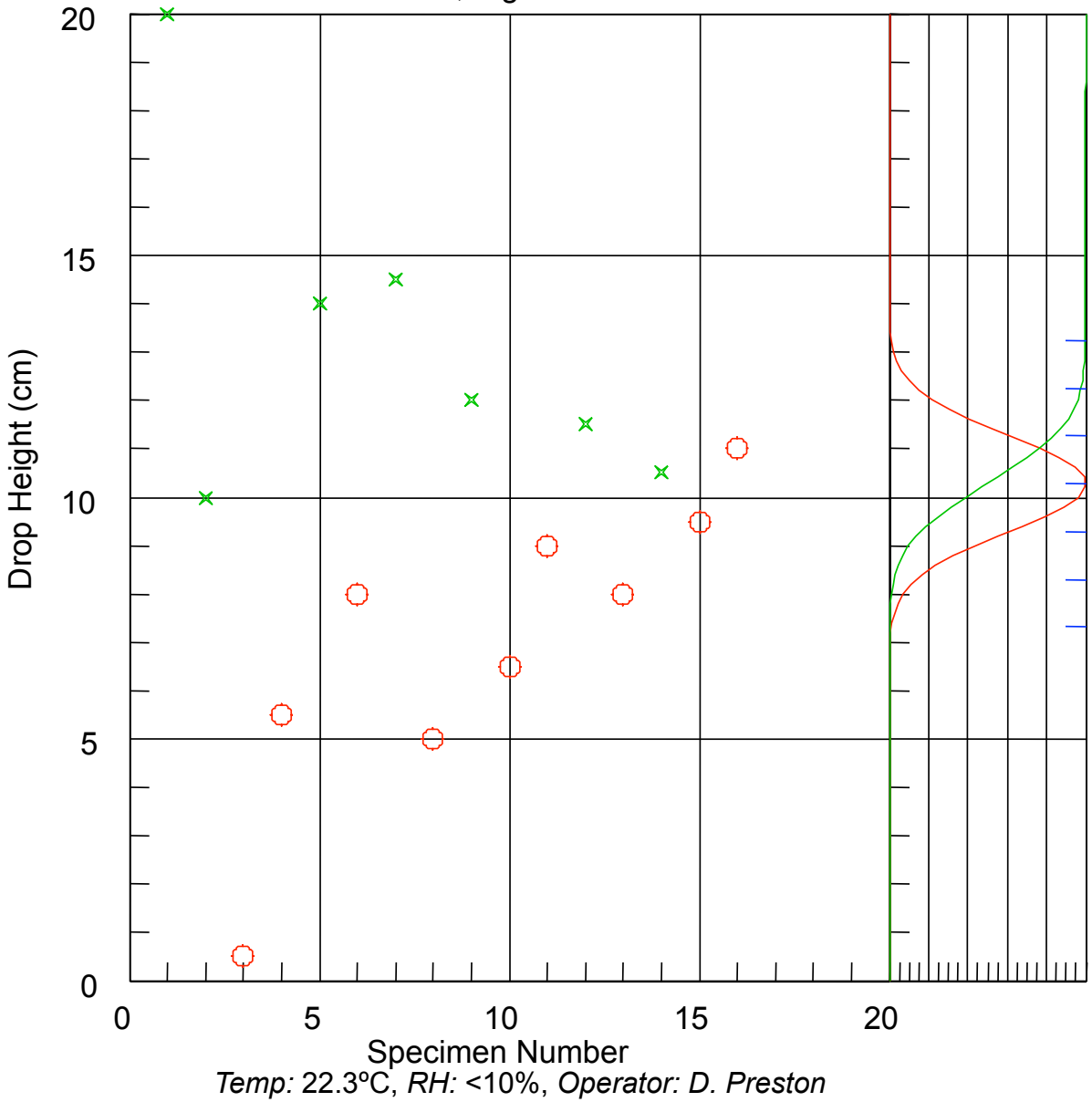


Temp: 23.4ºC, *RH:* 22.5%, *Operator: Pollard*

ERL Type 12 Impact Sensitivity: *Neyer D-Optimal Method*

Material: **KC Sugar Sieved**, Date: 04/28/2010

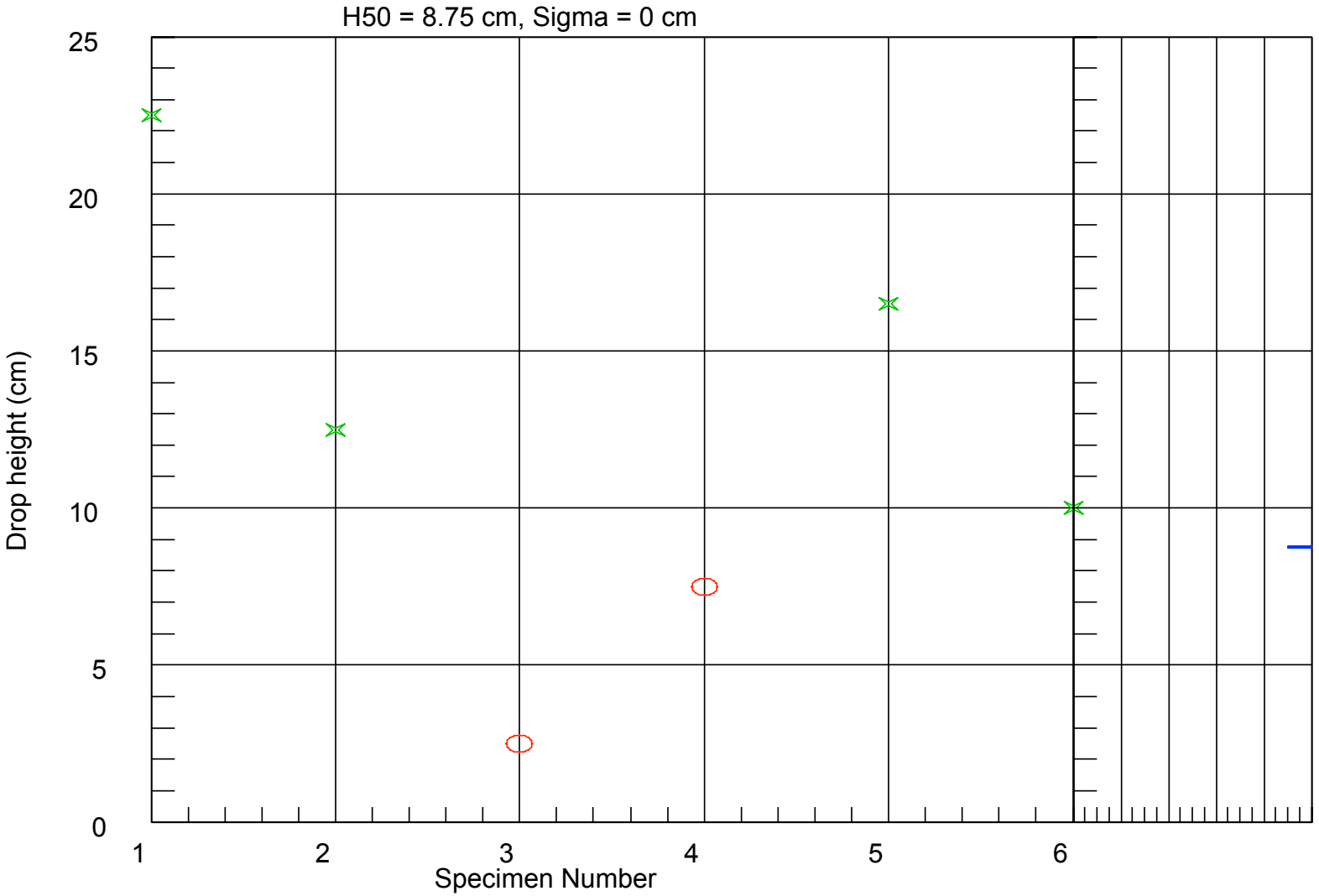
H50 = 10.2751 cm, Sigma = 0.987675 cm



Temp: 22.3ºC, *RH:* <10%, *Operator: D. Preston*

ERL Type 12 Impact Sensitivity: *Neyer D-Optimal Method*

Material: BNDD, Date: 08/04/2010



Temp: 21.2ºC, *RH:* 61.1%, *Operator: Pollard*

Bruceton vs. D-optimal Methods

Daniel Preston, WX-7

Introduction: Explosive Research Laboratory (ERL) Drop Tower

- Fabricated in house
- 2.5Kg drop weight
- Go's determined by 2 sound level meters
- An average reading of RMS pressure >119.5dB is a "Go"

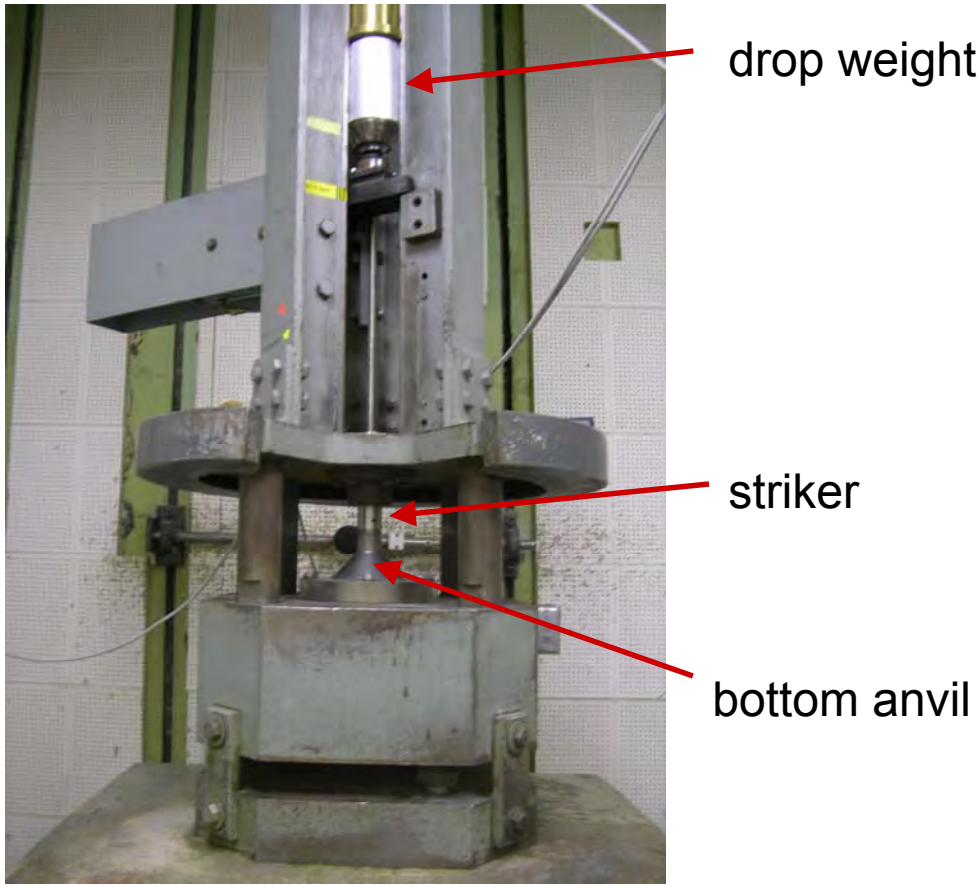


figure 1: drop weight impact machine

Introduction con't: type 12 vs. type 12B

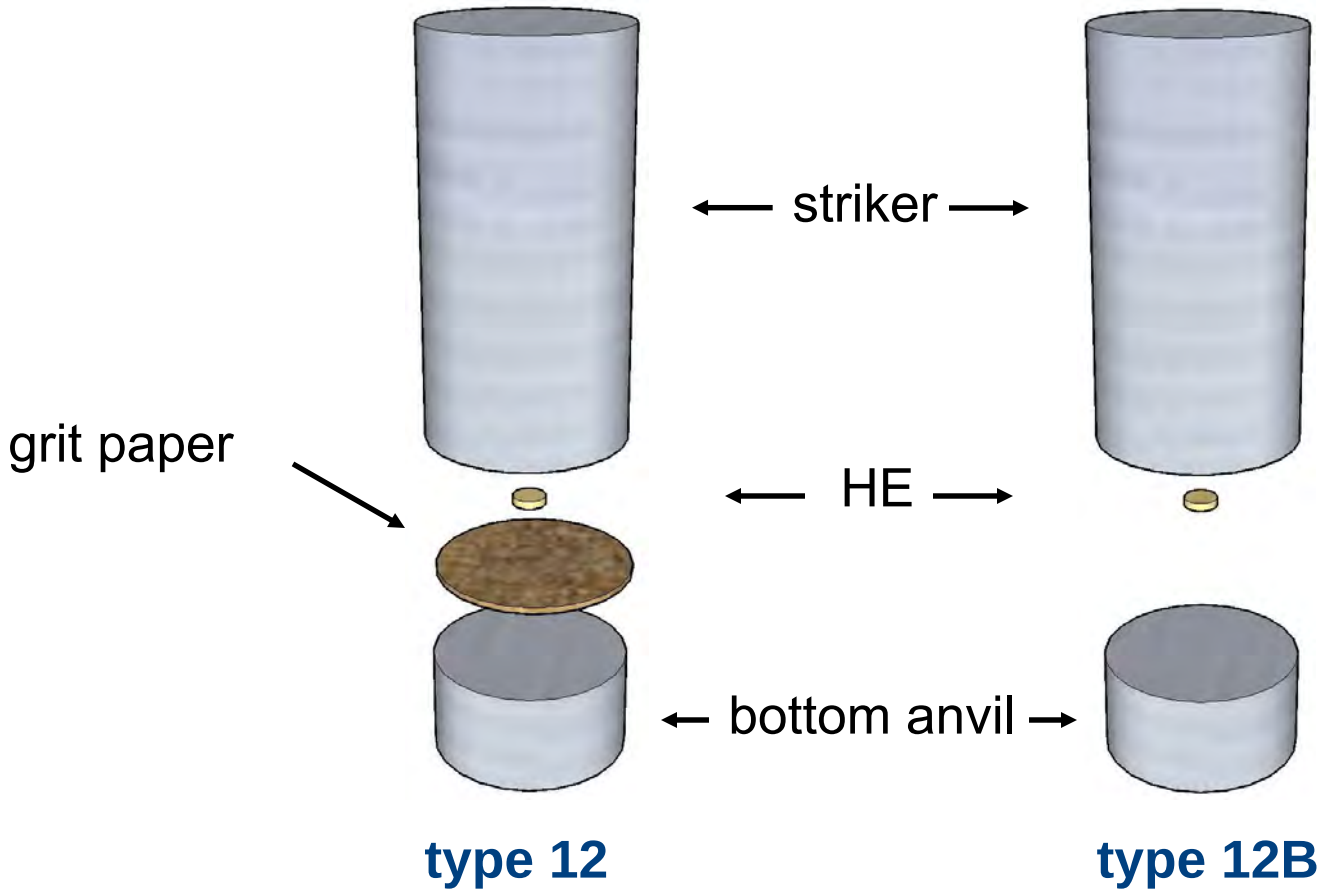


figure 2: type12 vs. type12B

Analysis method: Bruceton

- Developed in Bruceton PA at the Explosives Research Laboratory in the early 1940's
- H50's can be generated with a hand calculation
- Collects data only around the 50% level and does not test into the tails of the bell curve
- A standard deviation is generated but due to limited testing range it can be unreliable if you are not careful
- Typical ERL drop weight testing is done on a log scale generating a standard deviation in log units relative to the H50 offering little utility

Analysis method con't: Bruceton

ERL Type 12 Impact Sensitivity Data Sheet

Ht (log)	Ht (cm)	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	Σ E	Σ N
2.4548	285.0	E		E		E		E		E		E		E		E		E		E		E		E		E	13	0
2.4048	254.0		N		N		N		N		N		N		N		N		N		N		N		N		0	12
#NUM!																											0	0
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																										Totals:	13	12

figure 3: Limiting data collection scenario using Bruceton method

Analysis method con't : Neyer's D-optimal

- Targets 83% and 17% probability
- Software suggests successive testing heights
- Immediately produces graphical results
- Commercially available write protected software
- Minimizes data entry errors and transcription
- Decrease number of required drops for each test material on average by 50%
  - Decreases mass of material required to complete the evaluation
  - Decreases the labor cost for the testing

Analysis method con't : Neyer's D-optimal

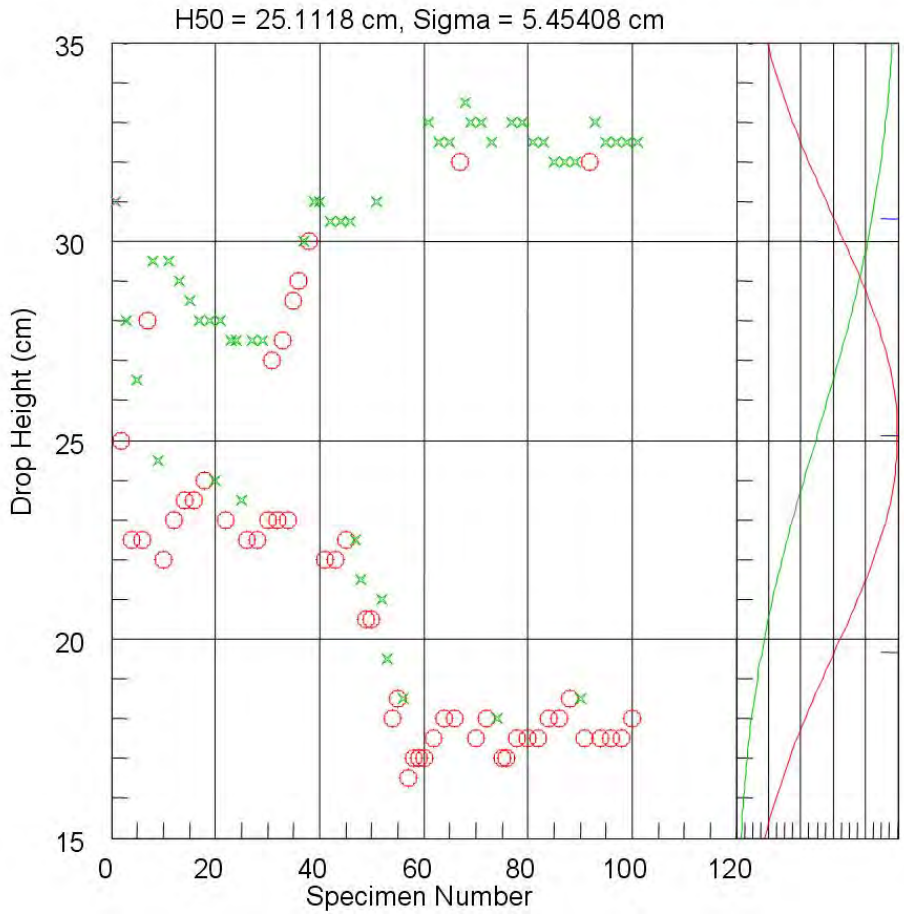
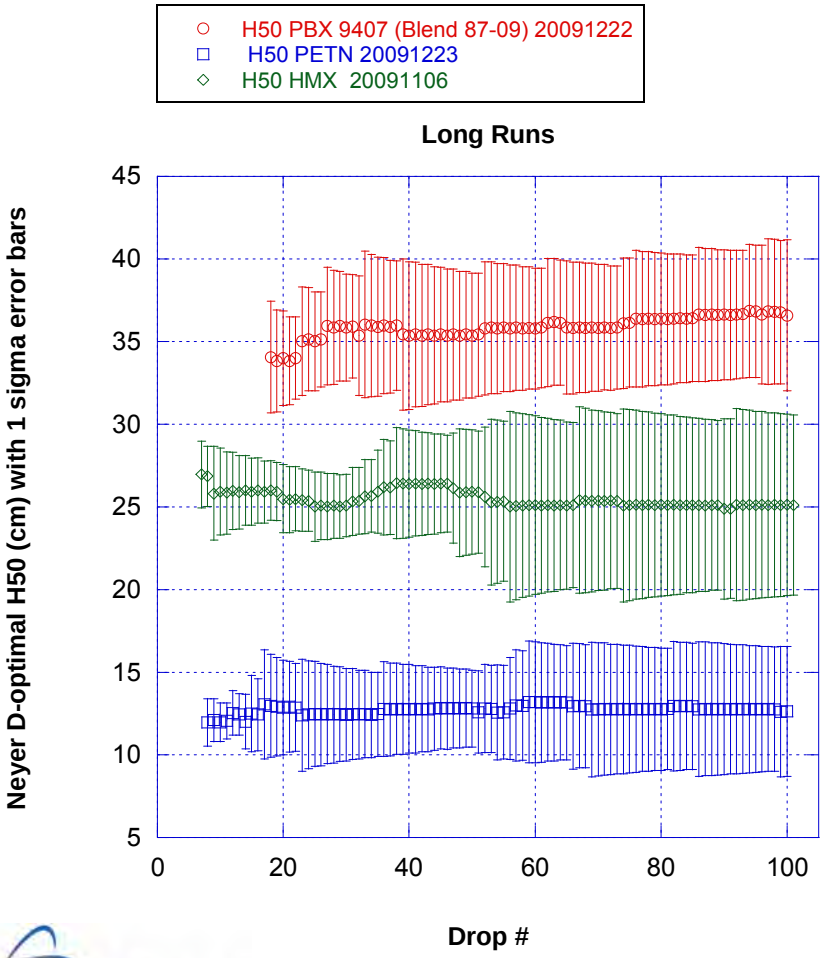


figure 4: HMX, 101 drops using D-optimal method

Choosing a D-optimal sample size



H50 average, cm

	PBX 9407	*PETN*	*HMX*
Neyer	36.8	12.9	25.7
Bruceton	35.2	12.8	23.2
Δ	1.6	0.1	2.5

NETZSCH

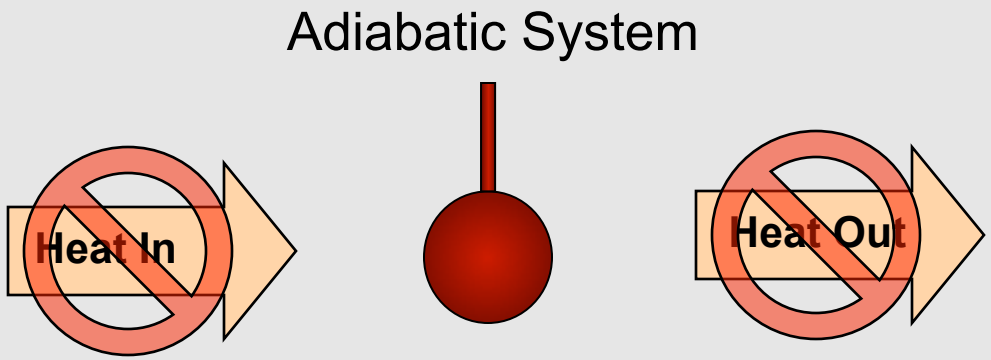
NETZSCH Instruments

APTAC Training, LANL April 2009

Slides provided by Peter Ralbovsky, Netzsch.

Adiabatic Calorimeters

- Adiabatic calorimeters are designed to minimize the heat energy loss or gain of the sample. Heat generated by the sample due to exothermic activity should not be lost to the environment. The energy released should be only be used to heat the sample (self-heating).



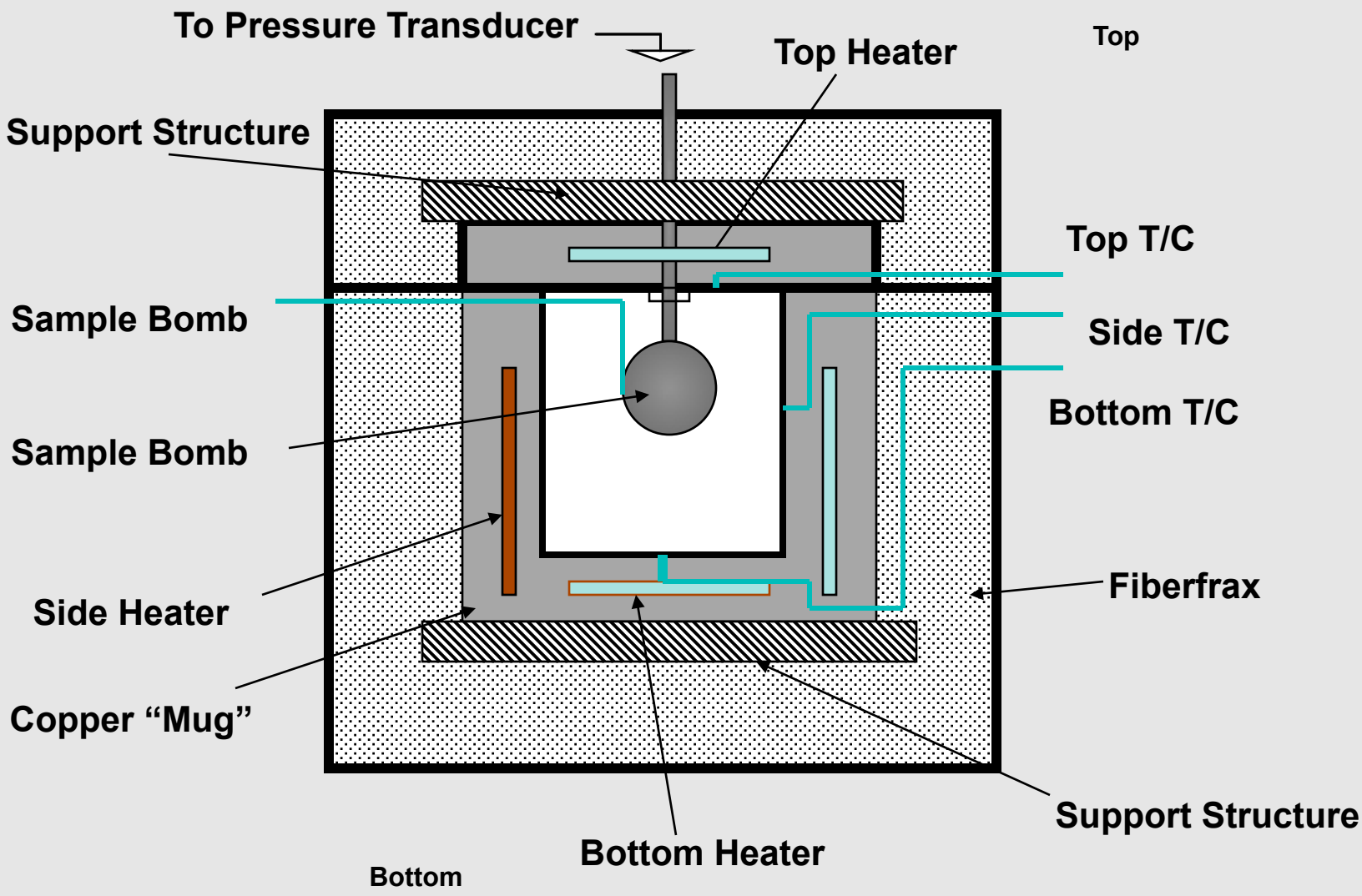
- All calorimeters have heat losses of one form or another. A well-designed calorimeter calibrated correctly will minimize these losses.

Adiabatic Calorimeters

NETZSCH

- We use three basic types of adiabatic calorimeters:
  - ARC®- The original ARC was developed by Dow in the 1970s and has been used widely around the world in chemical process safety
  - APTAC™- Developed by Dr. Chippett while at Union Carbide and at Arthur D. Little, Inc. This high performance adiabatic calorimeter not only tracks the sample temperature but also the sample pressure
  - New ARC®-The design of this new calorimeter was based on the APTAC system and lessons learned from the original ARC design
  - New ARC® Upgrade-The system uses the original ARC calorimeter and the NEW ARC electronics

Original ARC Calorimeter Design



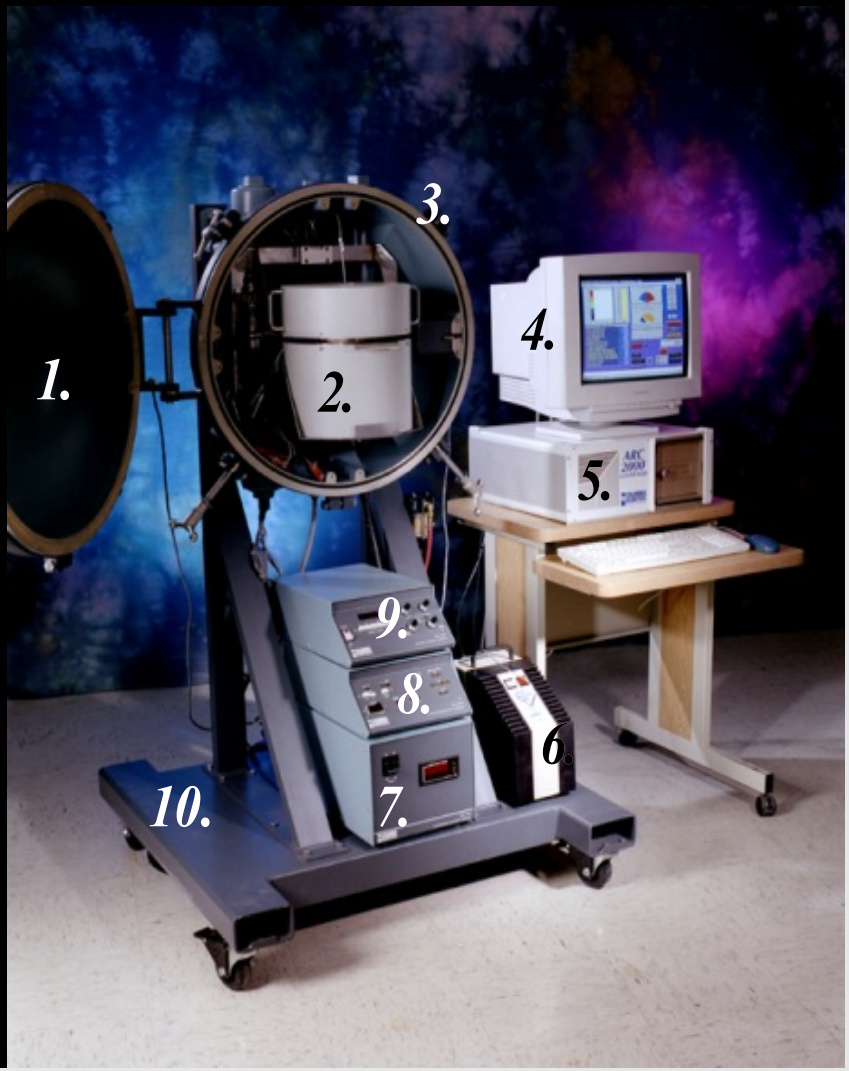
Original ARC Calorimeter

NETZSCH

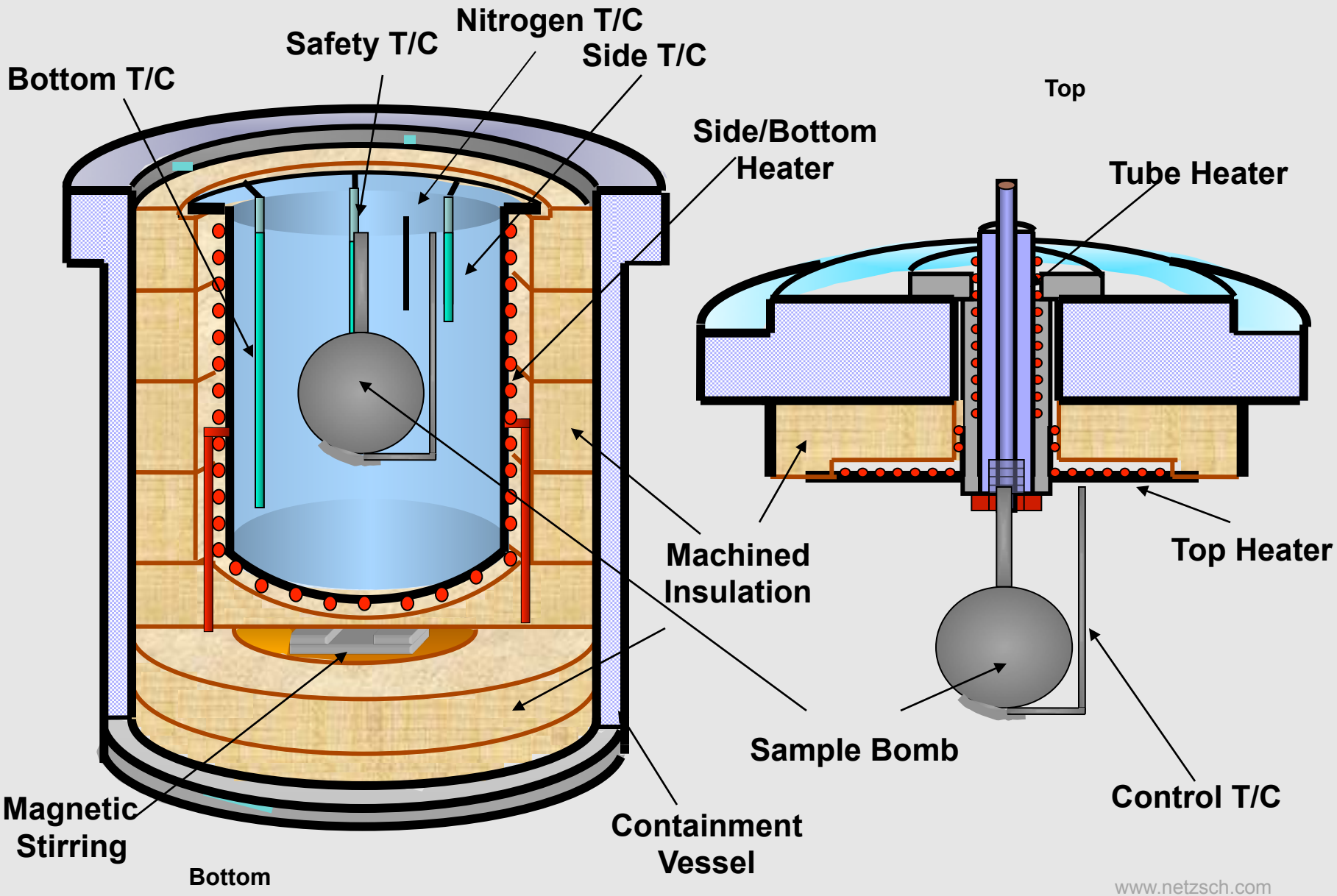
ARC® SYSTEM

1. Clamshell Door
2. Calorimeter
3. Containment Vessel
4. Monitor
5. ARC® 2000 Controller
6. Ice Point Reference Unit
7. Calorimeter Support Module (CSM)
8. Power Management Module
9. Stirrer Support Module (SSM)
10. Stand

A



ARC 254/APTAC™

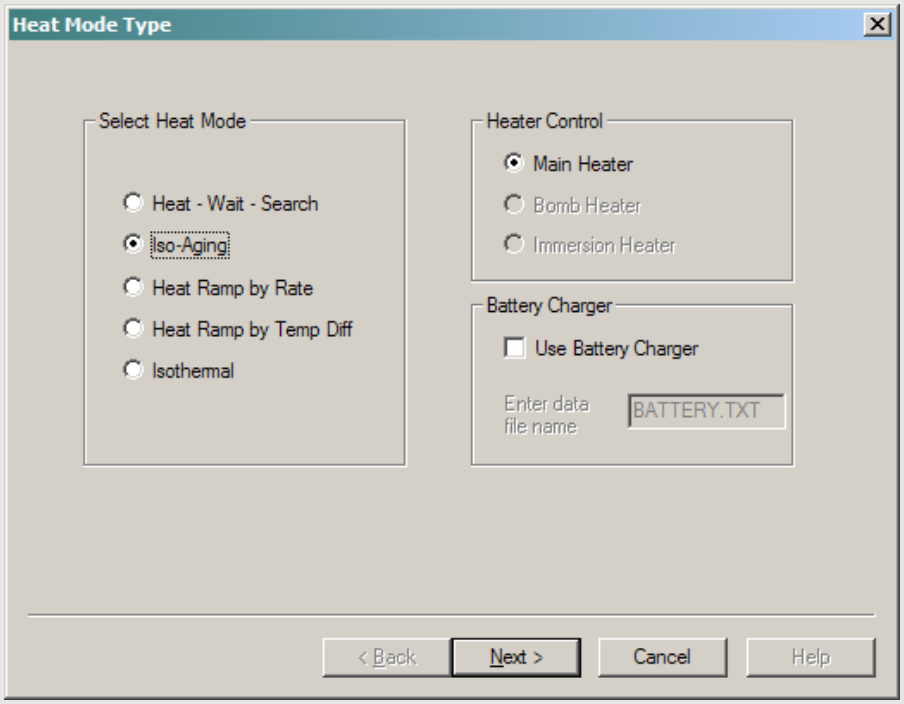


ARC254/APTAC

1. Primary Power
2. Heater Power
3. Control Power
4. Signal Conditioning
5. Calorimeter Assembly
6. Vent System (option)
7. Mixing Motor (option)
8. Computer
9. Monitor
10. Top Cover Assembly
11. Start Stop Assembly

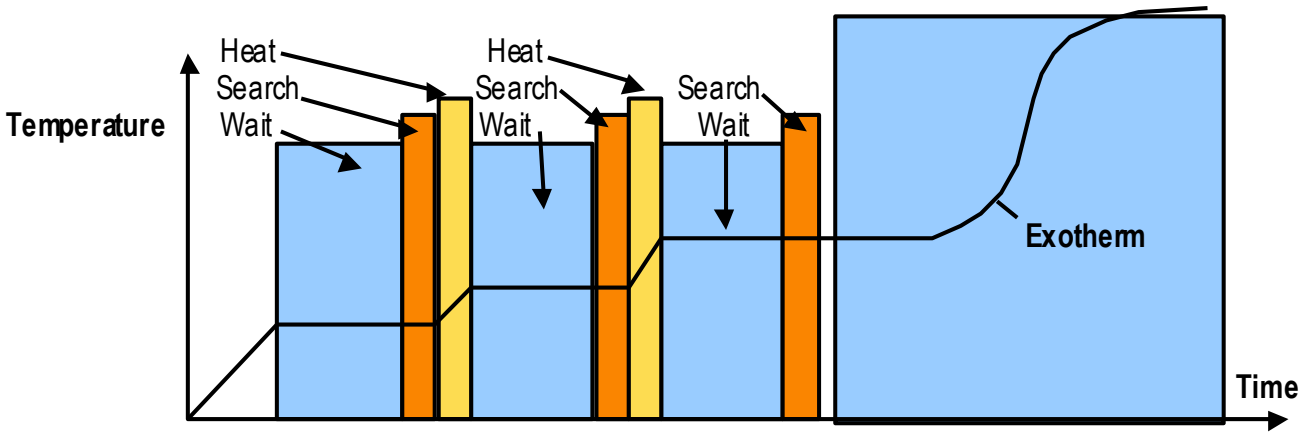
Modes of Operation

- Modes of operation
  - HWS™ (heat-wait-search™)
  - Anneal, Calibrate, Drift
  - Iso age (isothermal)
    - Iso fixed™
    - Iso track™
  - Ramp
  - Ramp Adiabatic

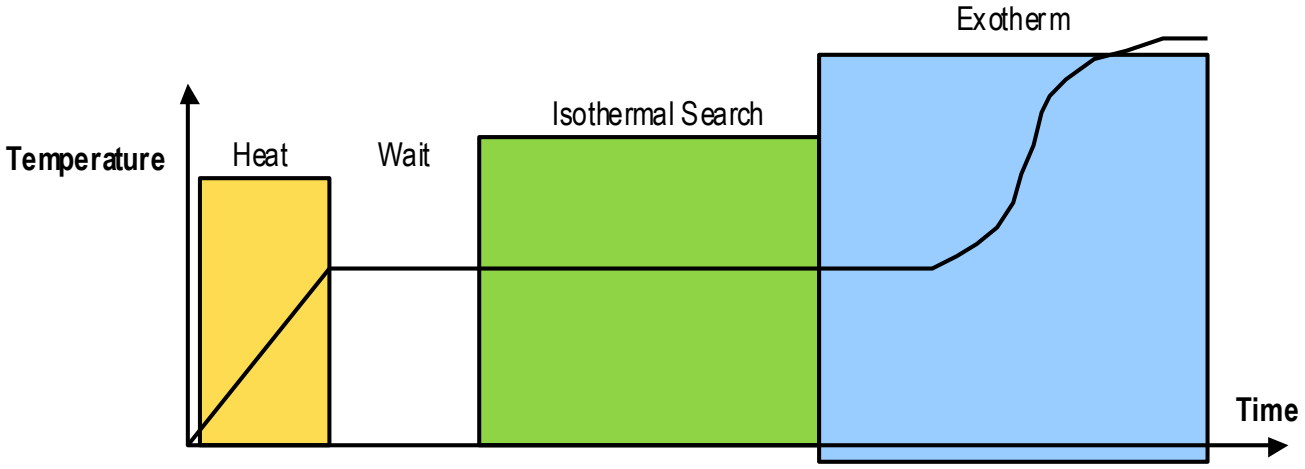


Agenda

Heat-Wait-Search *Operation*

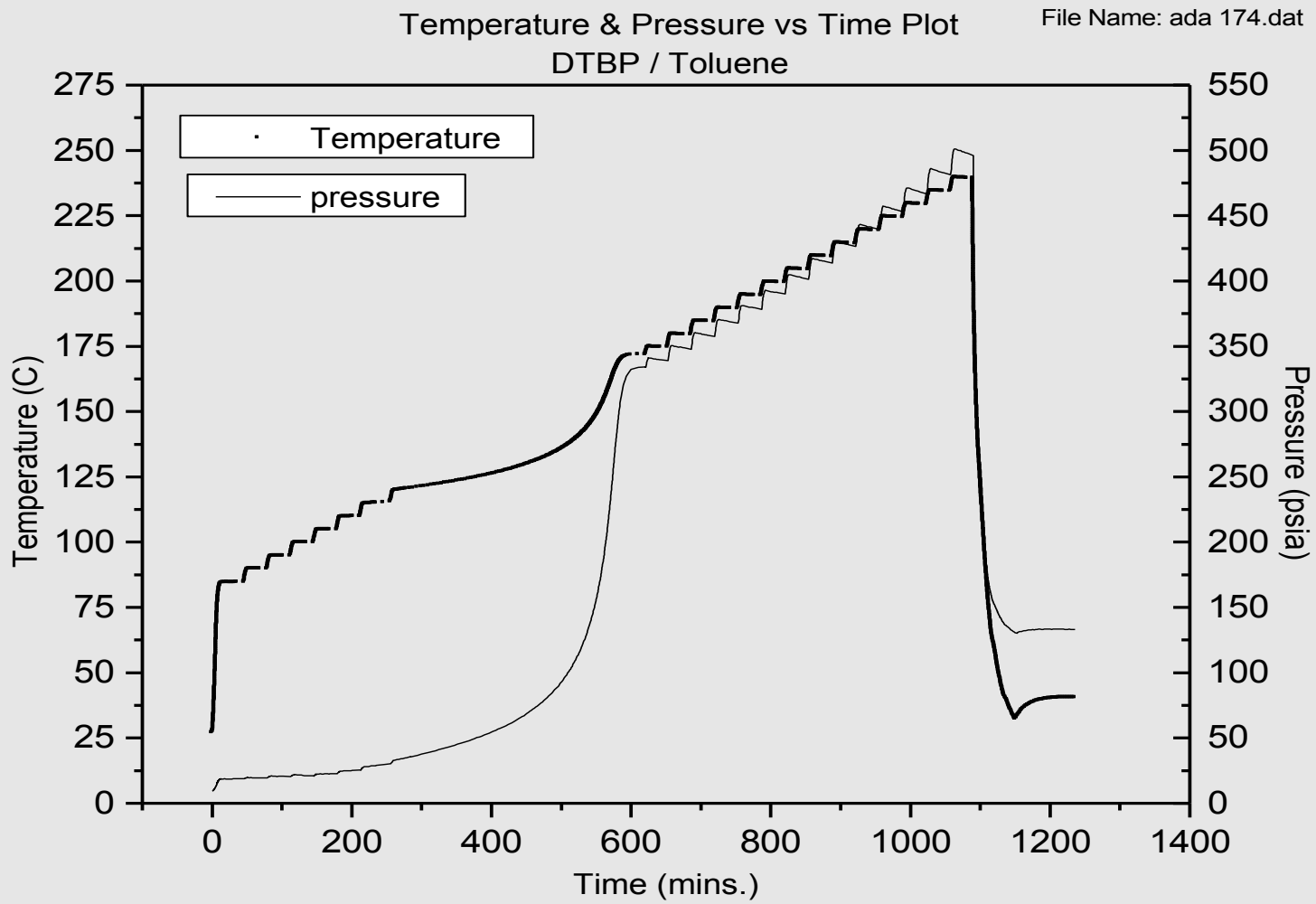


Isothermal Aging Option



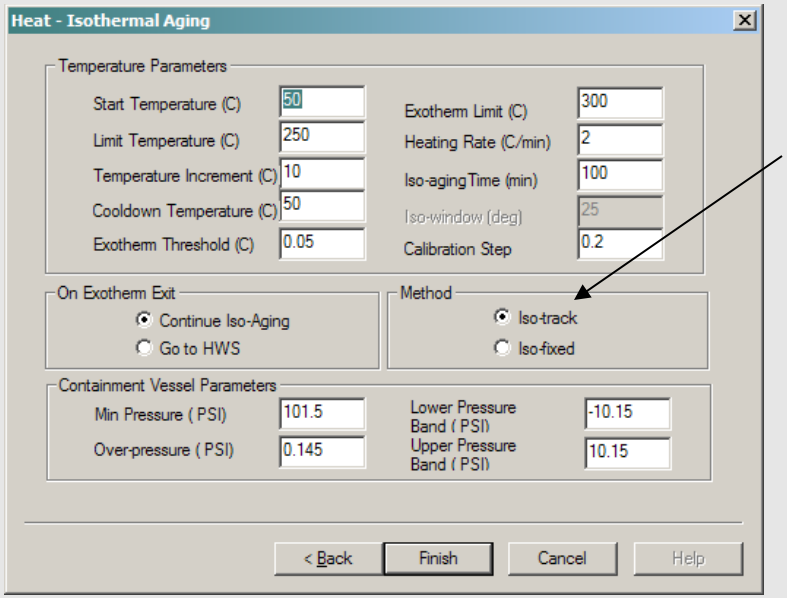
A

Standard Heat-Wait-Search Test



Iso-Aging Comparison

- Iso-Fixed Line™ Method
  - maximum temperature control
  - long term isothermal aging
  - good for storage stability
  - uses standard calibration
- Iso-Track Line™ Method
  - maximum exotherm sensitivity
  - short isothermal aging
  - good for autocatalytic investigation
  - needs isothermal calibration
    - Run calibration points around the iso-aging temperature
    - Drift rate of 0.01C/min over 10 hours is 6C
      - 0.01C/min x 10 hours x 60 min/hour = 6 C
      - If you start at 100C, 10 hours later you would be at 106C



Experimental Design Agenda

- Bombs Types
- Thermal Inertia
- Experimental Parameters
- Run Sheets/Databases
- Before, During, After the Run

Experimental Design- Bomb Selection

- There are a wide choice of bombs available (TIAX part numbers)
  - 851-3068 Titanium 1”ID x .032W 1/8” stem 10.2g
  - 851-3309 Titanium .5”ID x .020”W 1/8” stem
  - 851-3317 Titanium 1”ID x .020”W 1/8” stem, 9.5 g
  - 851-3316 Titanium 1”ID x .020”W 1/4” stem, 6.4 g
  - 851-3186 SS316 1”ID x .032”W 1/8” stem,15. 5g
  - 851-3070 Hastelloy C 1”ID x .032”W 1/8” stem, 19.1g
  - 851-8065 Hastelloy C/stir 1”ID x .032”W 1/8” stem,22.5g
  - 851-3322 Hastelloy C 1”ID x .032”W 1/4” stem, 21.0g
  - 851-3299 Ti Gr 2 1”ID x .035” 1/4” stem, bottom clip, 10.4g
  - 851-3329 SS316 1”ID x .032”W 1/4” stem, 17g
  - custom bomb design and materials (tantalum, SS304, etc..)

Bomb Selection- Thermal Inertia Phi-Factor

NETZSCH

- Thermal Inertia is an important factor to be considered with ARC® experiments. It is a function of the sample mass, bomb mass, and their heat capacities.

$$\phi = \frac{(M_o \times Cp_o) + (M_c \times Cp_c)}{(M_s \times Cp_s)} + 1$$

Where:
Mo = Mass of Bomb (g)
Cpo = Specific heat of bomb (cal /g C)
Mc = Mass of Clip (g)
Cpc = Specific heat of bomb (cal /g C)
Ms = Mass of the Sample (g)
Cps = Specific heat of Sample (cal /g C)

Bomb Selection – Phi Factor Example

NETZSCH

- A titanium bomb weighing 10.45g with a 1.67 316 stainless steel clip is loaded with 3.5g of Nitrobenzene. What is the Phi Factor at room temperature?

Cp of titanium = 0.12 cal/ g C
Cp of 316SS = 0.12 cal/ g C
Cp of Nitrobenzene = 0.33 cal/ g C

$$\phi = \frac{(10.4g \times 0.12cal/gC) + (1.67g \times 0.12cal/gC)}{(3.5g \times 0.33cal/gC)} + 1$$

= 1.28

Agenda

- Adiabatic Calorimeters
- Calibration
- Experimental Design
- **Standard DTBP Test**
- Trouble-Shooting
- SADT

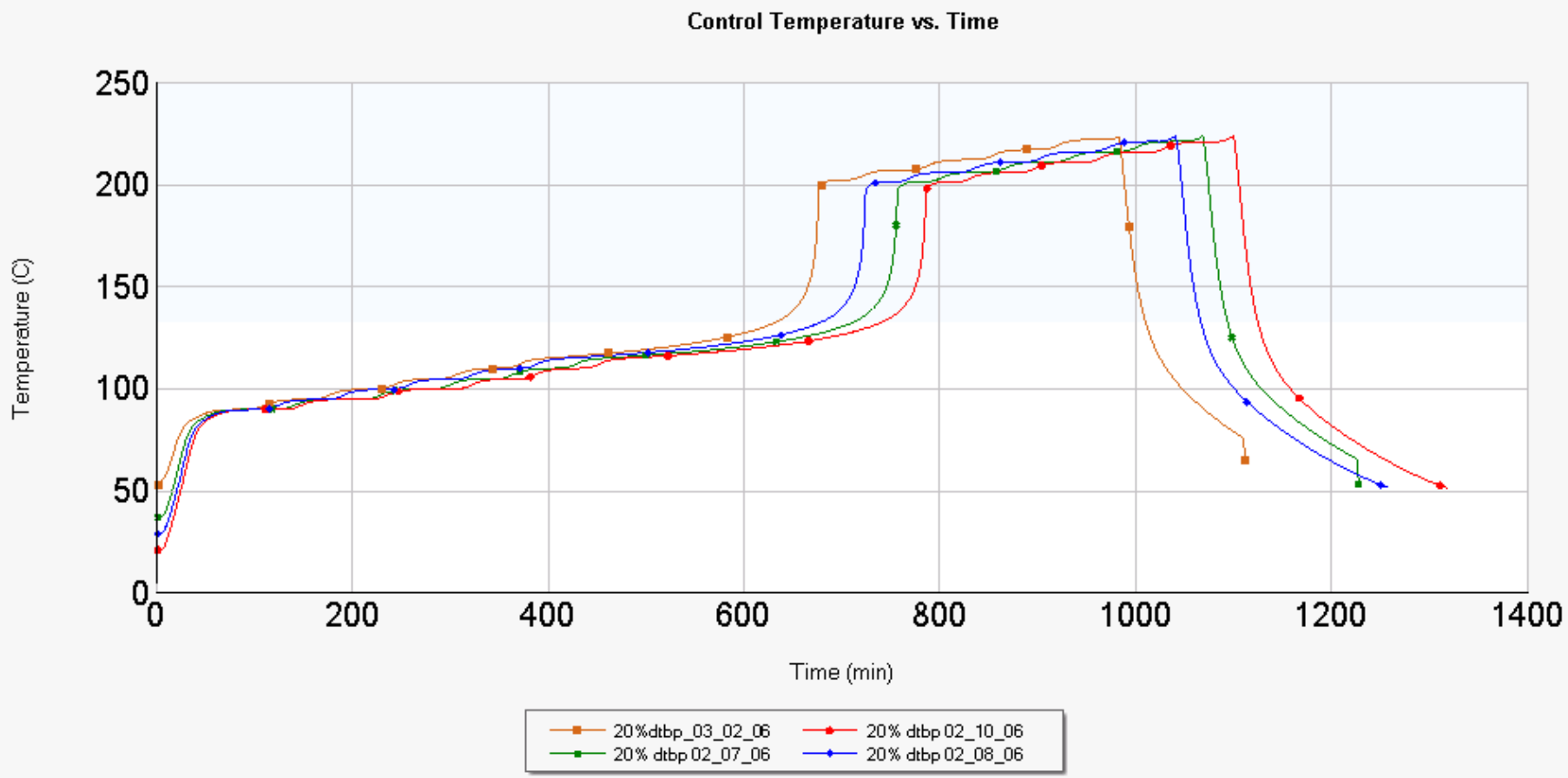
DTBP Standard ARC Test

- 20% DTBP (wt/wt) in toluene
- Sample size and bomb mass chosen so thermal inertia = 1.5

Component	Mass (g)	Specific Heat (cal /g °C
Bomb, Ti (851-3299)	~10.2	0.14
Sample	~5.6	0.5
Al foil	~0.25	0.22

- Experimental Settings
  - Start Temp 90C
  - Exo threshold 0.02C/min
  - Step size 5C
  - Limit Temp 225C

4 DTBP Test Runs



Agenda

- Adiabatic Calorimeters
- Calibration
- Experimental Design
- Standard DTBP Test
- Trouble-Shooting
- SADT

NETZSCH

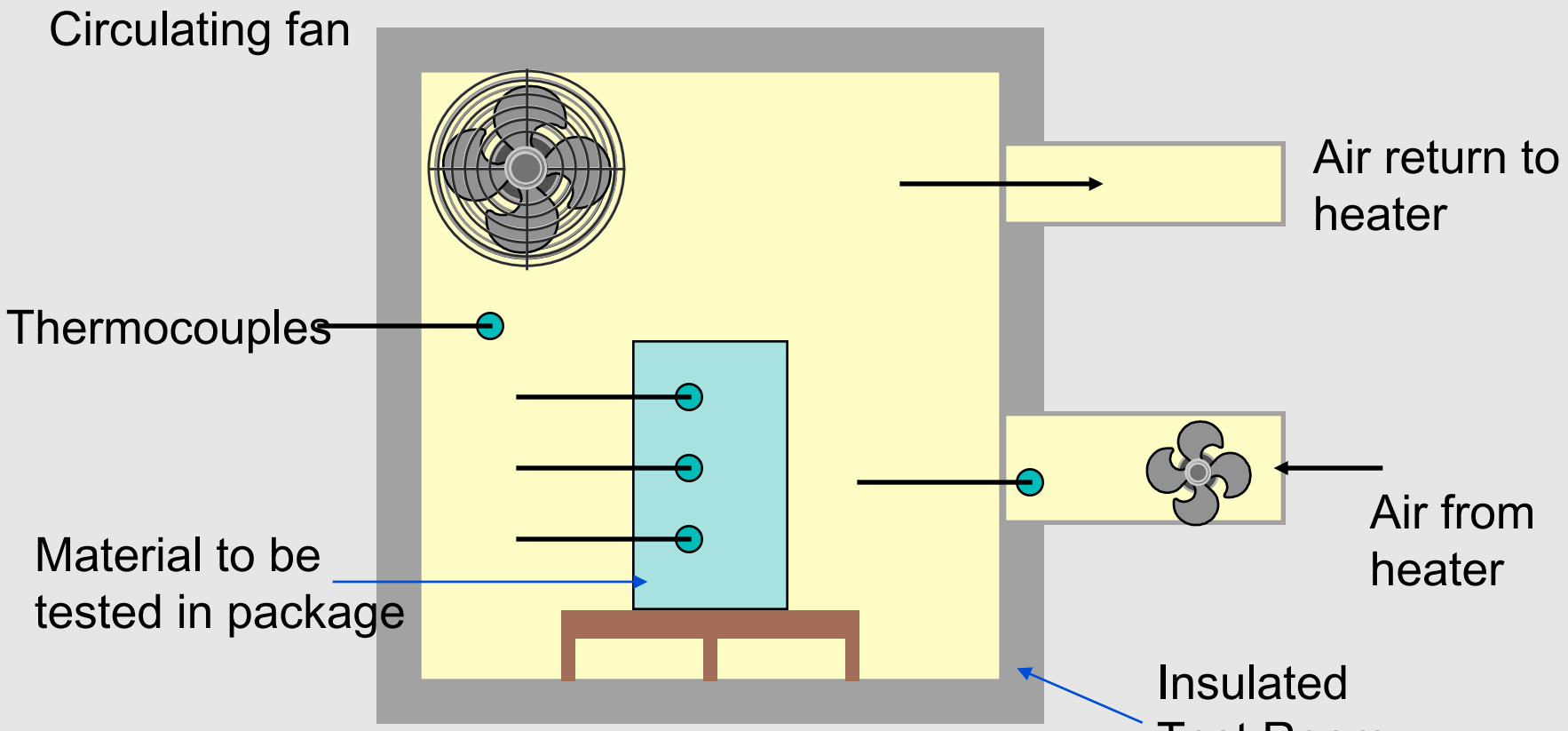
SELF-ACCELERATING DECOMPOSITION TEMPERATURE (SADT)

THE LOWEST AMBIENT AIR TEMPERATURE AT WHICH A SELF-REACTIVE SUBSTANCE WILL UNDERGO AN EXOTHERMIC REACTION IN A SPECIFIED PACKAGE IN A PERIOD OF SEVEN DAYS OR LESS

SADT Explained

- SADTs are measured to determine if a substance should be maintained in a temperature controlled environment during shipping.
- If the tested material exhibits thermal runaway at 55 deg C or less, then temperature control during shipping is required.

The US SADT Test



SADT Problems

- Each package type must be tested
- Uses large samples
  - Not always readily available
  - Potentially large amounts of (noxious/toxic) products
- Tests are expensive and time consuming.
- Need to be done in remote location.
- Only a small number of commercial facilities to do the tests.

ARC Test for SADT

- Can also use the ARC to determine the SADT.
- Obtain E, A, ΔH_r by analysis of ARC data
- Estimate heat transfer parameters relating to the actual shipping package
- Calculate the SADT using measured data and heat transfer data.

Assumptions

- Homogeneous system
- No reactant depletion (zero order kinetics)
- Simple reaction mechanism (single reaction)
- No mechanism change at the temperatures of interest (e.g. a phase change where reaction rates may be much higher in the liquid phase as opposed to the solid)
- Constant ambient temperature
- Constant physical properties
- Steady state
- High heat of reaction
- High activation energy

General Procedure

- Obtain the self-heat rate curve for the material from an ARC experiment
- Obtain the Time-to-Maximum-Rate (TMR) curve for the material
- Obtain the activation energy for the material
- Correct the TMR curve to a $\Phi = 1$
- Measure a system time constant from a cooling curve for the package $[(US/mC_p) = t_{NR}]$
- Use the time constant and the $TMR_{\Phi=1}$ curve to obtain T_{NR} and thus T_{SADT}

SADT Formulas

$$t_{NR} = mCp/US \qquad T_{SADT} = T_{NR} - (RT_{NR}^2 /E)$$

- t_{NR} = the time to reach maximum rate from the point of no return
- T_{NR} = the temperature of no return
- m = mass of package
- C_p = heat capacity
- U = heat loss characteristic
- S = surface area
- R = universal gas constant
- E = activation energy
- T_{SADT} = Self Accelerating Decomposition Temperature

Agenda

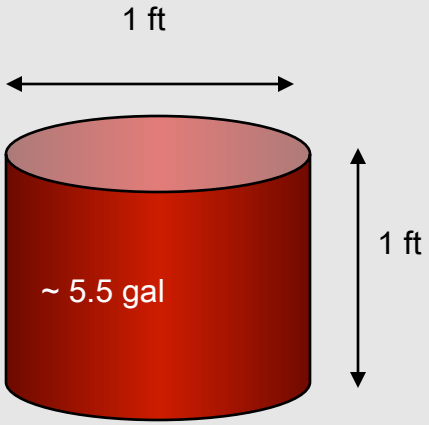
Constants

U =

- 2 btu/(hr*ft^2*°F) uninsulated, painted metal
- 0.5 btu/(hr*ft2*°F) insulated
- 5 btu/(hr*ft2*°F) windy
- 10 btu/(hr*ft2*°F) rainy

R = 8.314472(15) J · K-1 · mol-1

Calculating SADT Example



Problem: Calculate SADT for a cylindrical container with a 1 ft diameter top that is 1 foot tall containing 55 lbs of 20% DTBP in Toluene.

M = 55 lbs

Cp of DTBP = 0.5 cal/g/°C

Surface Area (S) of a cylinder = $2*(\pi r^2)+ (2\pi r)(h)$

$= 2(3.14159)(.5ft)^2 + 2(3.14159)(.5ft)(1\ ft)$

$S= 4.71ft^2$

Calculating t_{NR} Example

NETZSCH

$$t_{NR} = mCp/US$$

t_{NR} = (55 lbs)(.5 cal/g/C)/ (2 btu/(hr*ft2*°F)(4.71 sq ft))

55 lb, lbs = 24 948 gram

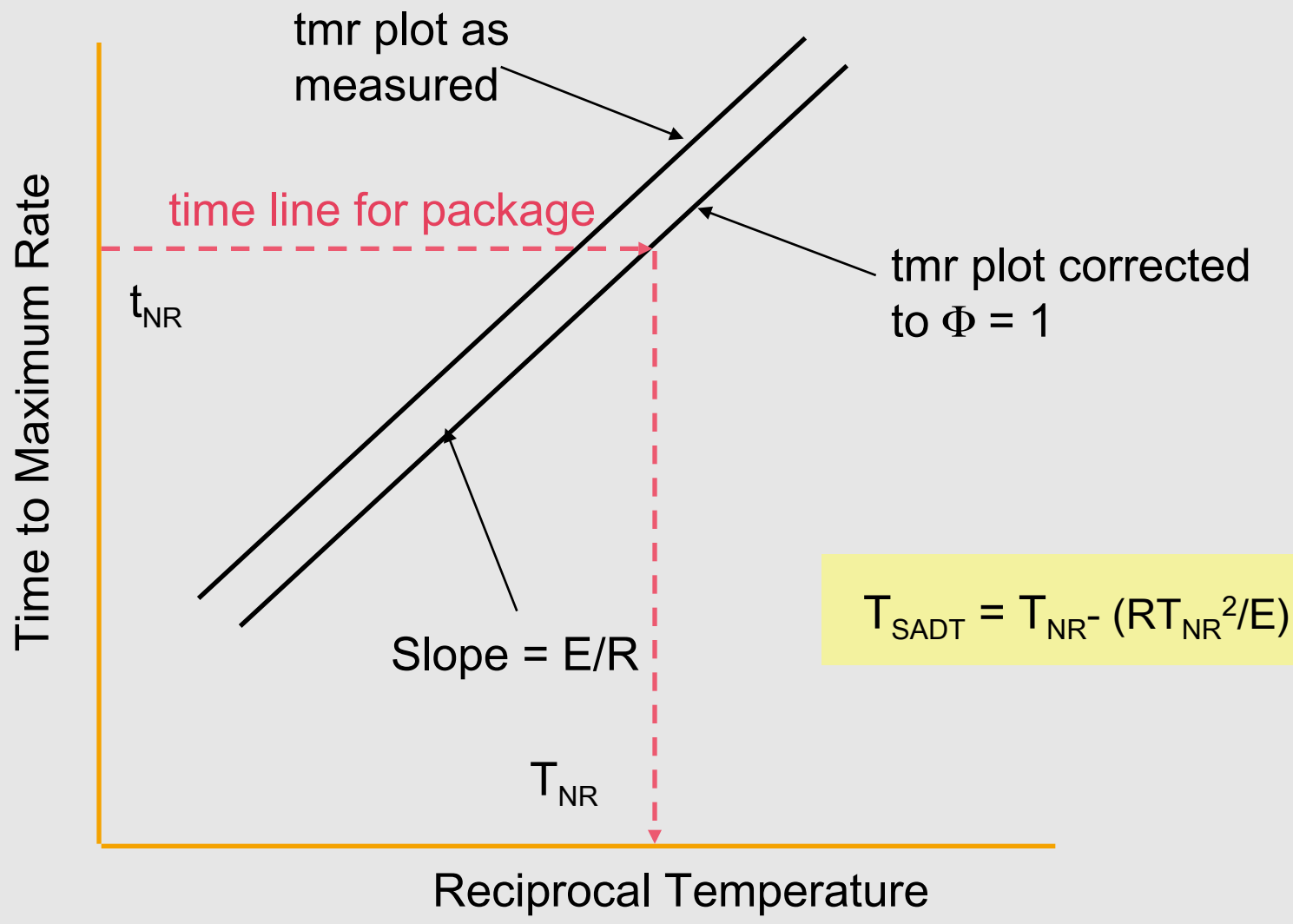
2 Btu = 504 calorie

1 °C = 1.8 °F

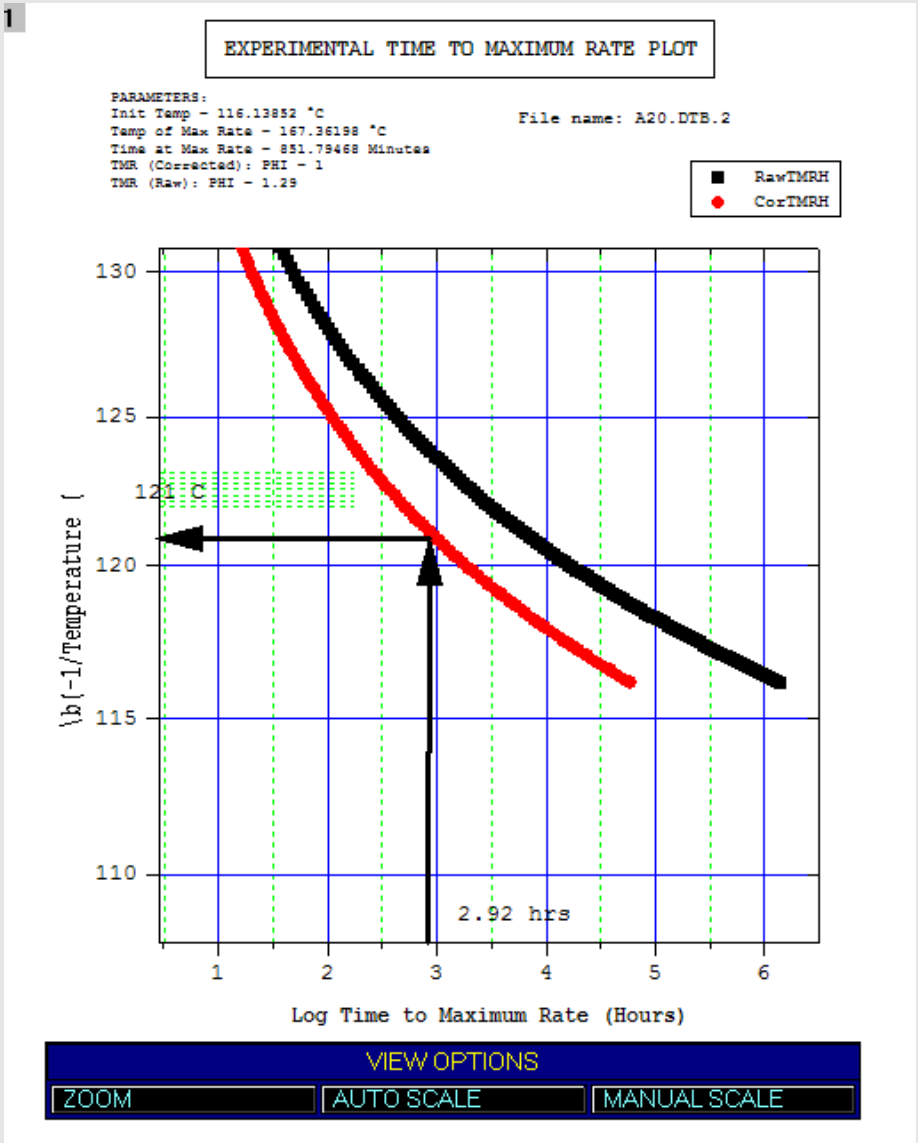
t_{NR} = (24, 948 g)(.5 cal/g/C)(1 C/1.8 F)/ (504 cal/(hr*ft2*°F)(4.71 sq ft))

$$t_{NR} = 2.92 \text{ hrs}$$

SADT Determination



Time to Maximum Rate Plot



SADT Determination

$$T_{SADT} = T_{NR} - (RT_{NR}^2 / E)$$

$$T_{NR} = 121°C\ (394K)$$

$$E = 37.5\ kcal/mol = 15{,}700\ J/mol$$

$$\boldsymbol{R} = 8.314\ J \cdot K\text{-}1 \cdot mol\text{-}1$$

$$T_{SADT} = 394K - (8.314J/K/mol\ (394K)^2 / 15700\ J/mol)$$

$$T_{SADT} = 38.8°C$$

Energetic Materials Research Group: Understanding the role low temperature physicochemical processes play in the performance, safety and aging response of energetic materials throughout their lifecycle

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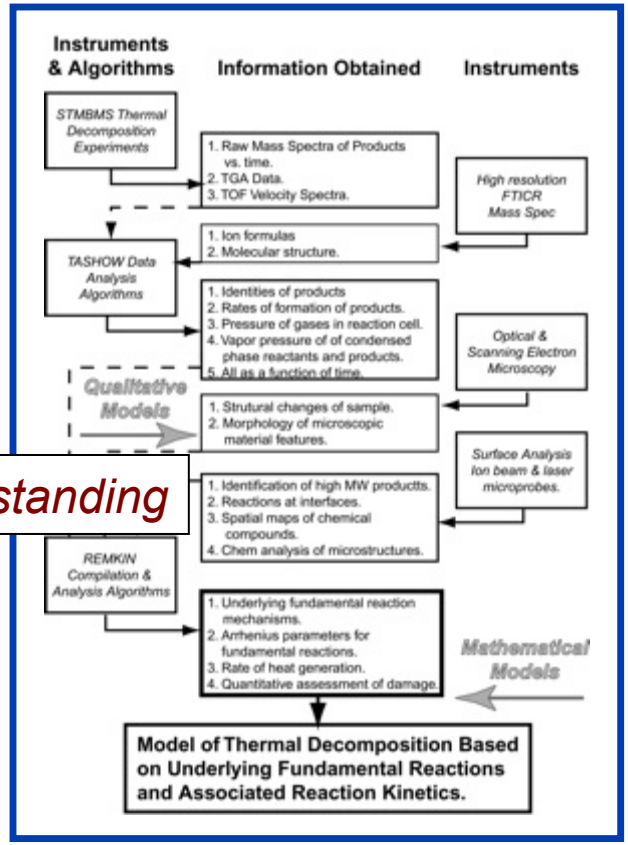
Dept 08128: Remote Sensing and Energetic Materials

Energetic Materials and Chemical Microanalysis Laboratories

Two laboratories and highly developed experimental and numerical algorithms enable accurate determination of decomposition mechanisms/ kinetics for any material of interest

Experimental and simulation methods are applied to develop predictive models



Understanding

Mathematical Models

STMBMS apparatus

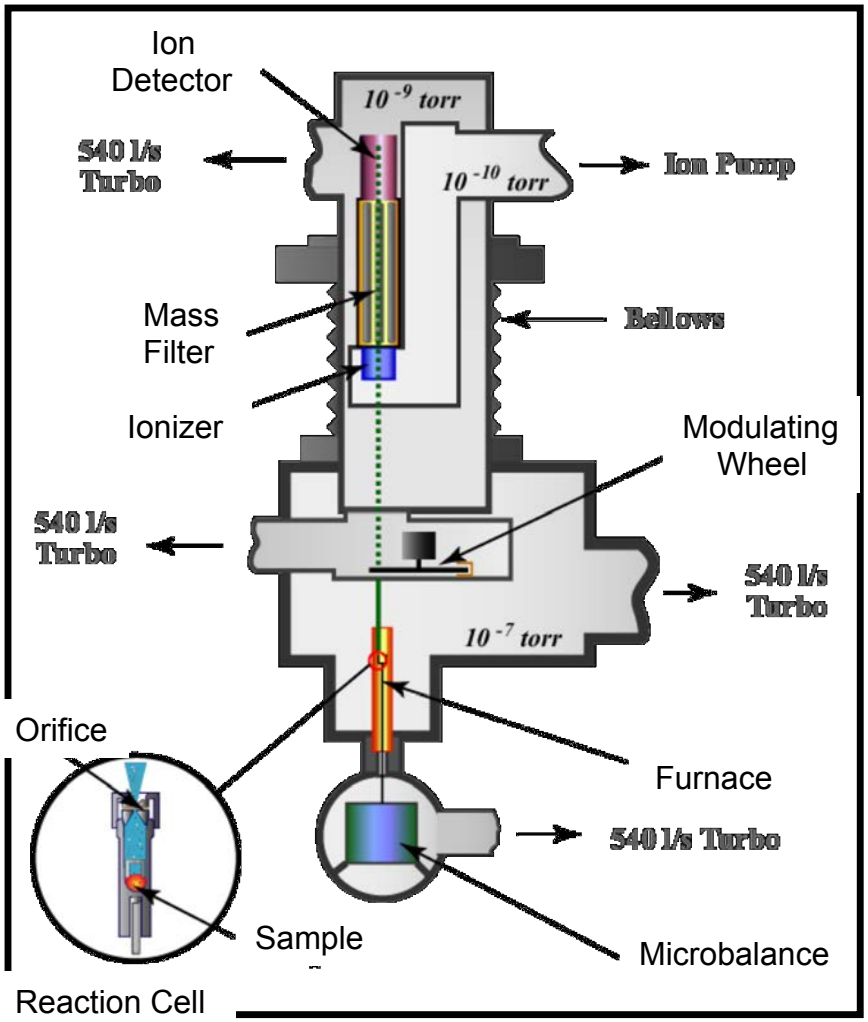
- Thermal decomposition studies

Surface analysis/FTICR MS

- High accuracy MS
- Chemical imaging
- Reactions at microscopic interfaces

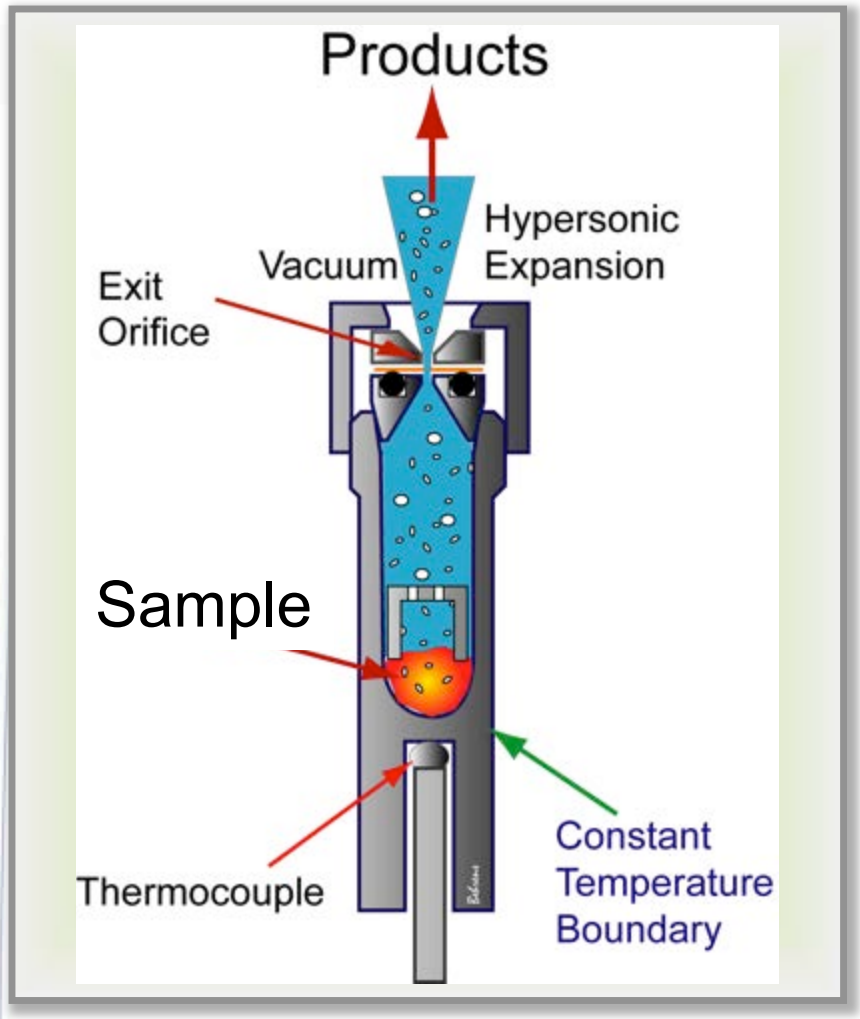
Simultaneous Thermogravimetric Modulated Beam Mass Spectrometer (STMBMS) provides sensitive measurements of the evolved gaseous products.

STMBMS Schematic



- **Data obtained includes:**
  - Identification of products
  - Rate of formation of products
  - Vapor pressures and sublimation rates at low temperatures.
- **Techniques used:**
  - Modulated beam mass spectroscopy
  - Thermogravimetry
  - Coupling of two measurements provides quantitated data.

Reactions of EM's are investigated under well controlled conditions in a reaction cell



- **Experimental features:**
  - Identify gaseous products
  - Measure concentration vs. time
  - Control:
    - Particle morphology
    - Pressure of gases
  - Measure morphological changes
- **Applications:**
  - Vapor pressure of explosives
  - Contaminants/compatibility
  - Elucidate reaction schemes
  - Reaction kinetics in condensed phase
  - Investigate ingredients: RDX/HMX, Binders, Oxidizers, etc.
  - Investigate materials:
    - Military Explosives, Gun propellants. HME's

Objective: Determine reaction mechanisms and kinetics that control reaction of energetic materials.

- **Challenges:**
  - Identify processes that actually cause changes in material.
    - What compounds?
    - Molecular vs. reactions at larger spatial scales
  - Collect data to understand and characterize these reactions.
  - Collect data to characterize the physical and chemical aspects of the reaction process.
  - Create mathematical models to characterize these processes.
- **Our approach:**
  - Use combination of high information content experiments coupled with modeling/simulation to address the challenges.
    - Our methods are based on mass spectrometry for identification and MS/TGA for quantification.
- **Our goals:**
  - Develop new knowledge of important reaction processes.
  - Develop reaction schemes for ingredients and materials (formulations).
  - Develop mathematical models to represent the reaction schemes.

Chemical Signatures of Explosives

Remote Explosives Detection and Identification (REDI) (joint project with LLNL)

Issues

- Remote detection of explosives key in protecting against IND's
- Passive detection best for broad area 'sweep'
  - Canine best passive detectors available
    - Limited detection range
- Accurate chemical characterization of explosives required to develop improved detection platforms

Results

- **SAND2008-7013:** *Signatures and Vapor Pressures of the Volatile Ingredients in Composite Explosives*
- Integration of explosive property, vapor/particulate transport, and sampling databases ongoing
- Development of Interactive Situational Assessment Tool (ISAT) to facilitate access and retrieval of all DB information started in FY10

Approach

- Use core capabilities to characterize vapors emanating from explosives
  - Identification of compounds
  - Measure vapor pressures and sublimation rates at low temperature
  - Develop unique chemical fingerprint for each explosive

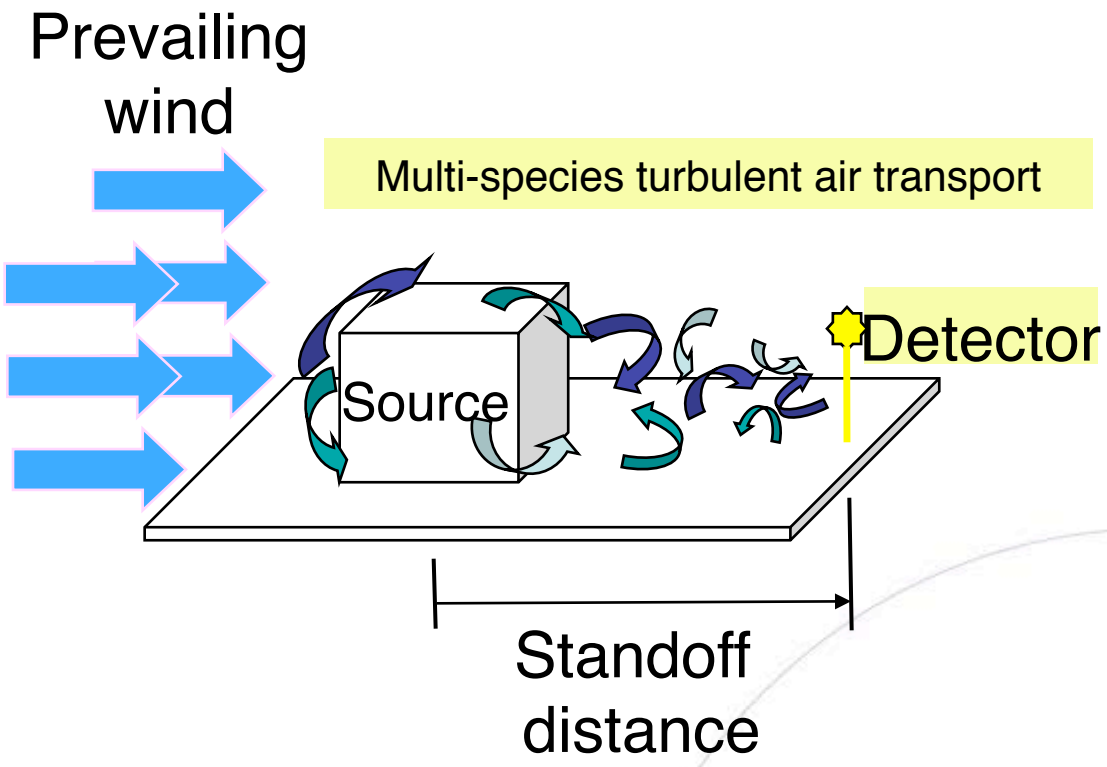
Conclusions

- Accurate chemical characterization leads to reliable explosive fingerprints
- Multi-source fingerprints more informative than single-component signatures
  - Detection, *Identification, and Ranging*
- Complexity of fingerprints requires effective data filtering
  - Data-driven interactive decision tool - ISAT

CRF

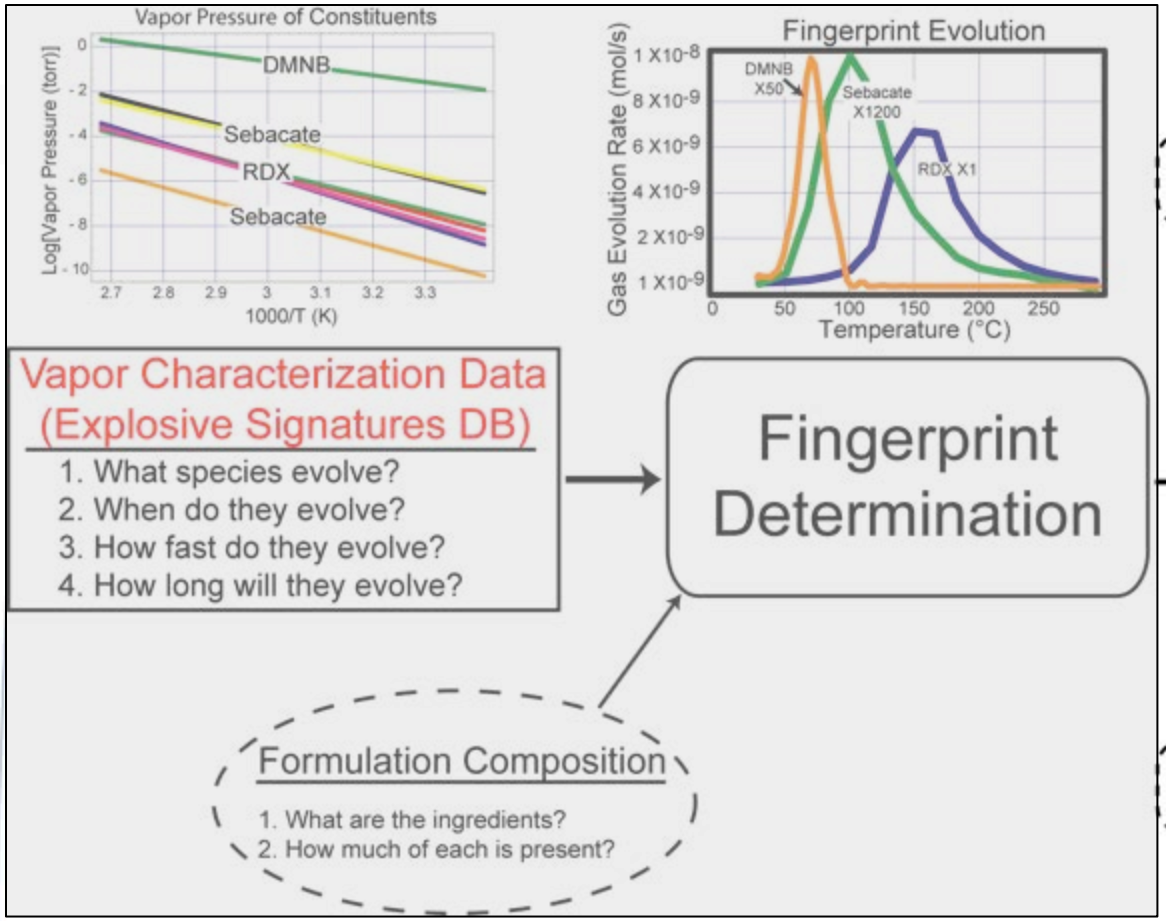
Background: Current technologies for remote detection of explosives are unreliable, have low sensitivity and poor selectivity

- **What information does the source provide**
  - Energy: light, heat, etc.
  - Mass: vapor, particulate
- **How does the information 'leave' the source**
  - Radiative, ablative, diffusive
- **How is the information convected away from source**
  - Radiative, convective, dispersive
- **How is the information detected**



⇒ The volatile species evolving from an explosive formulation can be used to form a unique vapor-phase chemical fingerprint for the explosive

Sandia group was responsible for measurements of vapor pressures and sublimation rates for all volatile ingredients evolving from an explosive as well as determination of viable vapor-phase chemical detection signatures



⇒The Interactive Situational Assessment Tool (ISAT) was developed to provide a platform to rapidly evaluate new explosive fingerprints

Summary

- **Sandia's Energetic Materials and Chemical Micro-Analysis research group is housed at the Combustion Research Facility at Sandia's Livermore, California site**
- **The group specializes in development of low temperature reaction models for new and existing EM formulations**
- **Questions addressed by the group's research are paramount to the EM community**
  - How do material interactions affect the performance of EM formulations?
    - What controls the IM behavior in IM compliant formulations?
  - What role does ingredient compatibility play in the lifecycle of a munition?
  - How does an abnormal external stimuli alter the safety of a munition?
    - Role of thermal decomposition of ingredients.
    - How morphology plays into development of localized reaction environments within the munition.
    - Creation of new reactive species within the EM.

Statistics: How to Deal With Them

Issue 1) Reporting results of sensitivity tests

- Parameterizes the response of the material to stimulus level (μ and σ values)
- Helps rank the materials relative to other well-known explosives (relative μ values)
- Determines how well-behaved the material is (σ relative to μ and other materials' σ)
- Provides thresholds for certain probability of reaction (by number of σ from μ)
- Can provide confidence levels for thresholds and distribution parameters

Question: What is best way to report data?

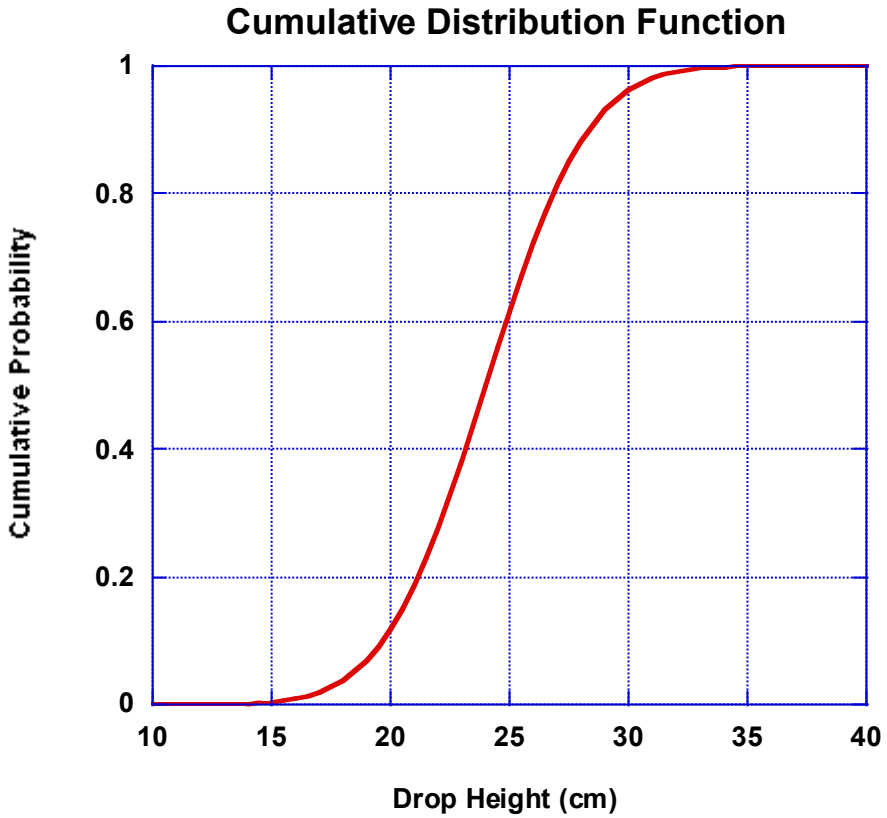
Issue 2) Comparing data from different labs

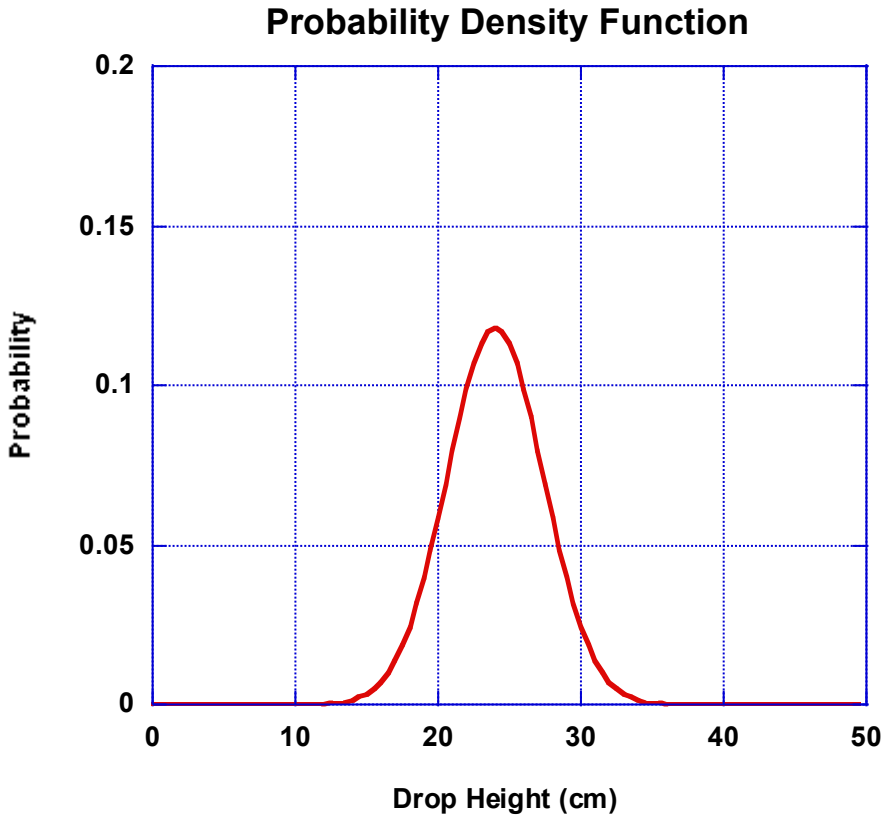
- Hypothesis tests of parameters of sensitivity tests.
- Want to know if "statistically significant difference" exists between one or more labs in the collaboration.
- Identify differences and maybe relate to methods, instruments, etc.

Question: What can we learn from these statistical comparisons?

Issue 1) Reporting Results of Sensitivity Tests

Assume a Gaussian distribution, Probe for μ and σ



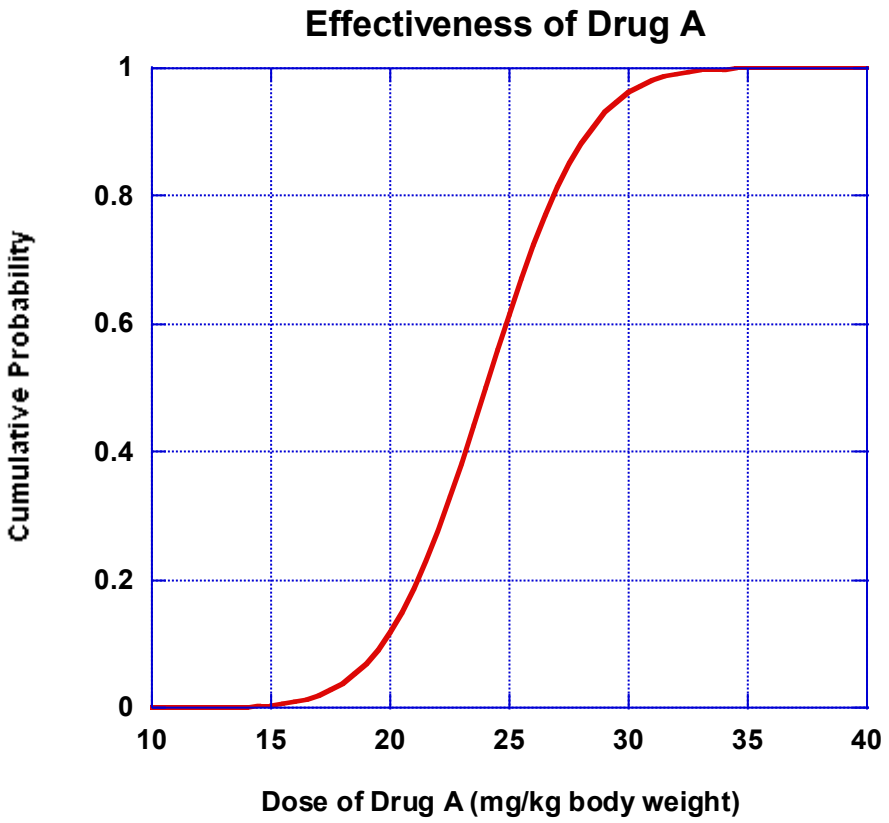


Probing regions of the Cumulative Distribution Function

Derivative of the CDF is the Probability Density Function

Analogy With Medicinal Effectiveness

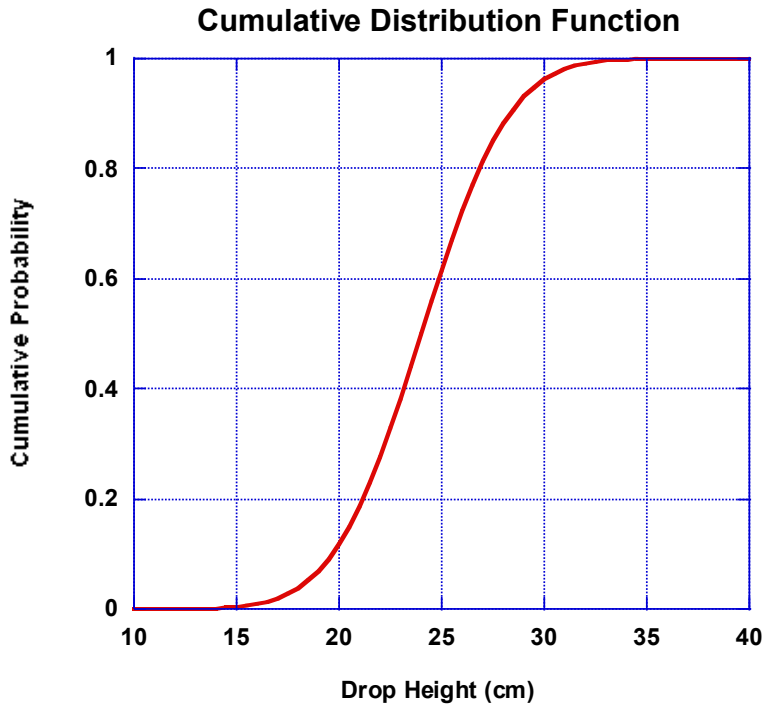
Much more work in Dose-Response Evaluation



- Easier to find volunteers or patients for evaluation than to reproducibly run 1000's of small scale sensitivity tests.
- Probit and Logit tests can be used effectively.
- Statistical (non-repeatable) response due to variety of factors related to test subjects
  - Metabolism
  - Baseline immune response
  - Recent diet/health
  - Genetics

Statistical Nature of Sensitivity Tests

Statistical when uncontrollable factors influence response



Impossible to run two identical tests. Variables include many factors.

- **Drop weight testing**
  - Material homogeneity
  - Sample pile distribution
  - Sample pile mass
  - Striker planarity/ rotation
- **Friction testing**
  - Material homogeneity
  - Sample pile distribution and mass
  - Pin and plate surface variations
  - Voltage / speed fluctuations
- **Spark testing**
  - Material homogeneity
  - Sample pile distribution and mass
  - Pathway of spark

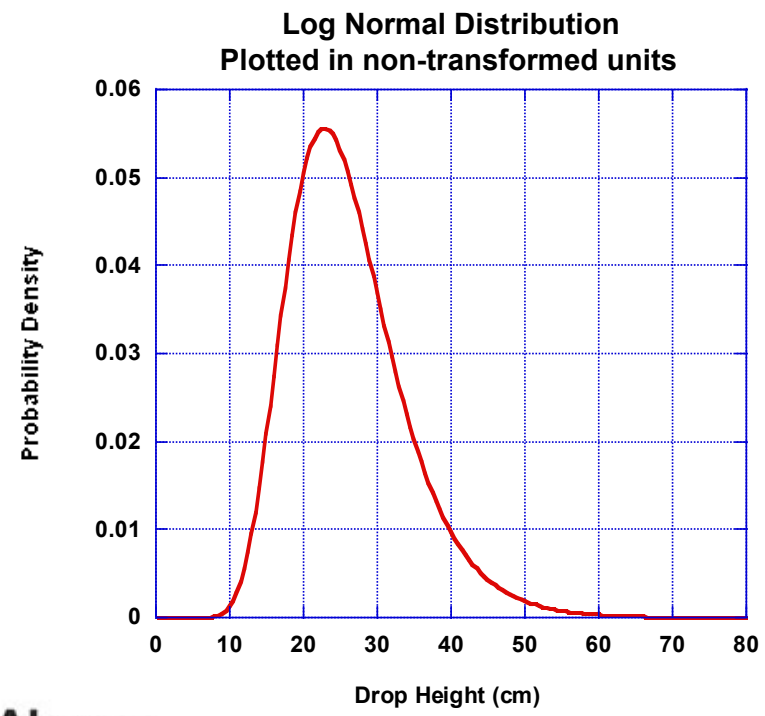
Guidelines for Reporting Results

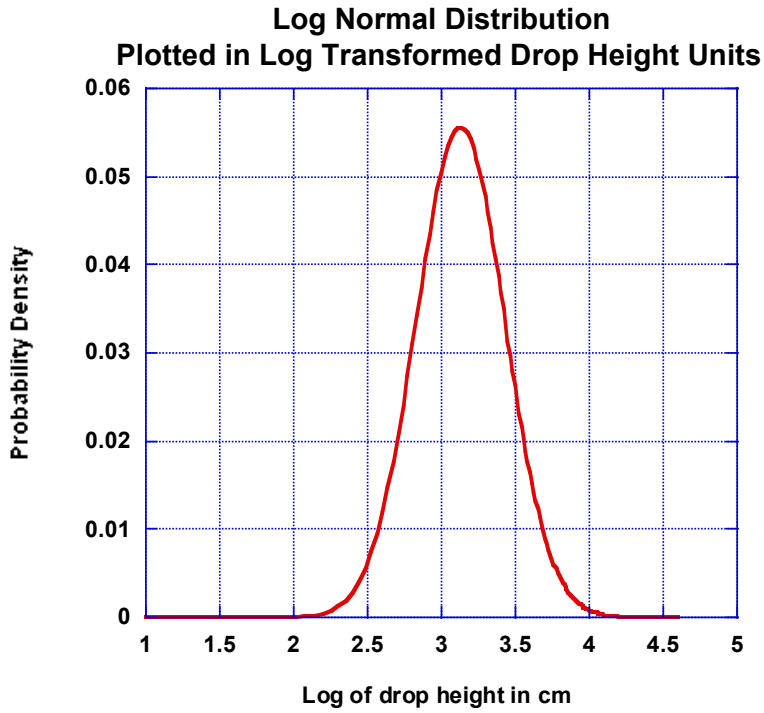
- Important to report how testing was carried out – number of tests, criteria for Go / No-Go evaluation, statistical model used to determine μ and σ or threshold / probability level.
- Minimum data is the parameter set μ and σ or the threshold / probability level.
- Sometimes useful to see the testing progression (when trying to understand lab-to-lab differences perhaps).
- Important to report how standard materials respond with your method to let others evaluate results relative to their methods.
- May be useful to note the confidence level associated with the parameter values reported.
- Reporting in common units is useful for rapid evaluation by other testing laboratories.

Standard vs. Log-Transformed Units

Why use log-transformed units at all?

- Easy comparison to other data sets from testing in log transformed units.
- Log normal distribution may be better model approximation (especially if Go response depends on product of many independent random variables.
- Can "clean up data set" if noise increases with stimulus level.





Reporting in Both Units

Testing in Non-Transformed Units

- μ transforms directly since both are relative to zero.
- σ is relative to μ and must be approximated.

$$\mu_{\log} = \log(\mu_{cm}) \qquad \sigma_{\log} = \frac{\log(\mu_{cm} + \sigma_{cm}) - \log(\mu_{cm} - \sigma_{cm})}{2}$$

Testing in Transformed Units

- μ transforms directly since both are relative to zero.
- σ is relative to μ and must be approximated.

$$\mu_{cm} = 10\text{^}(\mu_{\log}) \qquad \sigma_{cm} = \frac{10\text{^}(\mu_{\log} + \sigma_{\log}) - 10\text{^}(\mu_{\log} - \sigma_{\log})}{2}$$

- Replace Log with Ln if steps are Ln-transformed.
- If Log is used, analogy with log-normal is not technically accurate but still works

Issue 2) Comparing Data from Different Labs

If different labs find different values, is it significant?

If different labs find same values, how confident are we?

- Statistical testing can provide quantitative measure of significance.
- Has to be evaluated against common sense and knowledge of typical testing results.
- Simple eye-ball method is to look at means and whether standard deviations overlap.
- Established methods exist to help set required confidence levels and evaluate results from more than two labs.

t-Test Can Compare Two Means

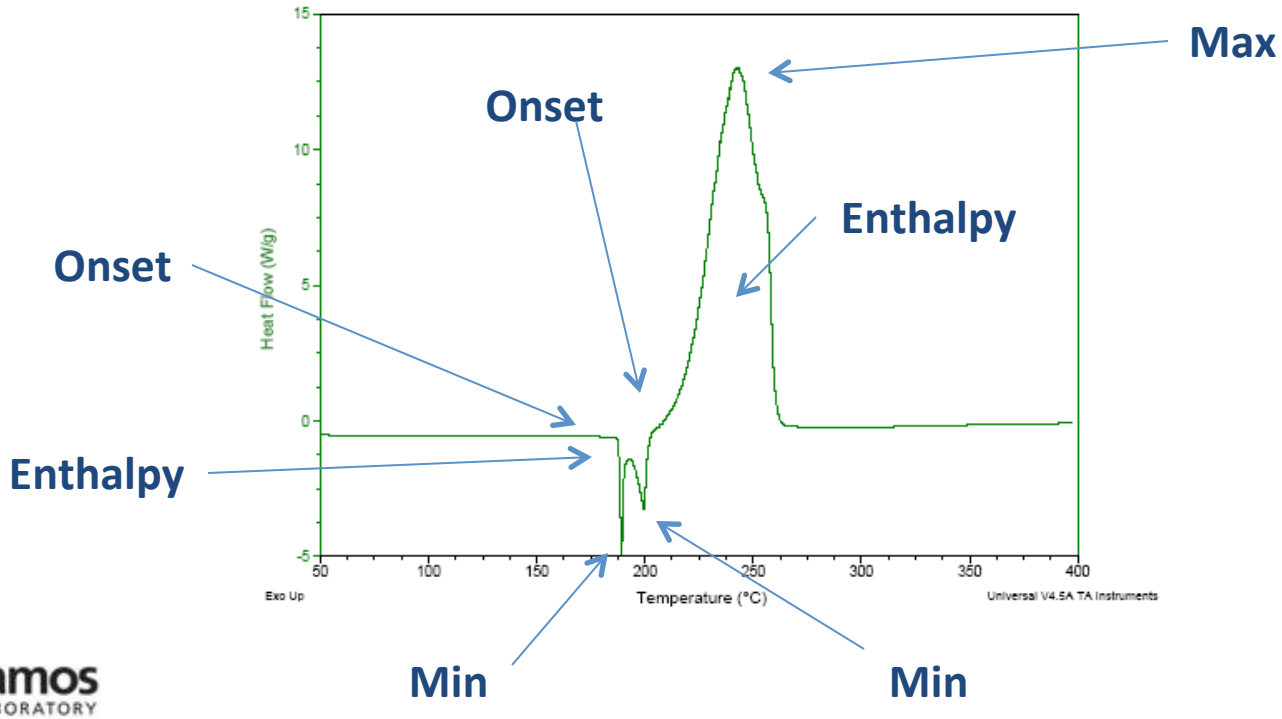
- t-Test is a hypothesis test that uses a function of mean and standard deviation to generate a test statistic to apply to t-distribution.
- t-distribution takes into account the decreasing uncertainty in standard deviation as a function of number of samples.
- Pick a confidence level of choice – determines how much area outside of the t-distribution can be left out and still have confidence that the means were the same – called α value.
- Test statistic for evaluating equivalence of two means is

$$t = \frac{DH_{50,1} - DH_{50,2}}{\frac{(n_2 - 1)\sigma_1^2 + (n_1 - 1)\sigma_2^2}{n_1 + n_2 - 2} + \sqrt{\frac{1}{n_1} + \frac{1}{n_2}}}$$

- The statistic gives a location and hence an area of the t-distribution. The remainder area is the p value and is compared to α to determine if means are the same within pre-chosen confidence level.

ANOVA Compares > Two Means

- ANOVA = analysis of variance. Similar approach to t-test but more complicated calculations.
- Pick a confidence level of choice – called α value – evaluate p value and compare the two.
- Example for three lab comparison of RDX DSC data.



Example from IDCA data (DSC of RDX)

ANOVA test of DSC features from RDX. Used $\alpha = 0.05$ (90% confidence level)

Feature	P-Value	Statistically Significant Difference	Largest Δ Between Labs	Reasonable single lab variation	Still Statistically Significant Difference
Endotherm 1 Onset	0.011	Yes	0.417 C	2 C	No
Endotherm 1 Minimum	0.720	No	0.246 C	2 C	No
Endotherm 1 Enthalpy	0.023	Yes	8.63 J/g	14 J/g (10%)	No
Endotherm 2 Minimum	0.032	Yes	0.973 C	2 C	No
Exotherm Onset	0.026	Yes	5.520 C	2 C	Maybe
Exotherm Maximum	0.507	No	0.950 C	2 C	No
Exotherm Enthalpy	0.018	Yes	82.4 J/g	200 J/g (10%)	No

Exotherm onset may be significantly different between labs. Could be due to pan type, ramp stability, sample mass.

Some Recent Thermal Issues IDCA

IDCA Quarterly Meeting

September 14, 2010

Mary Sandstrom

Drying of Ammonium Nitrate

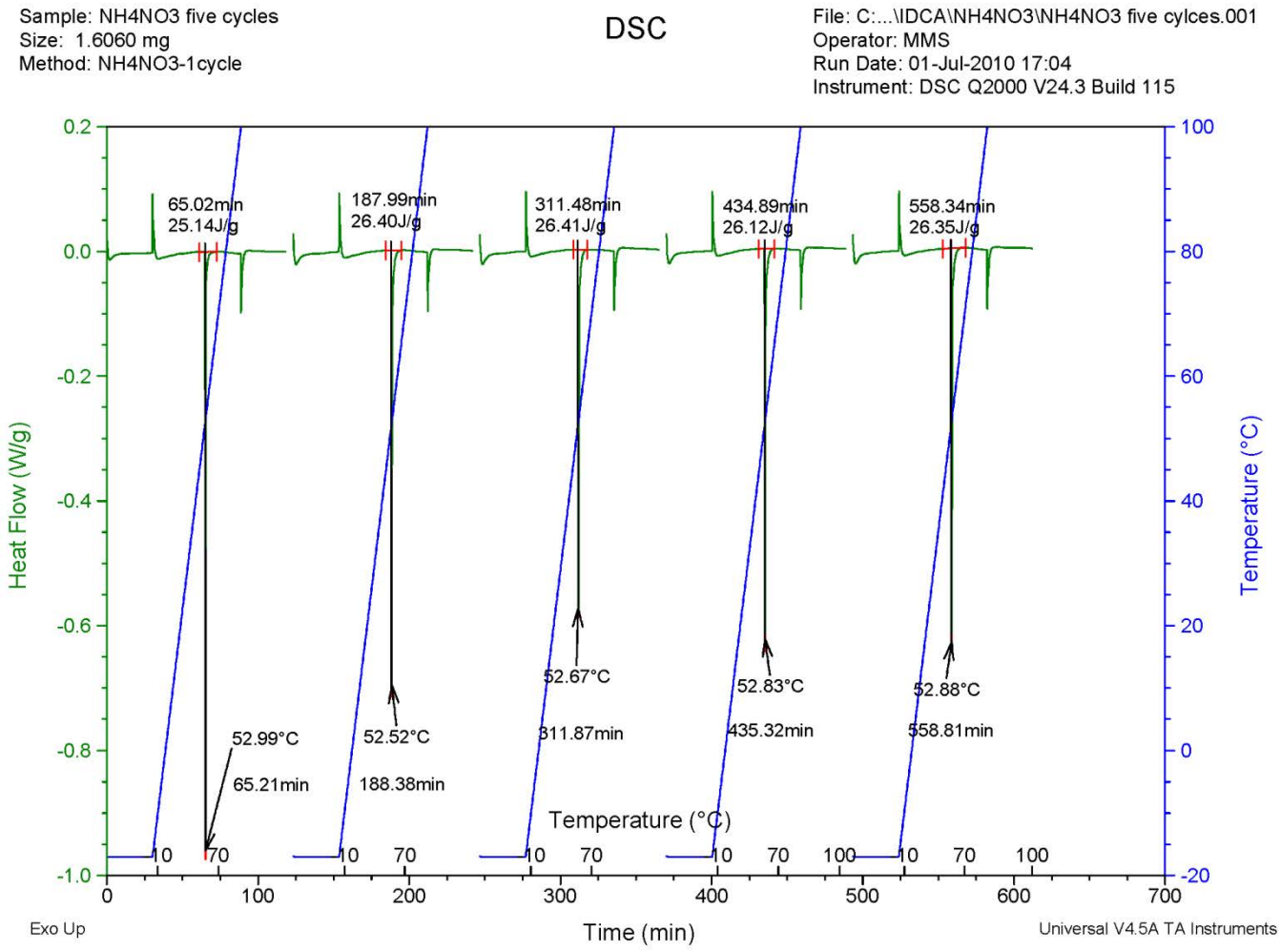
- Why do we care? (beyond the obvious reasons)
  - The obvious reason is that we all want to treat our materials the same way..
- AN becomes very sensitive towards shock in the presence of water (humidity) when it is subjected to temperature cycling through the 32°C phase change.
- KNO_3 (a phase stabilizer) and dessicants, such $Mg(NO_3)_2$ and $Al_2(SO_4)_3$ are added to AN to stabilize it against this phase change.

Phases Of Ammonium Nitrate

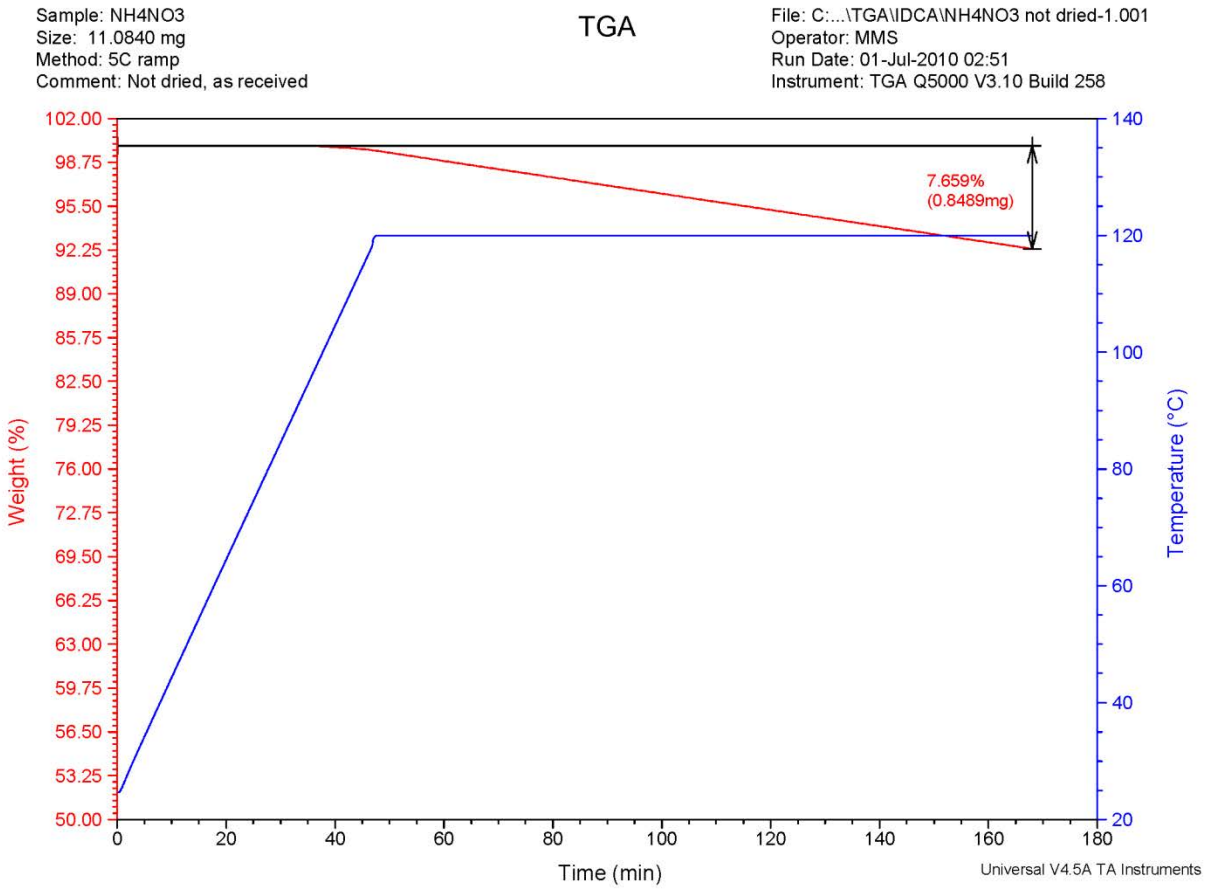
SYSTEM	TEMPERATURE (°C)	STATE	VOLUME CHANGE
-	> 169.6	Liquid	-
I	169.6 to 125.2	Cubic	+2.1
II	125.5 to 84.2	Tetragonal	-1.3
III	84.2 to 32.3	α-rhombic	**+3.6**
IV	32.3 to -16.8	B-rhombic	-2.9
V	-16.8	tetragonal	-

- Large volume change between the IV→III phase change creates a lot of pores upon thermal cycling. These heterogeneities are the source for the increased sensitivity (hot spots).
- As the water content of AN decreases is reduced below 0.2%, the IV→III phase transition temperature increases and the III→IV decreases; below 0.01% water, form IV does not form does not go to III at all resulting in a direct II →IV transition. (Sjölin, 1971).

DSC and TGA Data for IDCA Ammonium Nitrate Powders



DSC and TGA Data for IDCA Ammonium Nitrate Powders



Vacuum Thermal Stability

Jose Archuleta

Mary Sandstrom

VTS

- Determines material stability on the basis of gas liberated on heating the under vacuum.
- This can be the result of volatilization of the material or a chemical reaction.

VTS

- Vacuum thermal stability
- 0.2 g of material loaded into glass capillary tube.
- Tube is slightly evacuated and pressure is measured by mercury manometry
- Material is heated in silicone oil bath at a predetermined temperature (~100 or ~120 C, depends on material).
- After 48 hours, pressure rise corresponding to more than 2 ml of gas per 2 grams of material is considered to indicate thermal instability.

How Can VTS used to Characterize HMEs?

- Commonly used in compatibility testing
  - Each component is tested individually to determine thermal stability alone
  - Components are mixed to determine changes in stability
- Applying Arrhenius reaction principle, testing at elevated temperatures infers aging behavior.
- Testing of materials at different temperatures may give more complete information about the HME.

Issues related to thermal stability evaluation

- Not as much information from VTS as from ARC or APTAC or DSC or CRT
- Volatile materials typically can't be tested.
- No information on what is causing the volume change.

Lawrence Livermore National Laboratory

Overview of Some Thermal Safety Characterization Techniques at LLNL

Peter C. Hsu, John G. Reynolds, Gary Hust, Michael Howard

September 14-15, 2010

Presented at the IDCA program review meeting

Los Alamos, New Mexico

Lawrence Livermore National Laboratory, P. O. Box 808, Livermore, CA 94551
This work performed under the auspices of the U.S. Department of Energy by
Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344

UCRL-PRES-XXXX

Outline

- CRT (Chemical Reactivity Test)
- STEX (Scaled Thermal Explosion Experiment)
- ODTX (One-Dimensional Time to Explosion) system for the thermal ignition and thermal safety study
  - Thermal safety characterization
  - Description of the ODTX system
  - Recent experimental results
  - Summary

Tools for thermal safety characterization

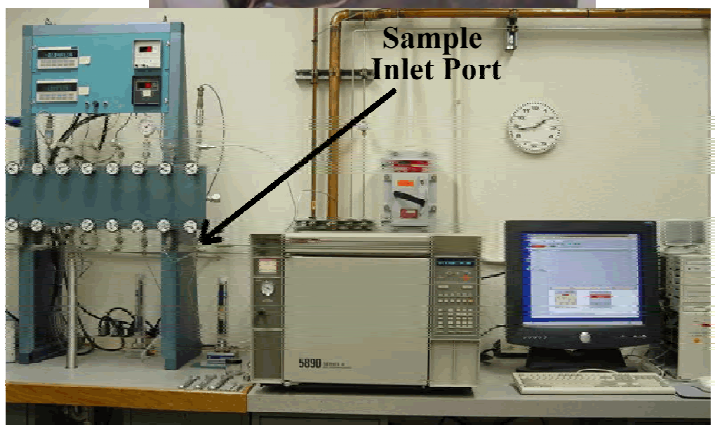
Understanding the response of energetic material to thermal event is very important for the storage and handling of energetic materials

Tools for thermal safety characterization at LLNL

- **Differential scanning calorimetry (DSC), 0.3 mg sample size**
- **Chemical reactivity test (CRT)/Vacuum thermal stability (VTS), 0.25 g sample size**
- **ODTX, 2 g sample size**
- **STEX (scale thermal explosion experiment), > 100 g sample size**

Chemical reactivity test for thermal stability and material compatibility

- CRT is used to measure the thermal stability of explosive and compatibility of explosive with alien materials by detecting the volume of gases emitted from heated samples. This information is useful when assessing long-term storage
- Main components include a crucible, a holder vessel, a vacuum pump, a silicone bath, and a GC. The crucible with sample is placed inside the holder vessel, which is evacuated, and backfilled with helium. The vessel is heated for 22 hours at 120 ˚C
- A sample that generates ≥ 4 cc/g is considered thermally unstable. Some data LX-17, 0.2 cc/g; PBX 9407, 0.42 cc/g; PBX 9407/615 Hysol (epoxy), 4.26 cc/g (not compatible)



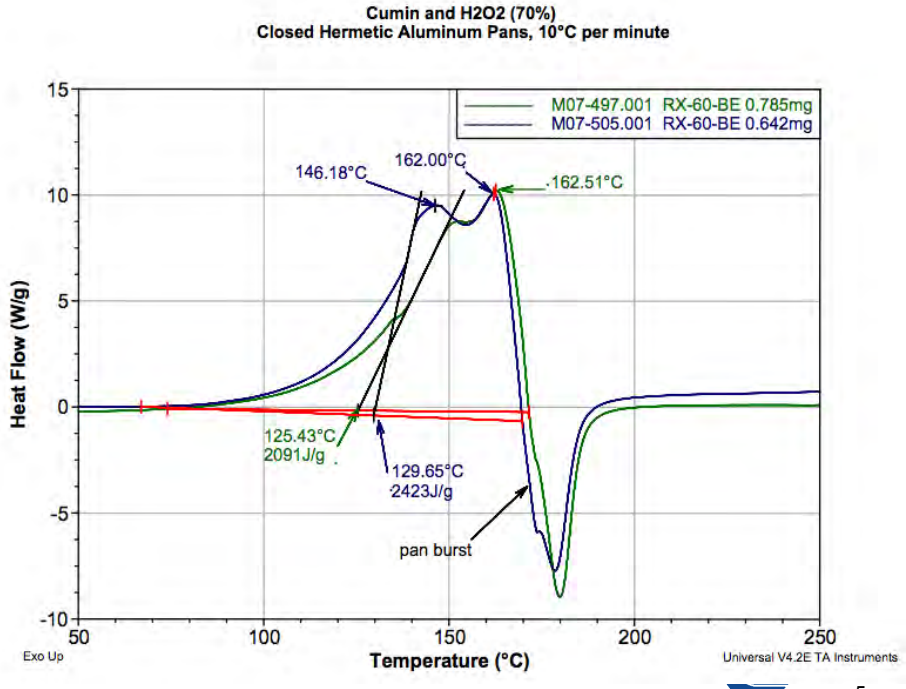
Thermal Stability <4.0 cc/g
Y or N ?

OK	No reaction observed
?	minor reaction, questionable compatibility (Excess gas > 0.75 cc/g HE)
#	Compatibility No Good (Excess gas > 1.5 cc/g HE) (Excess gas rounded to whole number in g/cc)

Category		no.	Explosive	Alien Material	DATE	Wt. EX (g)	Wt. Alien (g)	Temp. (˚C)	N_2 (cc)	O_2 (cc)	CO (cc)	NO (cc)	CO_2 (cc)	N_2O (cc)	Total (cc)	cc/g EX	Compat.? Stable?	Explosive Details/ stdev
Aliens	Ave.	A		615 Hysol	2/27/07		0.250	120	0.01	0.00	0.00	0.00	0.04	0.01	0.05	0.18	Y	Lot#6AC1294C
RDX Hi/Misc.	Ave.		PBX 9407		2/27/07	0.250		120	0.06	0.00	0.00	0.00	0.03	0.02	0.11	0.42	Y	B 808 Powder
TATB, hi %	Ave.		LX-17		2/27/07	0.250		120	0.03	0.00	0.00	0.00	0.02	0.00	0.05	0.20	Y	C-063
RDX Hi/Misc.	Ave.	A	PBX 9407	615 Hysol	2/27/07	0.250	0.250	120	0.18	0.00	0.01	0.05	0.13	0.70	1.07	4.26	4.00	Lot#6AC1294C B808 Powder
TATB, hi %	Ave.	A	LX-17	615 Hysol	2/27/07	0.250	0.250	120	0.00	0.00	0.00	0.00	0.02	0.00	0.03	0.13	ok	Lot#6AC1294C C063

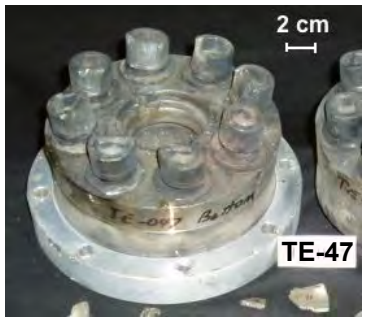
DSC for phase change, impurity, and decomposition enthalpy measurements

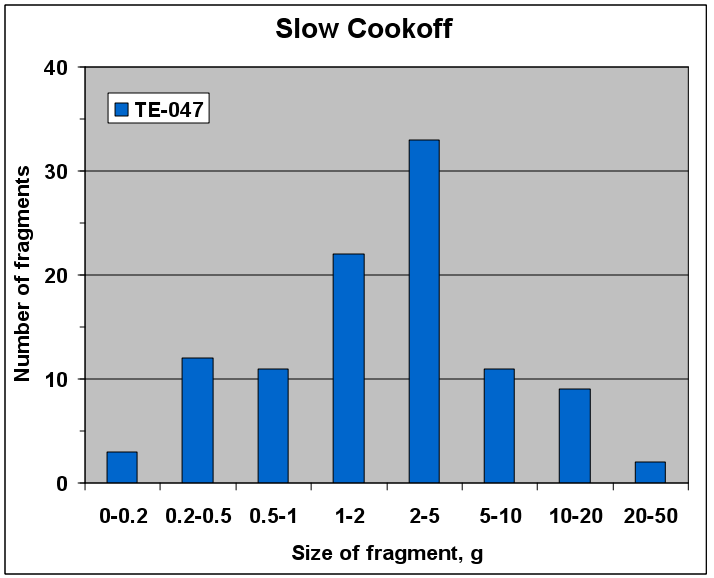
- DSC measures the difference in the heat flow between a sample and an inert reference measured as a function of time and temperature. For example, as a solid sample melts, heat is absorbed as the material undergoes the endothermic phase transition. Likewise, as the sample undergoes exothermic processes (such as decomposition), heat is released. By observing the difference in heat flow between the sample and reference, DSC is able to measure the amount of heat absorbed or released during such transition
- DSC curve peaks: TATB, 382 C, HMX, 280 C, lower peak temperatures for HP/fuel mixtures



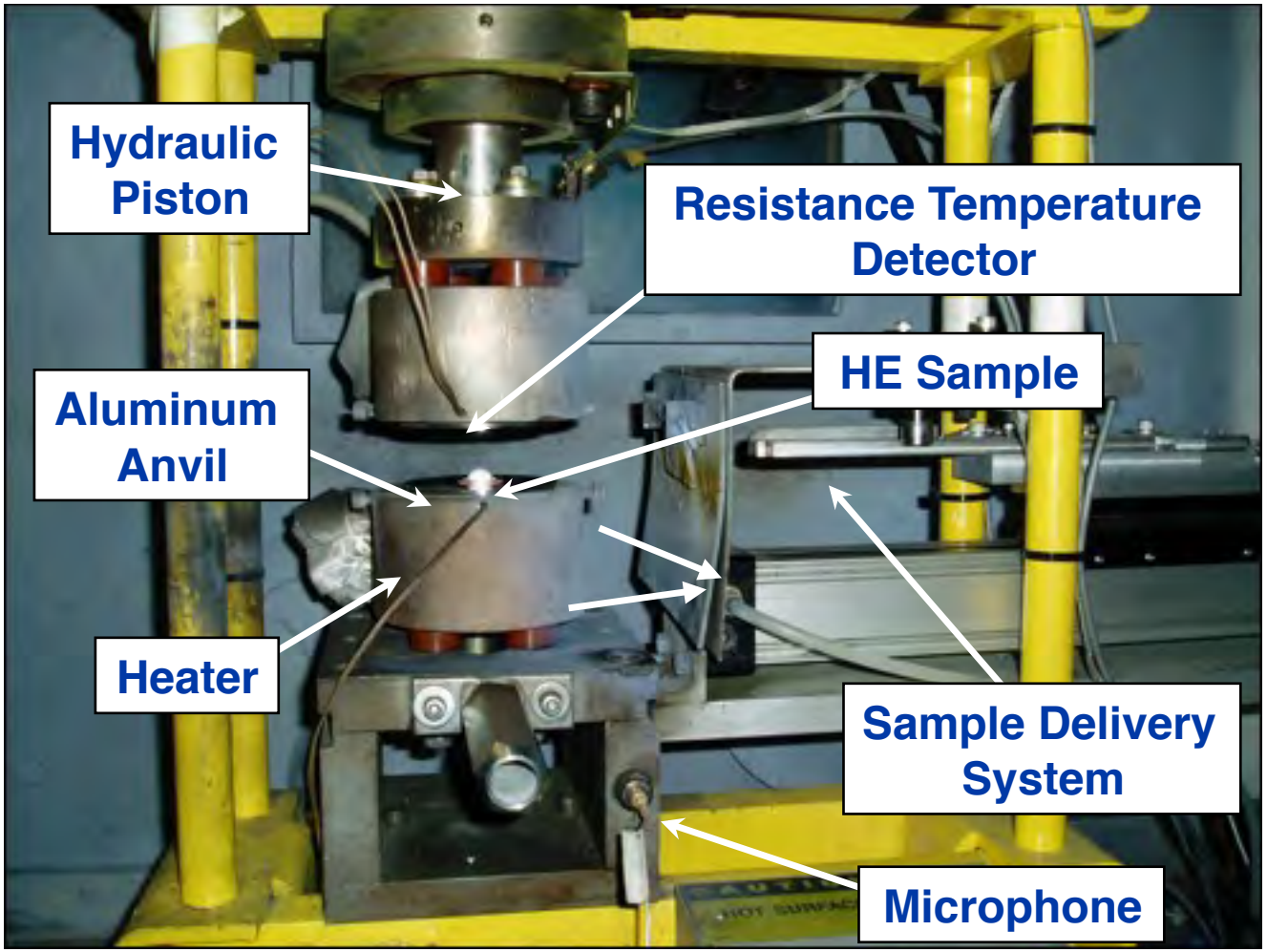
STEX- thermally ignition/explosion testing of cylindrical parts in a carbon steel vessel

- STEX can determine thermal ignition/explosion temperature and relative degree of violence
- We monitor temperature, pressure during experiments
- It is more expensive per shot, $70k (use > 100 g material each shot)



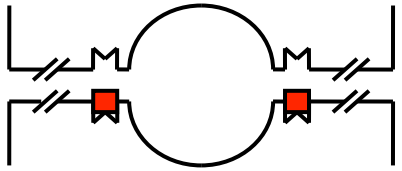


The ODTX system at LLNL



ODTX measures time to explosion and threshold ignition temperatures.

Crucial information obtained on the thermal sensitivity and kinetics.



Hermetically seal sample with:

- Cu o-ring
- Al knife-edge

Using ODTX to generate threshold thermal ignition temperature, kinetic parameters, and thermal violence

The ODTX testing generates two important technical data for energetic materials mixtures

(1) Threshold temperature at which thermal ignition would occur (T_{li}) – important for safe storage and handling

Some liquid HMEs may ignite at temperature as low as 72 °C!!

The air temperature may be greater than 72 °C in

-Parked vans with window up in summer time

-Storage containers in hot climates (Death Valley, Iraq etc.); metal containers may reach 80 °C (170 °F) when air temperature is 49 °C (120 °F)

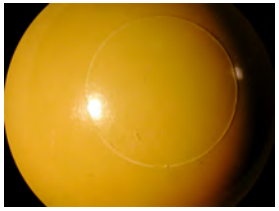
(2) Times to thermal explosion data at temperatures above T_{li} for activation energy and frequency factor of thermal decomposition kinetics

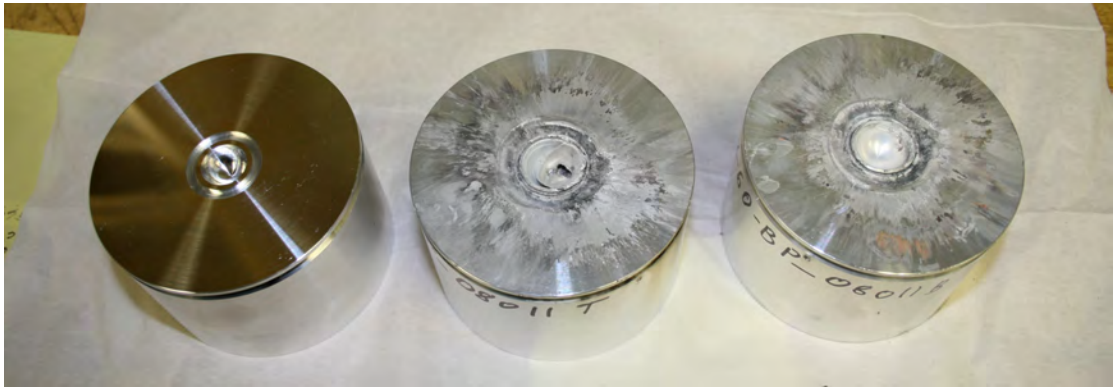
(3) We monitor the thermal ignition/explosion violence by measuring the increase of aluminum cavity volume

Each ODTX shot cost ~ $3k

Samples of any configurations (pressed parts, powder, pastes, and liquid) can be tested in the ODTX system

- 12.7-mm diameter spherical samples
- Aluminum shell is used for holding powder, pasty, liquid samples
- Aluminum anvils are preheated before sample is delivered
- Anvil cavity volume is monitored to determine the relative degree of thermal ignition violence

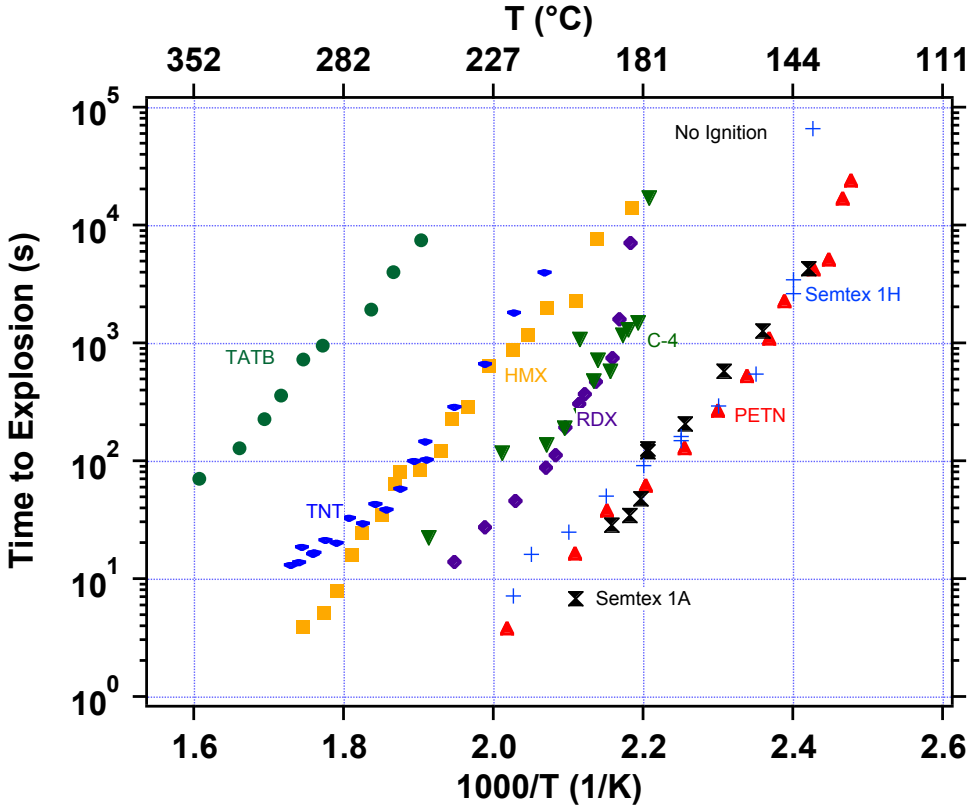




HP/fructose, 65%/35%

ODTX data for commonly-used high explosives

- **Thermal sensitivity: PETN> RDX> HMX (TNT)> TATB**
- **ODTX results were similar to those of more sensitive ingredients in the formulation; i.e. C-4 similar to RDX, Semtex 1A and 1H similar to PETN**



Pasty materials tested in the ODTX system

Samples	Material information	Test date
C-4	RDX and Semtex oil	2002
Semtex 1A	PETN, Semtex oil, and binder	2006
Semtex 1H	RDX, PETN, Semtex oil, and binder	2009

ODTX data for seven homemade HP/fuel liquid explosives

- Some liquid HMEs are very sensitive to thermal ignition
- Some could ignite at temperature as low as ~ 70 °C
- Extreme measures need to be taken when storing liquid homemade explosives in hot climates or in parked vans with windows closed in the summer time

LMD- HP/diesel

LMF- HP/fructose

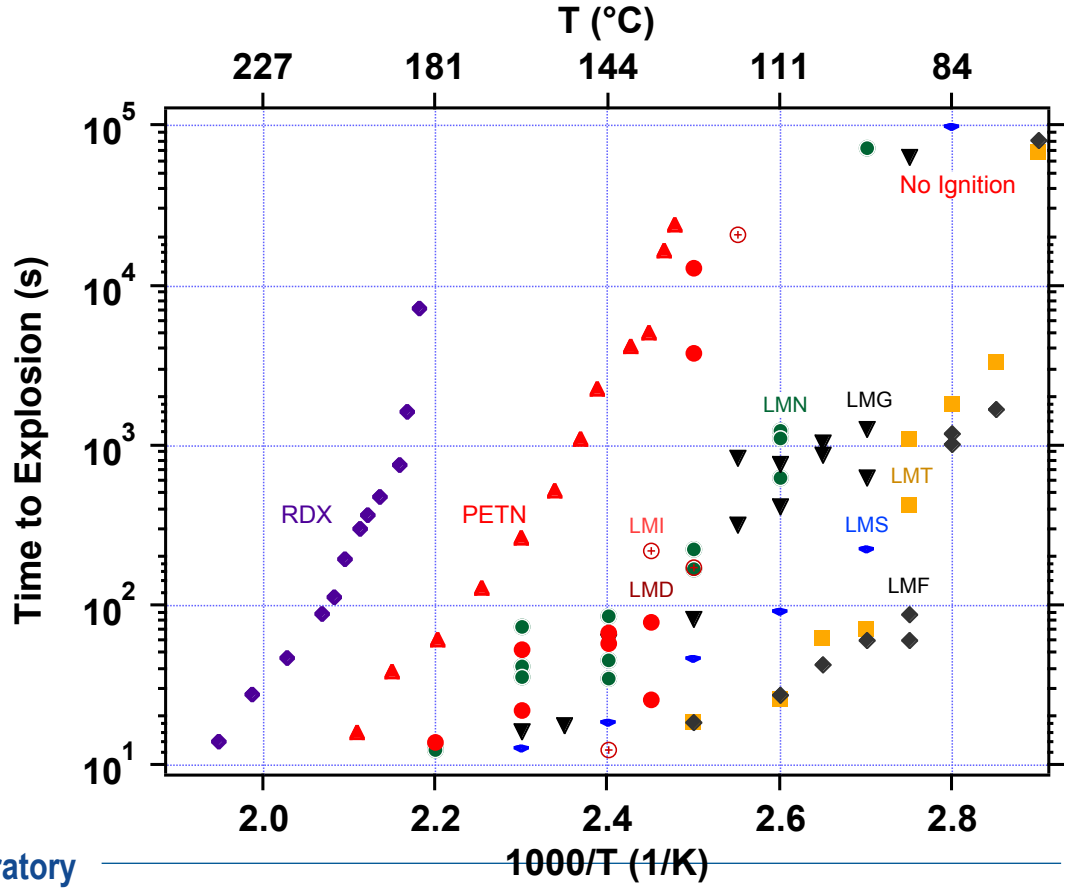
LMG- HP/glycerol

LMI- HP/isopropanol

LMN- HP/nitromethane

LMS- HP/sugar

LMT- HP/tang (drink mix)



Compositions, threshold temperatures (12.7-mm spherical samples), and kinetic parameters

Some homemade liquid explosives are very thermally sensitive.

Threshold temperature as low as 72 °C was observed!!

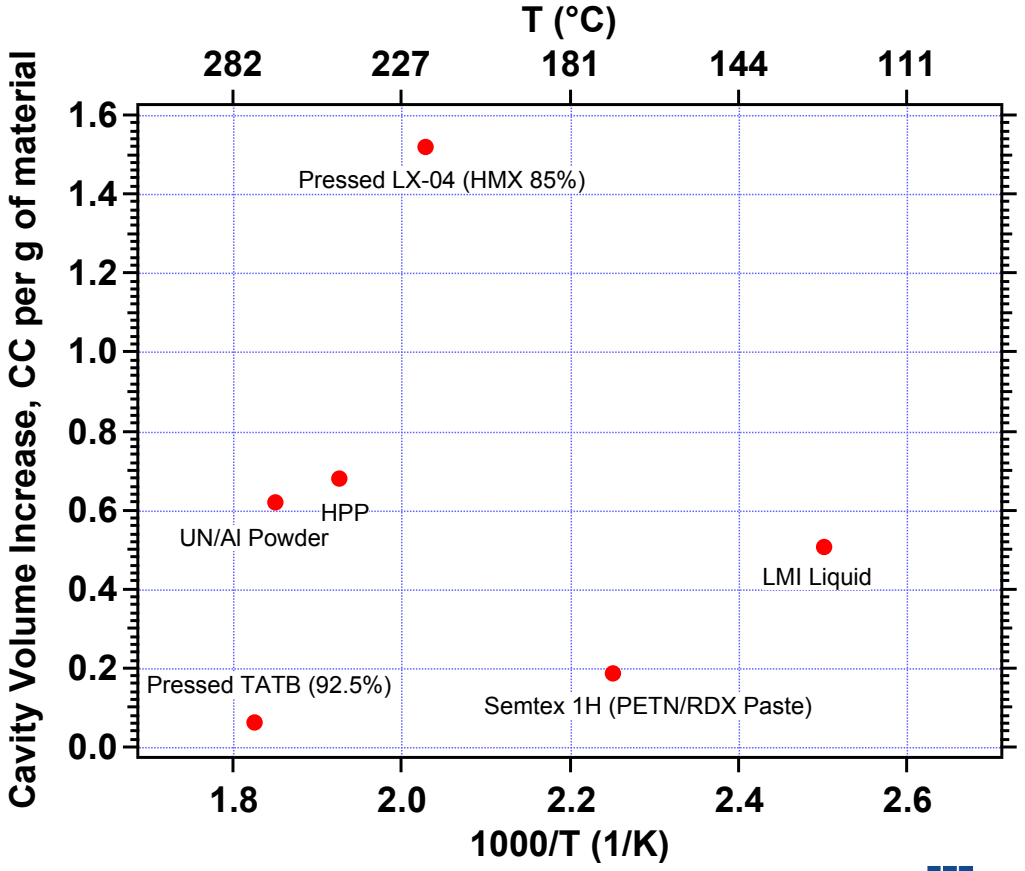
*** HP used was 90%HP/10% water**

Name	Compositions	Threshold thermal ignition temperatures, °C	E, kJ/ mole	A second^{-1}
LMD	HP*/diesel/others	112	145	4.7×10^{14}
LMF	HP/fructose	72	117	9.9×10^{12}
LMG	HP/glycerol	91	106	6.5×10^{10}
LMI	HP/isopropanol	119	N/A	N/A
LMN	HP/nitromethane	97	117	3.7×10^{11}
LMS	HP/sugar	84	92	1.3×10^{9}
LMT	HP/tang (drink mix)	72	116	1.3×10^{13}

Dent analysis for relative degree of thermal ignition violence

- After thermal ignition, spent anvils were scanned for cavity volume
- Cavity volume increase is an indication of thermal ignition violence

Material	Average volume increase, cc/g	Relative degree of violence
LX-04, pressed	1.52	1
HPP, casted	0.68	0.45
UN/Al, powder	0.62	0.41
LMI, liquid	0.51	0.34
Semtex 1H, paste	0.19	0.13
TATB, pressed	0.07	0.05



Option:Additional Information

Summary

- The ODTX system is a useful tool for studying thermal safety of homemade explosives
- Samples of all configurations (solids, powders, pastes, and liquids) can be tested in the system
- The homemade liquid explosives we have tested show higher thermal sensitivity than PETN. Some energetic liquids could ignite at temperatures as low as ~70 °C. Thus, operational handling and storage of energetic liquid mixtures in hot climates or conditions require careful planning and execution. Measures must be taken for safe storage of these mixtures to avoid incidental thermal ignition
- The ODTX testing can also generate useful data for determining relative degree of thermal ignition violence of homemade explosives

Collaborations are welcome

Collaborations are welcome. Please contact

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Thank you!!