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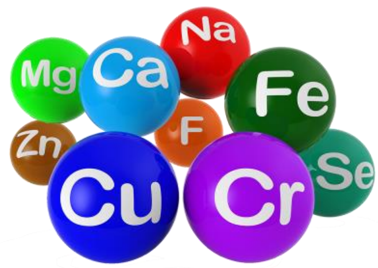

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Upcoming ACS Webinars®

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Thursday, June 25, 2015

"Accelerating CNS Positron Emission Tomography (PET) Ligand Discovery"

Lei Zhang, Senior Principal Scientist, Pfizer Inc.

David Donnelly, Senior Research Investigator, Bristol-Myers Squibb

Thursday, July 7, 2015

"The Entrepreneurial Chemist: Bridging the Bench and the Boardroom"

Tashni-Ann Dubroy, Chemist and Entrepreneur, Tea and Honey Blends

Steven Isaacman, CEO and Founder, PHD Biosciences

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Past ACS Webinars®

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"Chemistry of Fireworks"

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"Advanced Pyrotechnics: Flash, Sound, and Smoke"

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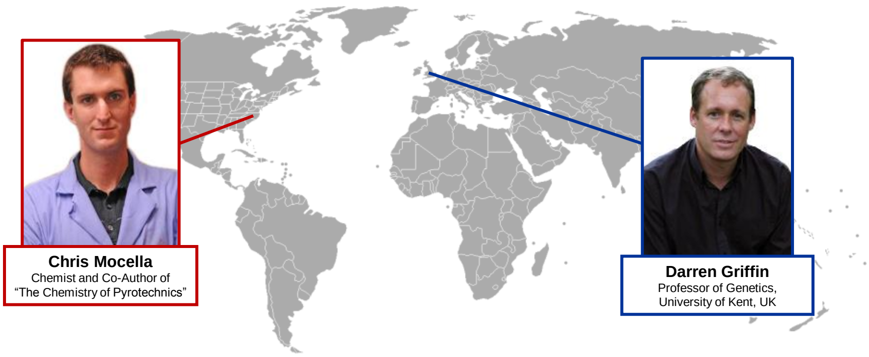
"Advanced Pyrotechnics 2: Ignition, Sensitivity, and Analysis of Energetic Materials"



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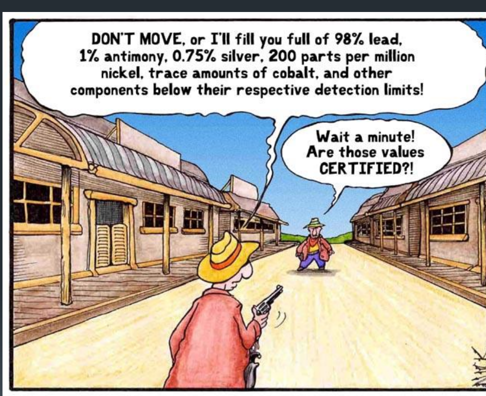
Advanced Pyrotechnics 2:
Ignition, Sensitivity, and Analysis of Energetic Materials



Analytical Chemists in the Wild West

Chris Mocella
ACS Webinar, June 2015

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Review: Basics of Pyrotechnics

- Oxygen source (oxidizer) + electron source (fuel)
  → Products + Energy
- Energy Output =
  - Light (color)
  - Sound
  - Pressure
  - Motion
  - "The effect"

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Ingredients for Pyrotechnic Mixes

- **Oxidizing Agents** (oxygen rich, occasionally fluorine)
- **Fuels** (organic, metallic, other)
- **Color ingredient**
- **Intensifier**
- **Binder** (small %, can also act as a fuel)

- Charcoal + KNO_3 + Sulfur = Black Powder
- Light a match → CO_2, H_2O, K_2O, N_2, SO_2, "soot", and

ENERGY!

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Principles of Ignition

- **Ignition:** The ability to ignite/initiate the material using an *external stimulus* (with respect for stability of the material in the absence of the stimulus)
- For ignition to occur, a material must be heated to its *ignition temperature*, where the reaction will initiate and propagate
- The stimulus can be heat or flame, spark, as well as friction or impact, or some manner of *transferring energy* from the stimulus to the material, heating the chemicals
- What happens when sufficient stimulus is applied?

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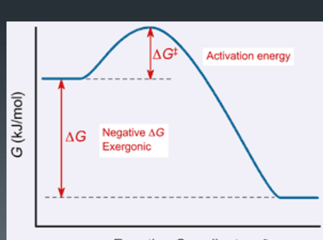
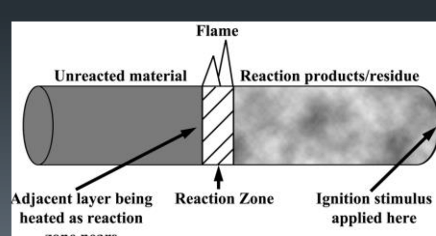
Ignition: Complexity and Propagation

- Upon sufficient stimulus, the materials will undergo a complex sequence of events, such as crystalline changes, melting, boiling, decomposition, interaction of liquid/vapor phases or fleeting decomposition products.
- These complex products and interactions take place on the materials and also in any visible flame.
- If the necessary activation energy has been applied, the reactions occur, more heat is evolved to give stimulus to unreacted material, propagating the reaction.





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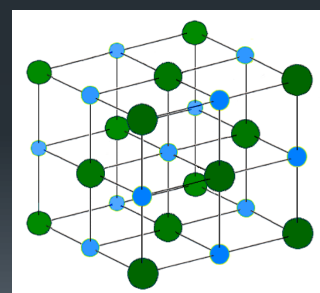
Ignition: Physical States

- **Requirement for ignition:** either the oxidizer or fuel to be in a liquid or vapor state to allow interaction
- Many oxidizers are **ionic solids** (KNO_3), and the "looseness" of the lattice is important in determining reactivity:
- Increased temperature, the vibrational motion of the lattice increases
- Liquid fuel components can more easily diffuse into the lattice, even if the oxidizer is still solid, and begin to interact below the melting or decomposition temperature



Audience Survey Question

ANSWER THE QUESTION ON BLUE SCREEN IN ONE MOMENT

Tammann Temperature is significant because?

- It is approximately two times the melting point in kelvin
- It is temperature at which the mobility and reactivity of the molecules in a liquid state become appreciable
- It has 70% of the vibrational freedom present at the melting point and can cause ignition in a reaction
- It is ideal temperature for ignition of any material

Tammann Temperature

- Prof G. Tammann proposed that this diffusion is significant at "halfway" to the melting point (the "Tammann temperature") and has 70% of the vibrational freedom present at the melting point → often sufficient for reaction leading to ignition
- KNO_3 melts at 334 ºC (607 K), but the Tammann temperature is 30.5 ºC (303.5 K), just a hot day in August!

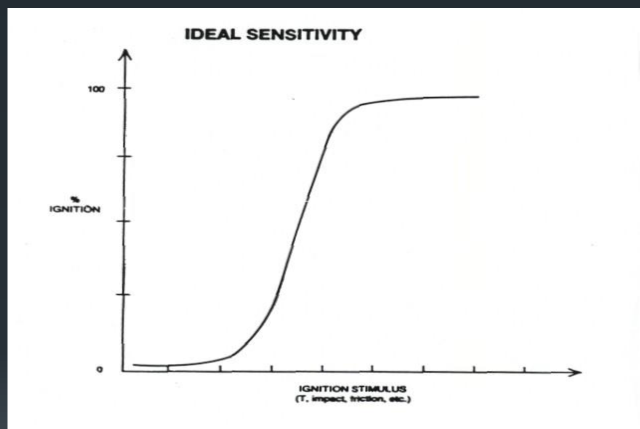
Oxidizer	Formula	Melting point, ºC	Melting point, K	Tammann temperature, ºC
Sodium nitrate	$NaNO_3$	307	580	17
Potassium nitrate	KNO_3	334	607	31
Potassium chlorate	$KClO_3$	356	629	42
Strontium nitrate	$Sr(NO_3)_2$	570	843	149
Barium nitrate	$Ba(NO_3)_2$	592	865	160
Potassium perchlorate	$KClO_4$	610	883	168
Lead chromate	$PbCrO_4$	844	1117	286
Iron oxide	Fe_2O_3	1565	1838	646
Magnesium metal	Mg	651	924	189

Sensitivity Analysis

- An energetic material must be sensitive to ignition if it is to be of any use
- But the safe handling and storage of the material must be of highest importance
- Understanding a material's sensitivity is extremely important for storage and use, and therefore full sensitivity testing should be run on any new composition as a standard matter of course

- Thermal sensitivity
- Electrical/spark sensitivity (including static electricity)
- Impact sensitivity
- Friction sensitivity

Ignition Sensitivity Curve



A specified level of energy is applied – does ignition occur?
→ Ignition is a statistical event, therefore sensitivity is statistical

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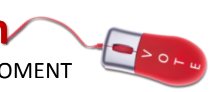
ANSWER THE QUESTION ON BLUE SCREEN IN ONE MOMENT



Which of the following are viable Pyrotechnic Sensitivity Tests?

- Impact, sample, static, reference, and shock
- Zap, pow, boom, kapow, and bam
- Friction, thermal, booster, acceptor, and shock
- Impact, friction, electrostatic, thermal, and shock
- Audio, visual, scratch & sniff, tactile, and tongue

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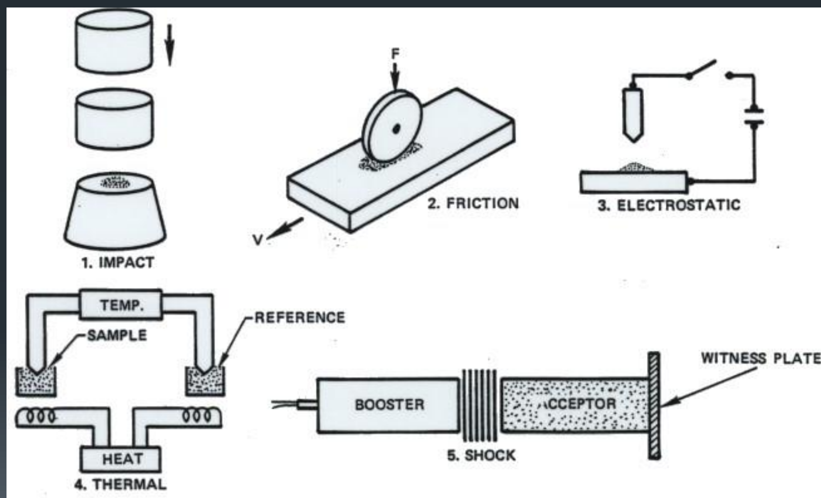
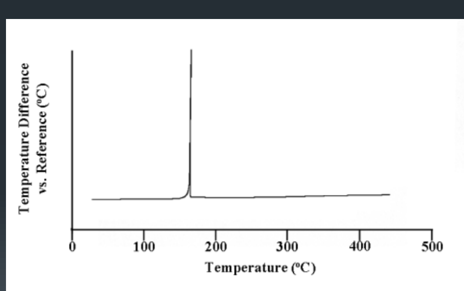
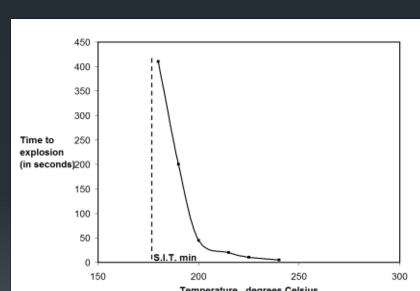
Types of Sensitivity Tests



Thermal Sensitivity

- At what temperature does the system ignite?
- Probably the best understood of all phenomenon
- Measured through DTA, DSC, time-to-ignition studies





Nitrocellulose – DSC and Time-To-Ignition Study

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Spark Sensitivity

- Usually measured with a needle electrode (cathode) that approaches a sample sitting on a grounded surface (anode)
- The energy of the spark is controlled by varying capacitance and voltage and is measured in Joules $J=1/2\ CV^2$
- Humans generate ~15-20 mJ (0.020 J) of energy, enough to ignite some compositions and many organic solvents (acetone, ethyl ether, methanol, etc)
- Conductive materials (metals) tend to increase the spark sensitivity of compositions
- Adding non-conductive materials (diatomaceous clay) can reduce the spark sensitivity (but also adversely affect the performance)

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Spark Sensitivities

Composition	Ignition Energy (J)
RDX	> 4.5
$Mg/NaNO_3$/binder 55/40/5	> 4.5
Si/KNO_3 50/50	> 0.45 < 4.5
$Al/KClO_4$ 22.5/77.5	> 0.04 < 0.45
Mg/BaO_2/Binder 12/86/2	> 0.001 < 0.045
B/MoO_3 25/75	0.00025

Source: J.M. Jenkins (UK); Lecture Notes (1980)

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Static Electricity

- Every effort should be made to eliminate static electricity from the manufacturing and storage processes!

Studies reveal that at the first hint of OSH paperwork, 82.3% of scientists are able to voluntarily jettison their short-term memories.

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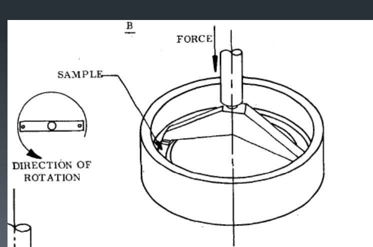
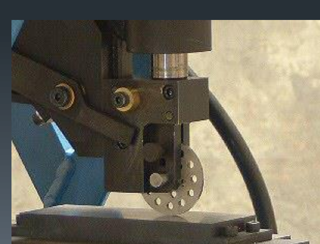
Friction Sensitivity

- A very important test, as many chances for friction to occur appear in production: mixing, pouring, pressing – generation of hot spots or interaction of materials at a chemical level
- Grittiness of the material can increase sensitivity (sometimes desired, sometimes not)
- Rotary friction – yields numerical value
- Sliding surface – yields a fire/no-fire result at a specific force





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Rotary Friction Sensitivities

Composition	Ignition Energy ($ft\text{-}lb^2/s$)
IM 28 Incendiary	19
Barium Nitrate 40	
Potassium Perchlorate 10	
Mg/Al Alloy 50	
SW522 Smoke	52
Potassium Perchlorate 20	
Potassium Nitrate 20	
Aluminum 20	
Zinc Dust 40	
M22 Flash Mixture	74,357
Magnesium (200/325) 75	
Teflon 10	
Viton 15	

Source: Aikman, et al; PEP 12, p.17 (1987).

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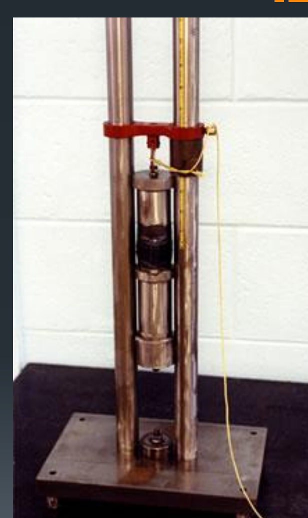
Impact Sensitivity

- The DOT and DoD use the Bureau of Explosives (BoE) impact machine to determine impact sensitivity
- A specified weight is dropped from a specified height a specified number of times
- Cannot re-use a non-ignited sample (pressed)
- Usually reported in 10% or 50% ignition values, or minimum observed
- Generation of “hot spots” in the material



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Impact vs. Friction Sensitivity

% Comp. $Zr/KClO_4$	Impact Sens. Height of 50% Explosion (cm)	Friction Sens. Pistil Load upto which Insensitive (Kgf)
10/90	115	36.0
20/80	106.5	36.0
30/70	106.25	36.0
40/60	90.0	14.4
50/50	92.5	10.8
60/40	99.1	5.4
70/30	92.5	4.8
80/20	103.0	3.6
90/10	94.0	2.0

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Factors Affecting Sensitivity

- Homogeneity
- Particle morphology and size
- Grain size of blended material
- Residual moisture or organic solvent
- Formula and percent composition
- Presence of grit, foreign material, acids, bases
- Chemical incompatibility (acids, moisture, etc)

- Changes to ANY ONE of these will affect sensitivity

- Be warned of static electricity!

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Instrumental Analysis

- Modern instruments and methods have provided pyrotechnicians with substantial new abilities and a wealth of information.

Ability to Study and Analyze:

- Chemical makeup and purity
- Ignition processes
- Sensitivity to ignition
- Micro-structure of solids and mixture layouts
- Thermal/barometric behavior and output
- Reaction products
- Quantification of visual and auditory effects
- Effects of external stimuli (environment, time) on compositions

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Some Instrumentation and Techniques

- Differential Thermal Analyzer (DTA)
- Differential Scanning Calorimeter (DSC)
- Spark Sensitivity Device
- Impact/Shock Sensitivity Device
- Friction Sensitivity Device
- Microscopy
- Particle Size Analyzer
- Fourier-Transform Infrared Spectrometer (FTIR)
- Ultraviolet-Visible Spectrometer (UV-Vis)
- Thermogravimetric Analyzer
- X-Ray Crystallography
- X-Ray Diffraction
- Gas chromatography
- Atomic Emission Spectroscopy
- Optical Emission Spectroscopy
- Raman Spectroscopy
- Nuclear Magnetic Resonance (NMR)
- X-Ray Fluorescence Spectroscopy
- Moisture analysis
- Calorimeter
- Barometer
- Voltameter
- Liquid Chromatography
- Mass Spectrometry
- Atomic Absorption Spectroscopy
- Flame Ionization Detector
- Footcandle Light Meter
- Volume Unit Meter
- Densitometer
- Ion-Mobility Spectrometry
- Neutron Diffraction Crystallography
- Pyrolysis Effluent Gas Detection (EGD)
- Melting point apparatus

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Emission Spectroscopy Uses

- Quantifying color output of colored compositions
- But remember: the human eye is not an electronic spectrometer, it is much more complicated!
- What looks like a fantastic green on the computer may be "rather meh…" to the human eye, or vice-versa.

- Optical Emission Spectroscopy (OES) - determination of purity of compounds, including identification of impurities with quantification

→Extra sodium causing too much yellow to overpower, too much strontium in the barium compound, etc.

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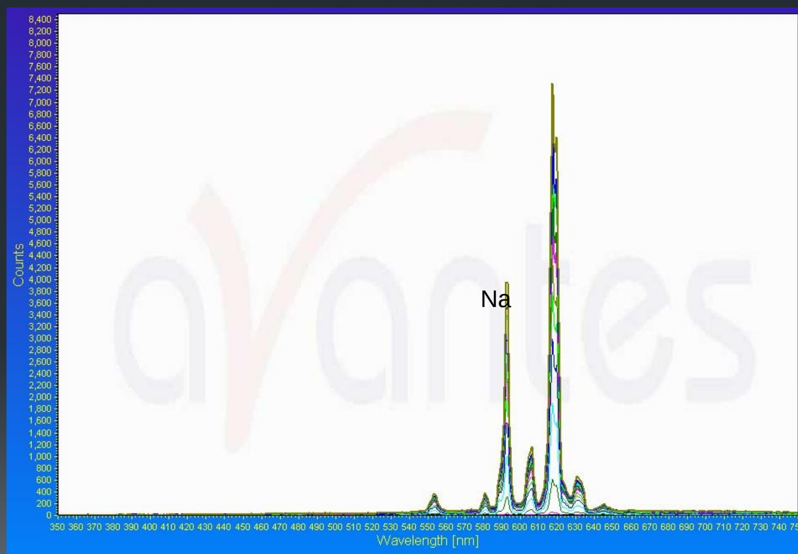
Red Flare Emission Spectrum



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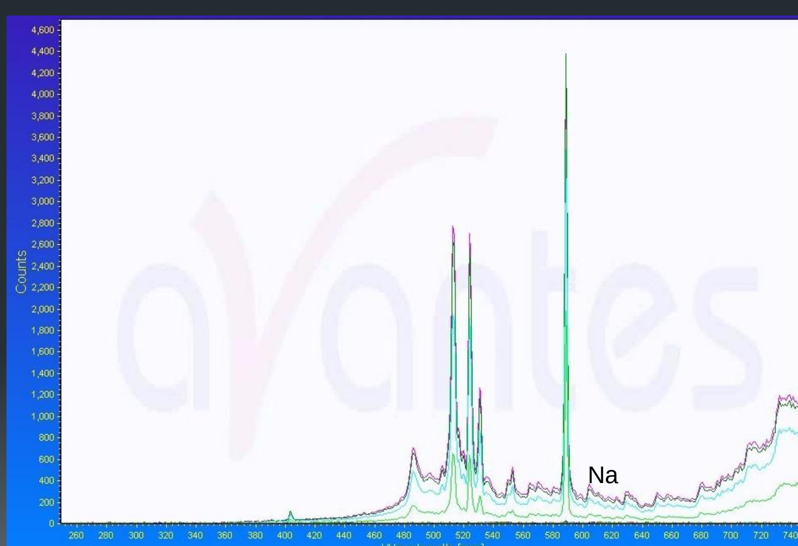
Green Flare Emission Spectrum



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Microscopy

- "Looking small"
- Using microscopes to enhance visualization material that may not be visible with the naked eye
- Optical - standard magnifying glass/microscope
- Electron – using a beam of electrons to illuminate the specimen
  - TEM – transmission electron microscope (older) – maps the resulting diffracted electrons to form the image
  - SEM – scanning electron microscope (modern) – analyzes resulting emissions to determine map of the target
- Scanning – using a physical probe to scan the surface
  - STM – scanning tunneling microscopy
  - ATM – atomic force microscopy

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KNO_3 under a Microscope

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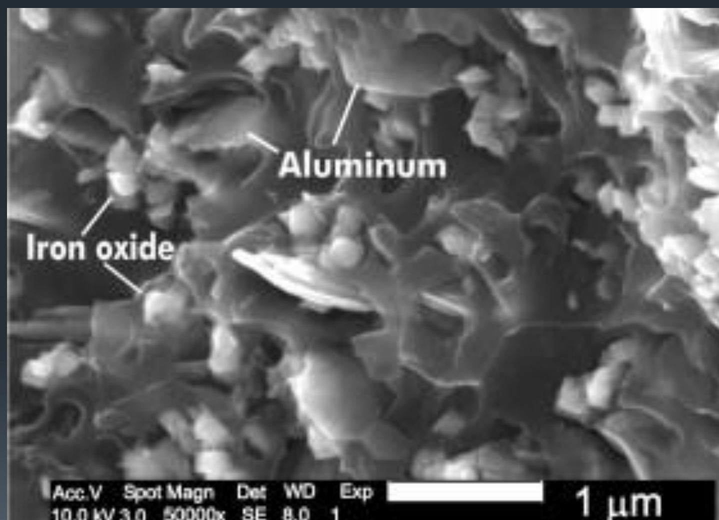
SEM Of Thermite - Al/Fe_2O_3



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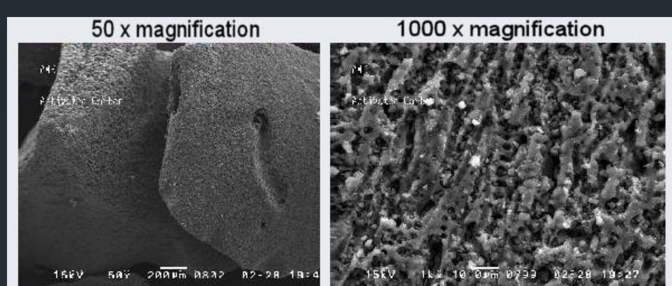
Optical/SEM of Activated Charcoal



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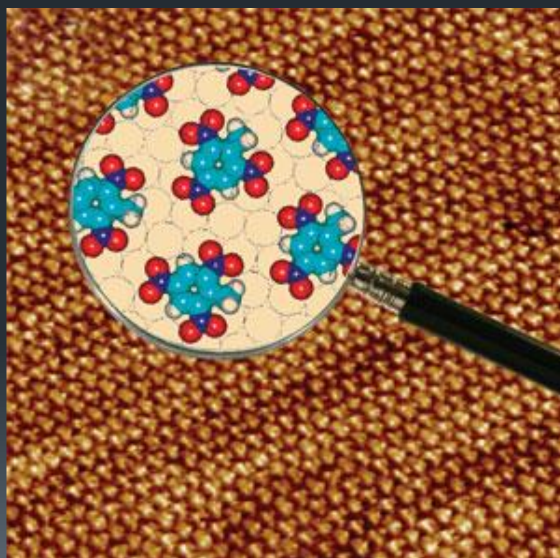
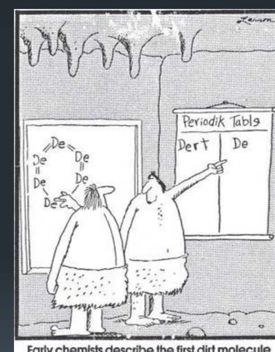
STM of TNT





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Thermoanalysis

- Study of the thermal properties of compositions is exceedingly valuable to the pyrotechnician:

- Ignition temperature/time-to-ignition
- Burning temperature
- Calorimetry
- Differential Thermal Analysis (DTA)
- Differential Scanning Calorimetry (DSC)
- Thermal Gravimetry (TG)
- Evolved Gas Analysis (EGA)
- Pyrolysis – Analysis of effluent gas

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Ignition Temperature

- Measured temperature of ignition of a composition
- Decomposition or activation of materials to allow interaction
  - Release of oxygen/oxidizer
  - Fuel in a state to be oxidized
- Rate of heat release must be sufficient to sustain further burning
- Measured by direct heat application (when did it burn?), DTA, or DSC

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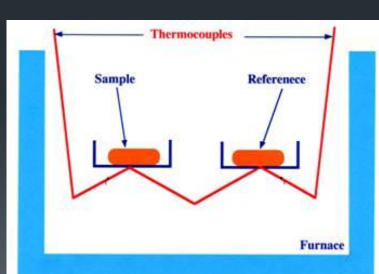
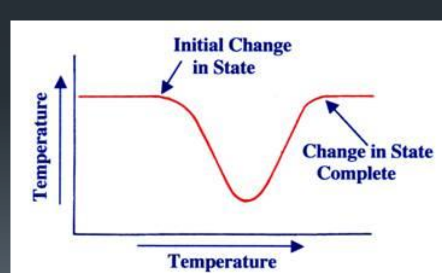
DTA

- Differential Thermal Analysis – measures the difference in temperature between an analyte and reference sample (that just gets hot at a steady rate)
- Endotherm – analyte not increasing in temperature with reference
- Exotherm – analyte hotter than reference





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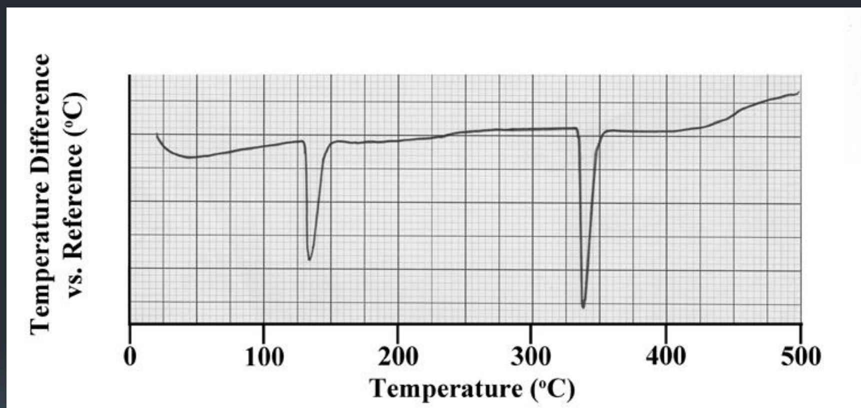
Thermogram of Potassium Nitrate



130 °C – rhombic to trigonal crystalline transition (requires energy/heat)
334 °C - melting

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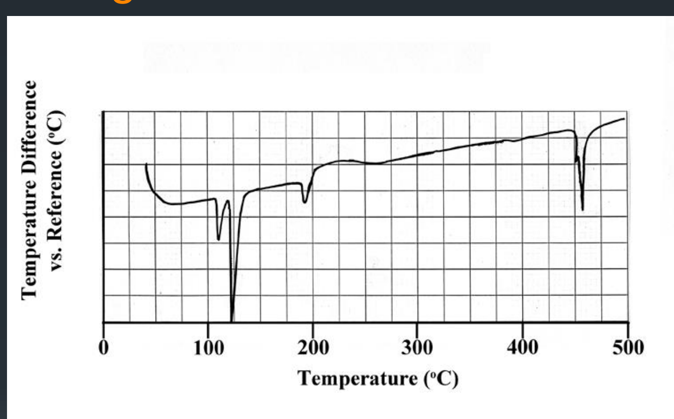
Thermogram of Sulfur



105 °C – rhombic to monoclinic crystalline change
119 °C – melting
180 °C – fragmentation of liquid S8 into smaller units
450 °C – vaporization

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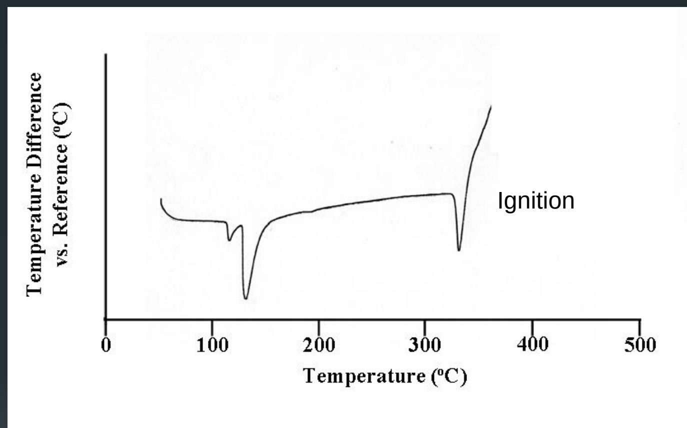
Thermogram of Black Powder



105/119 ºC – Solid phase transition and melting of sulfur (overlap)
130 ºC – rhombic to trigonal crystalline transition
334 ºC – potassium nitrate melting, followed by exotherm (ignition)
→ Release of oxygens from KN major player in ignition

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Conclusion: Analyzing your Composition

- Microscopy
- Suite of sensitivity tests
- Thermal analysis / ignition temperatures
- Functional analysis (did it work?)
- Analysis of desired output:
- Color – spectroscopy
- Light/Obscuration – photometry/light meter
- Gas generation – TGA/gas analyzer
- Sound – sound level meter/loudness meter
- Chemical analysis/Forensics – Chromatography/mass spec, IR, UV-Vis, Raman, x-ray fluorescence, x-ray diffraction, &c

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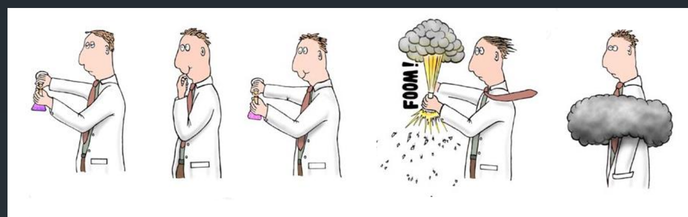
Safety!



- All pyrotechnic compositions are sensitive to some form of stimulus: heat/flame, spark, shot, friction, shock
- Every effort needs to be made to handle materials safely
- Do not experiment with chemicals that you do not understand!

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Other Resources

- A.A. Shidlovskiy, Principles of Pyrotechnics
- T. Shimizu, Fireworks, The Art, Science, and Technique
- J.A. Conkling, C.J. Mocella, Chemistry of Pyrotechnics
- Journal of Pyrotechnics, Pyrotechnic Chemistry
- American Pyrotechnics Association
- Pyrotechnics Guild International
- **Local hobbyist clubs**

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Audience Survey Question

ANSWER THE QUESTION ON BLUE SCREEN IN ONE MOMENT

What is your favorite memory of a fireworks show?

- Independence Day (U.S.)
- Bonfire Night/Guy Fawkes Night (U.K)
- Setting off snappers and bottle rockets as a kid
- New Year / Chinese New Year
- [Can’t tell you, we bent some laws doing it, but it was AWESOME!]

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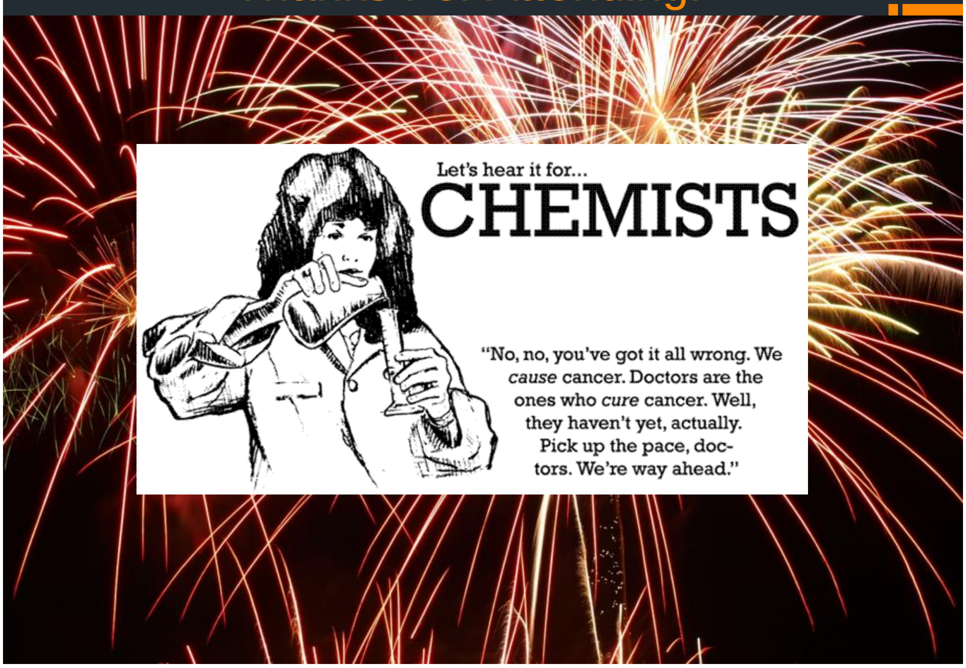
Thanks For Attending!



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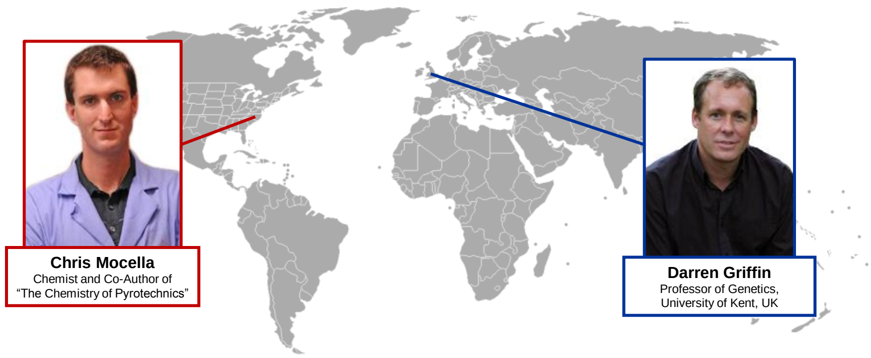

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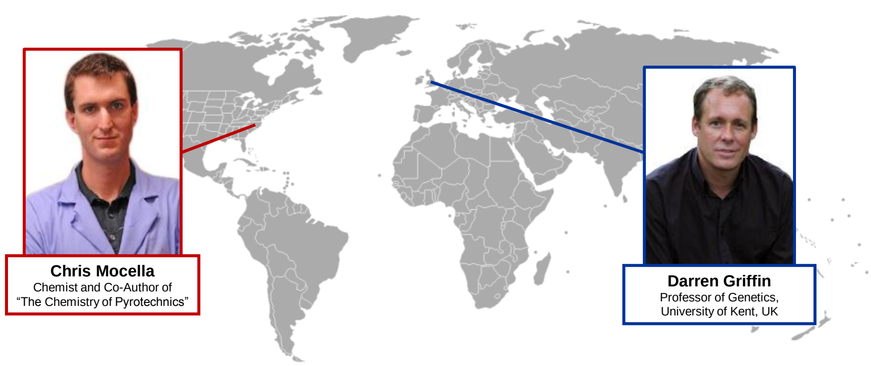

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