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14. ABSTRACT

This presentation covered an overview of AFRL's rocket propulsion laboratory and discussed advanced chemical propulsion for spacecraft. It discussed hydrazine, state-of-the-art rocket fuel, hydrazines and flammability, energetic ionic liquids, chemical propellant development, hydrazine replacement monopropellant objectives, relevant monopropellant properties, AF-M1028A monopropellant composition and physical properties, thruster tests of AF-M1028A, ionic liquids as explosives, predictive toxicology, predictive methods expected payoff. AFRL continues efforts in energetic ionic liquids (IL) research, because IL-based propellants can convey unique capabilities, and energetic ILs have intriguing explosive properties. IL material properties promise significantly improved performance and reduced toxicity compared to hydrazine fuels.

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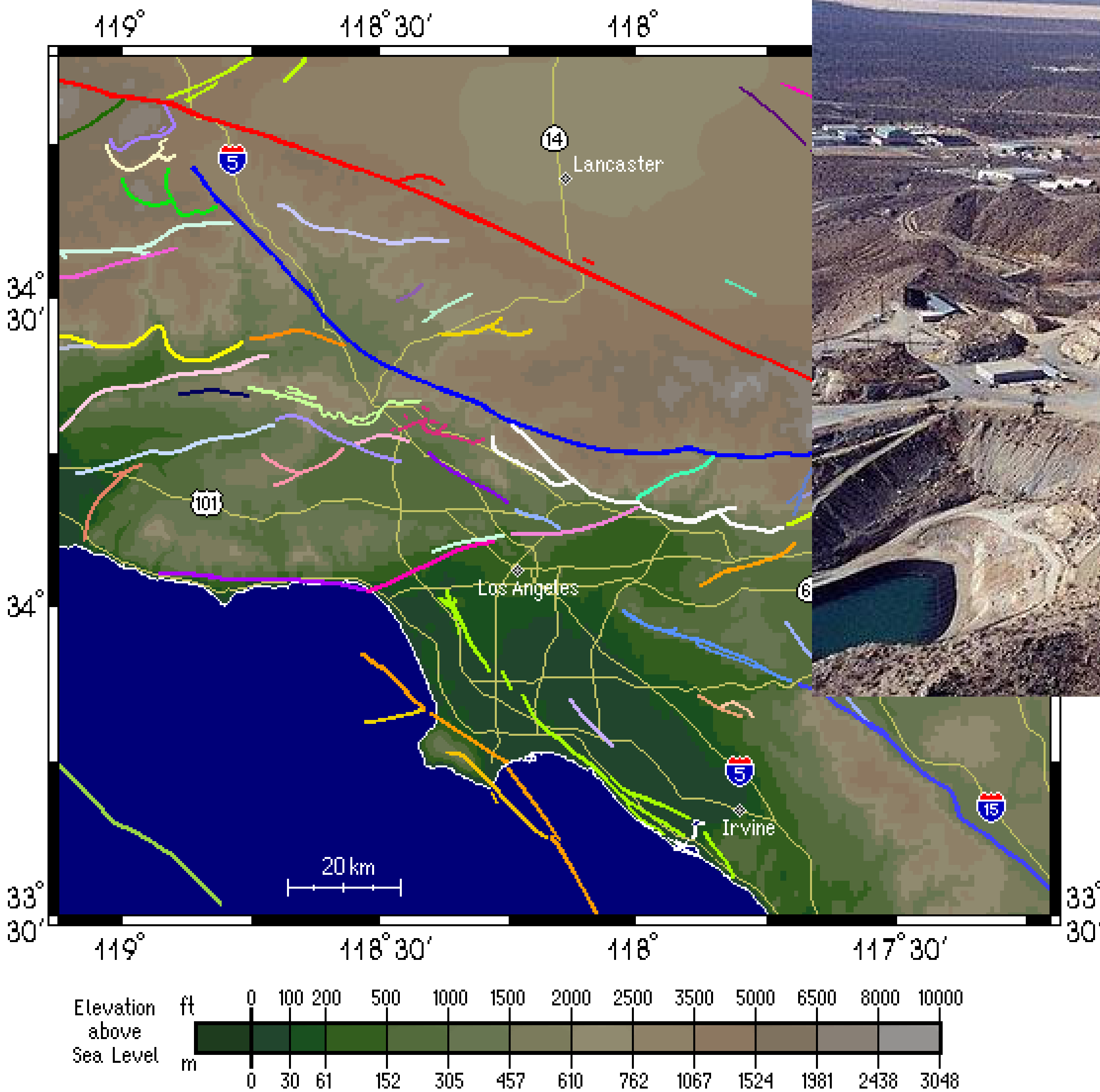
R&D of Energetic Ionic Liquids

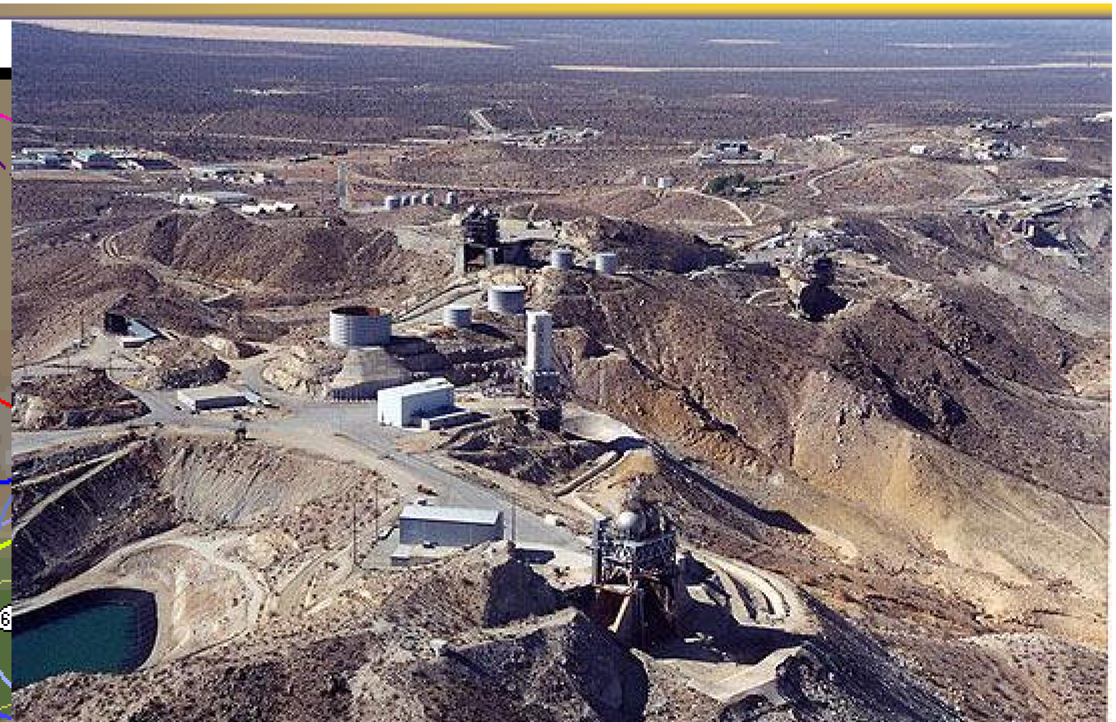
Symposium in Honor of Robin D. Rogers:
Industrial and Engineering Chemistry Fellow

243rd ACS National Meeting
San Diego CA
March 2012

Tom Hawkins
AFRL/RZSP

Where is AFRL's Rocket Propulsion Laboratory?





Images: Southern California Earthquake Data Center, California Institute of Technology; The Center for Land Use Interpretation

Propellant Laboratory Complex
Area 1-30

Advanced Chemical Propulsion For Spacecraft & Hydrazines

Communication (Iridium)

Global Positioning & Navigation (NAVSTAR GPS)

Weather (NASA TRMM)

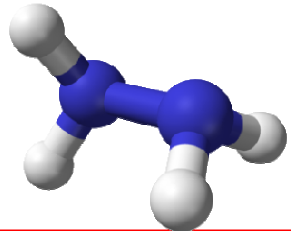
Spacecraft /Satellite propulsion employ hydrazines in both monopropellants and bipropellants

Reduced toxicity can give:
- lower handling cost
- lower transport cost
- more rapid response

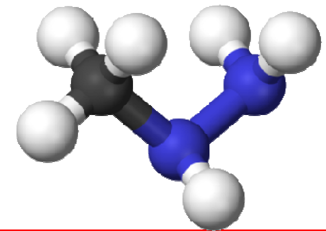
Higher performance gives:
- longer lifetime
- faster response time
- larger payloads

Hydrazine – State of the Art Rocket Fuel

Hydrazine



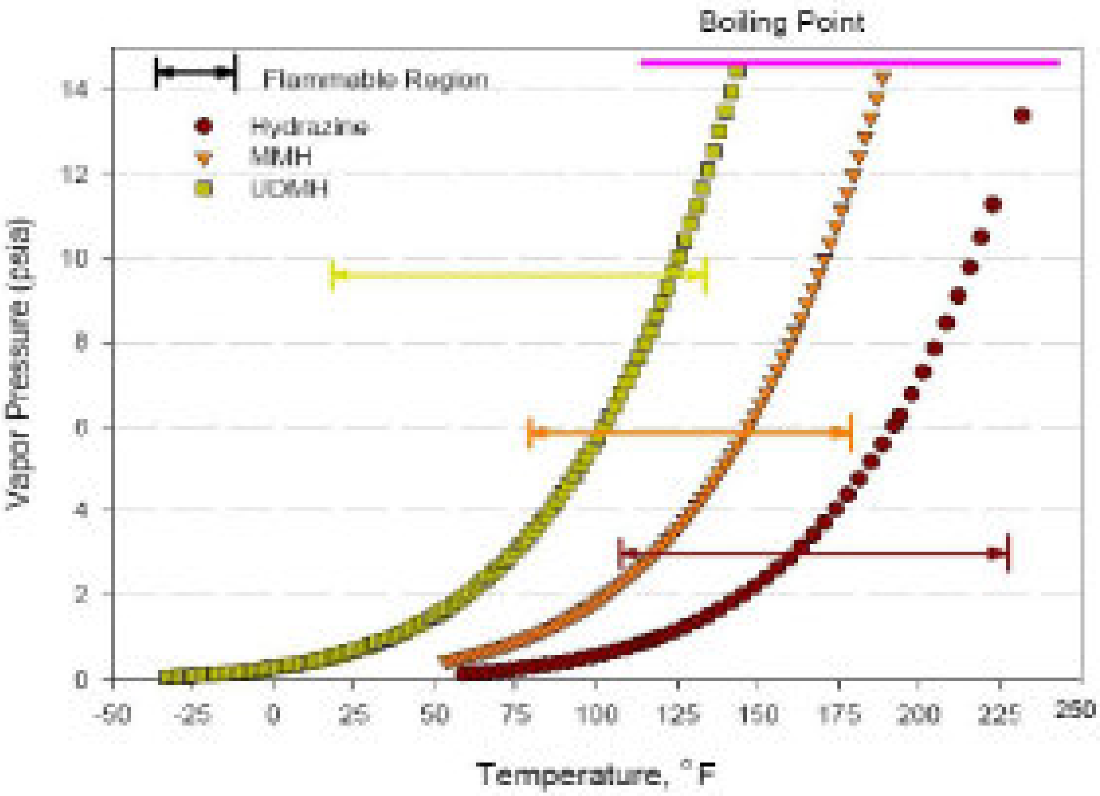
Monomethylhydrazine



- ❑ **Hydrazine fuel vapor toxicity can increase testing/operations costs:**
  - **System Handling/Fueling by certified crews in high level PPE**
    - **$0.5M in equipment & scheduled PPE QA**
    - **3 weeks of Level A training**
  - **Monitoring system requirement in the field**
- ❑ **Vapor toxicity can limit transportation options**

Hydrazines also bring additional hazards to operations

Hydrazines & Flammability



Hydrazines Spill and Fire Summary*

Fuel Incidents:

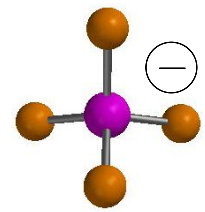
24	Total
8	Led to a Fire
2	Led to an Explosion
7	Led to Injuries (minor to death)
12	Led to Hardware Damage

***NASA/TP 2009-214769**

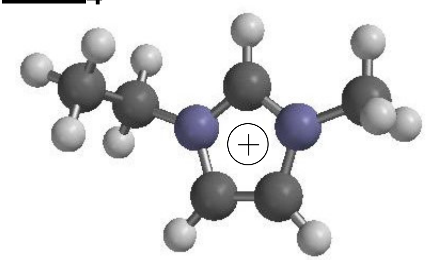
- **Hydrazine, MMH and UDMH pose flammability hazards at temperatures easily achieved at storage and operation conditions**
- **Take advantage of ultra-low vapor pressure of ILs**

Energetic Ionic Liquids
Avenues to Lower Toxicity & Higher Performance

- **History**
  - An ionic compound that has a melting point at or below 100ºC
  - Seminal work at USAFA (Wilkes et.al.)
  - Industrial solvents, green chemistry
    - Low vapor pressure, low vapor toxicity
    - Wide solubility ranges

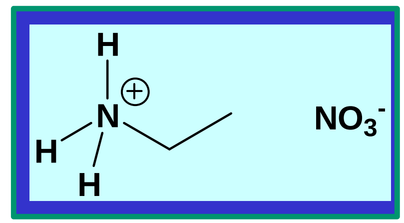


$AlCl_4^-$



EMIM cation
(1-ethyl-3-methylimidazolium)

- **ILs as *Energetic* Materials**
  - First energetic ILs: chemical oddities
  - AFRL realizes chemical structure manipulation leads to new classes of highly, energy dense materials (HEDM) for advanced propulsion

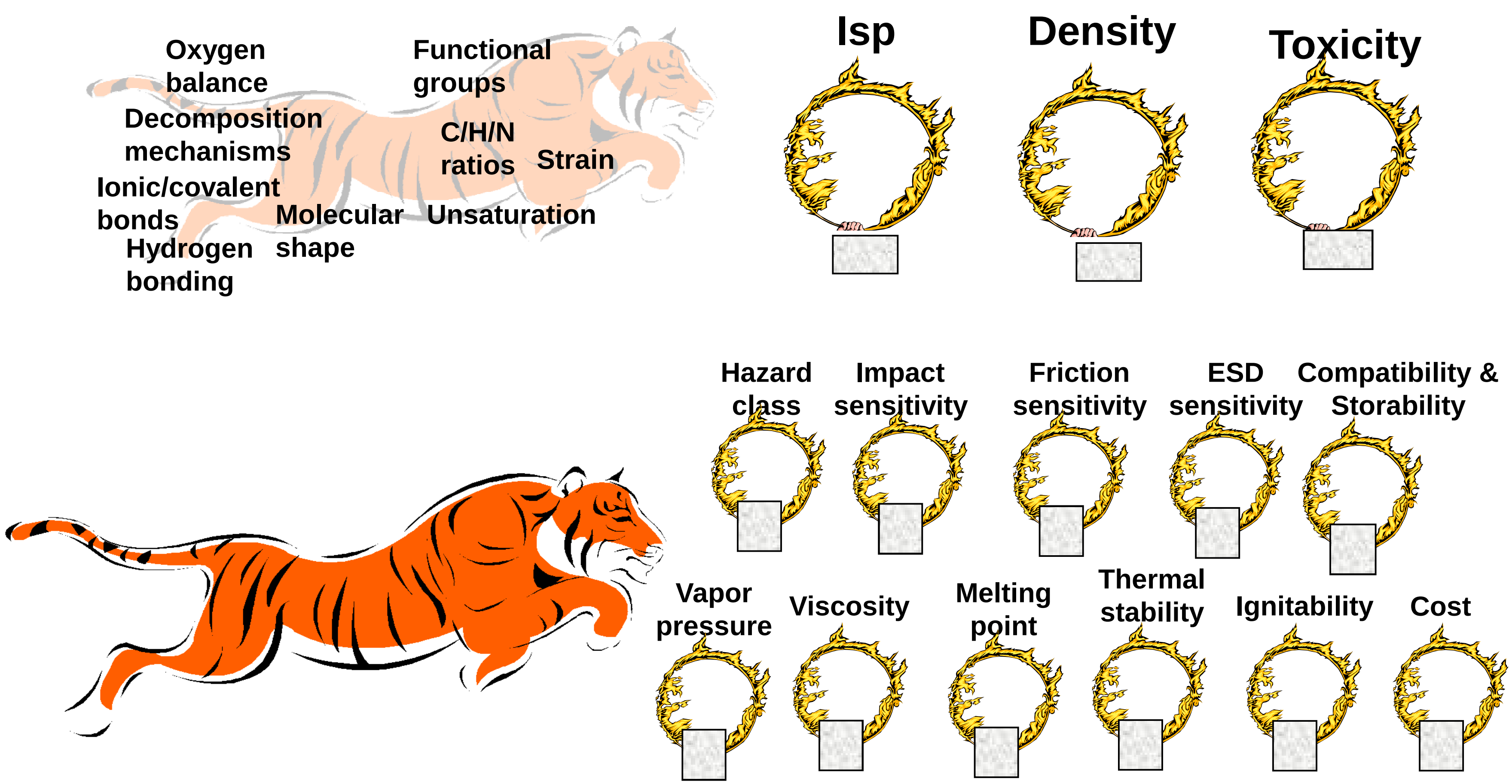


Liquid propellants:
Spacecraft thrusters
DACS/ACS
Booster engines

Take advantage of ultra-low vapor pressure of ILs to produce new classes of Green Propellant Fuels

Chemical Propellant *Development*

There is more to it than performance & toxicity



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Hydrazine Replacement Monopropellant Objectives

- Challenging first level property requirements

Characteristic	Objective
Isp	242 lbf-sec/lbm
Density	≥ 1.00 g/cc
Vapor toxicity	No SCBA required in handling
Exhaust carbon content	No soot in exhaust
Melting point	< 1^{O}C
Detonability	No propagation in lines of < 0.75 inch diameter
Impact sensitivity	> 20 kg-cm minimum (E_{50})
Sliding Friction	>300 N (Julius Peters –BAM)
Adiabatic compression	No explosive decomposition
Thermal stability	< 2% by wt. decomposition (DOT)

Relevant Monopropellant Properties

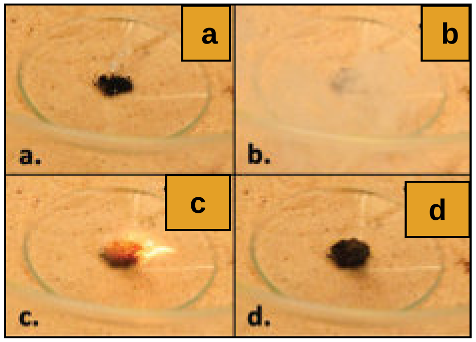
Properties	HEHN	Hydrazine
Viscosity (cps, 20C)	94	0.94 (a)
Surface Tension (dyn/cm, 20C)	81	68 (a)
Melt point, °C	<-45 (glass)	1 (a)
Catalyst ignition	Yes	Yes
Clean Combustion or Decomposition	No, Soot	Yes, No Soot

(a) Hydrazine and Its Derivatives , E.W. Schmidt, ed., J.W. Wiley & Sons, 2001

$$[HOCH_2CH_2N_2H_4]^+ \; NO_3^-$$

HEHN; ρ= 1.42 g/cc; MP <-25C

Reactivity of HEHN on catalyst



R. Rogers et.al., *Chem. Commun., 2010, 46, 8965–8967*

With this in mind, AFRL chose to:

- Balance O/F by incorporating hydrazinium nitrate/ammonium nitrate eutectic
- Take advantage of catalytic reactivity of hydrazinium nitrate (IL) oxidizer
- Use diluent (water) as effective means to lower hazards, combustion temperature and viscosity
- Achieve Hydrazine monopropellant performance

AF-M1028A Monopropellant Composition & Physical Properties

Property	AF-M1028A	Desired Objective
Composition	HEHN/HN/AN/H_20	--
Specific Impulse $_{vacuum}$ (Pc =300psi; exp=50:1)	242.5 sec	242 sec
Density	1.38 g/cc	≥ 1.00 g/cc
T_{melt}	-7 C	< 1 C
Vapor Concentration Hydrazines ; 8-hr, TWA	< 10 ppb	< 10 ppb

Overall: AF-M1028A meets initial physical and toxicity property objectives

AF-M1028A
Small-Scale Hazards

Test	AF-M1028A	Desired Objective
Detonability	Negative (deformed plate)	Negative (deformed plate)
Impact Sensitivity (Olin-Mathiesen)	> 86 Kg-cm	>20 (E_{50}) Kg-cm
Sliding Friction (Julius Peters –BAM)	352 N	>300N
Thermal (50 ml beaker @75^{o}C/48 hours)	No reaction Wt. Loss < Wt. Volatiles	No reaction Wt. Loss< Wt. Volatiles
TGA (75^{o}C/48 hours)	0.86 Wt % , Excluding Volatiles	<2.0 Wt%, Excluding Volatiles
Electrostatic Discharge	>1J	>1J

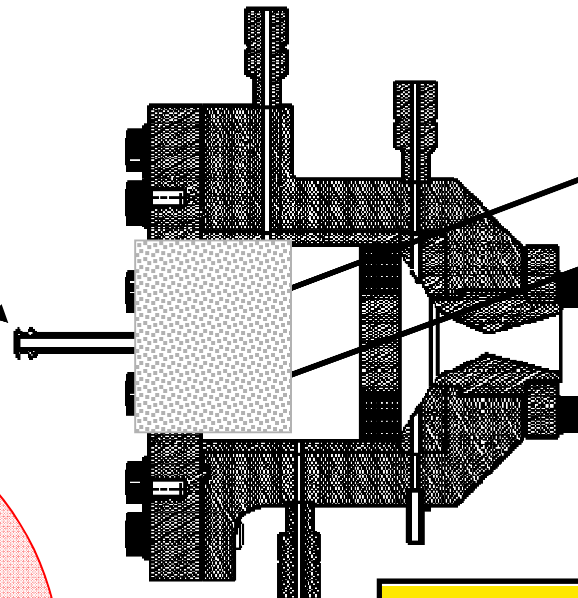
Overall: AF-M1028A has acceptable small-scale hazard properties

Thruster Tests of AF-M1028A

Proof of Principle

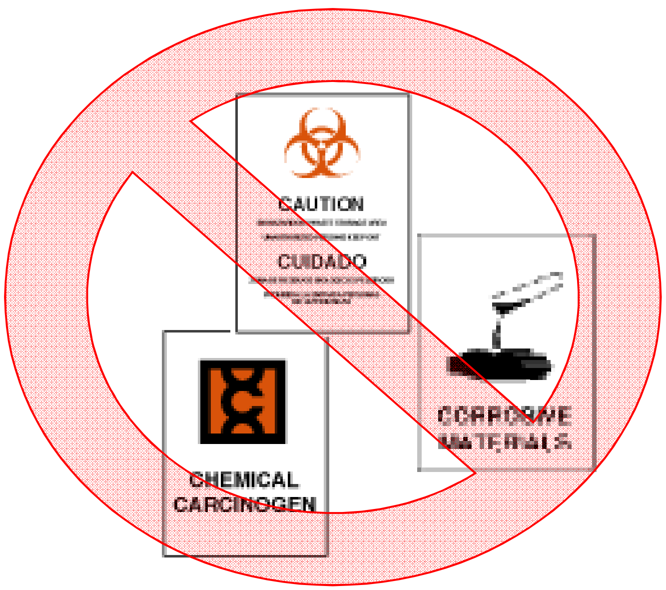
Propellant

- AF-M1028A Objective
- Specific Impulse equals Hydrazine



Thruster Materials

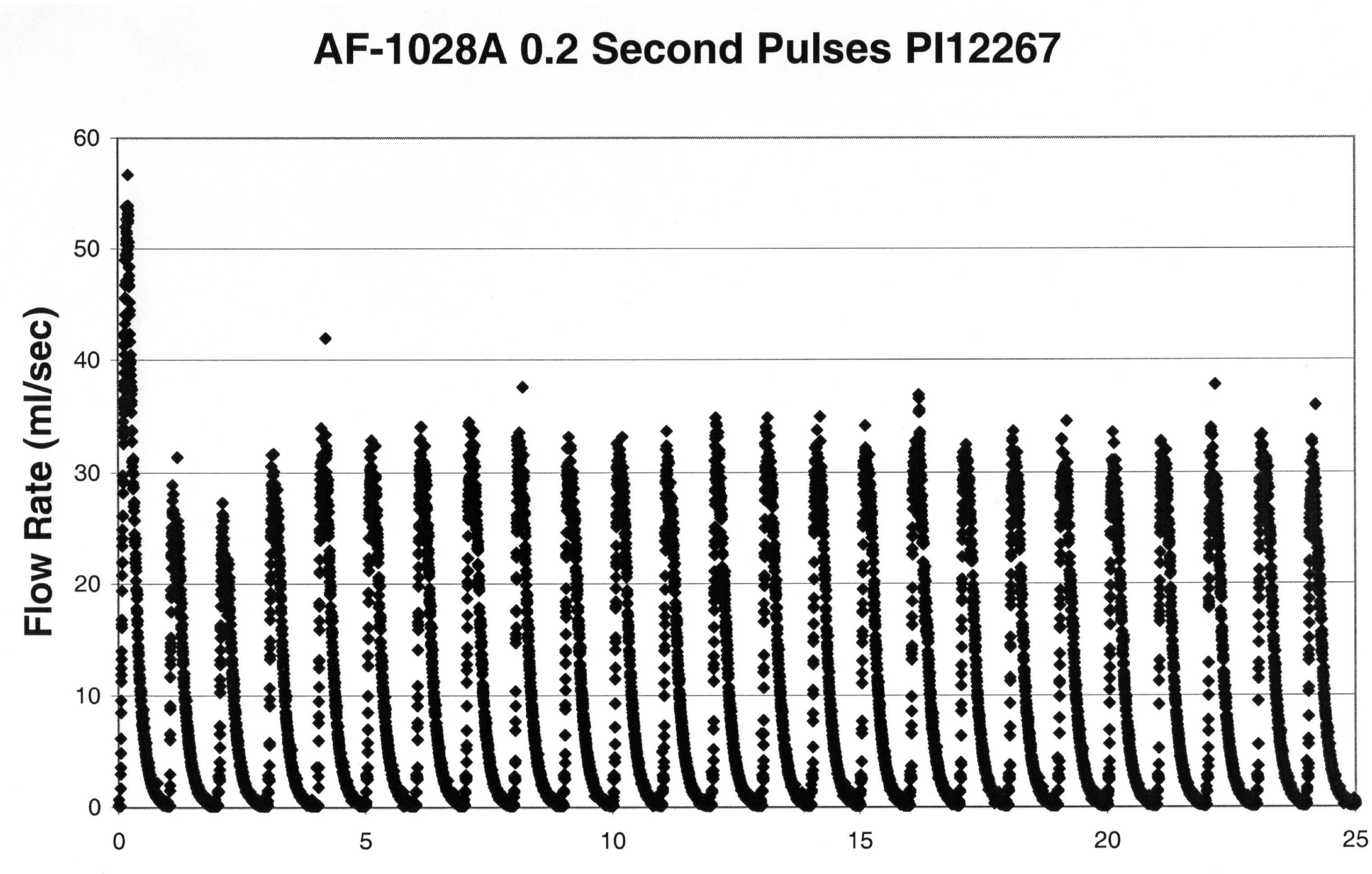
- S-405 (Ir/Al_2O_3)
- Catalyst/Substrate to Support Firing for short pulses



Potential Transition Opportunities

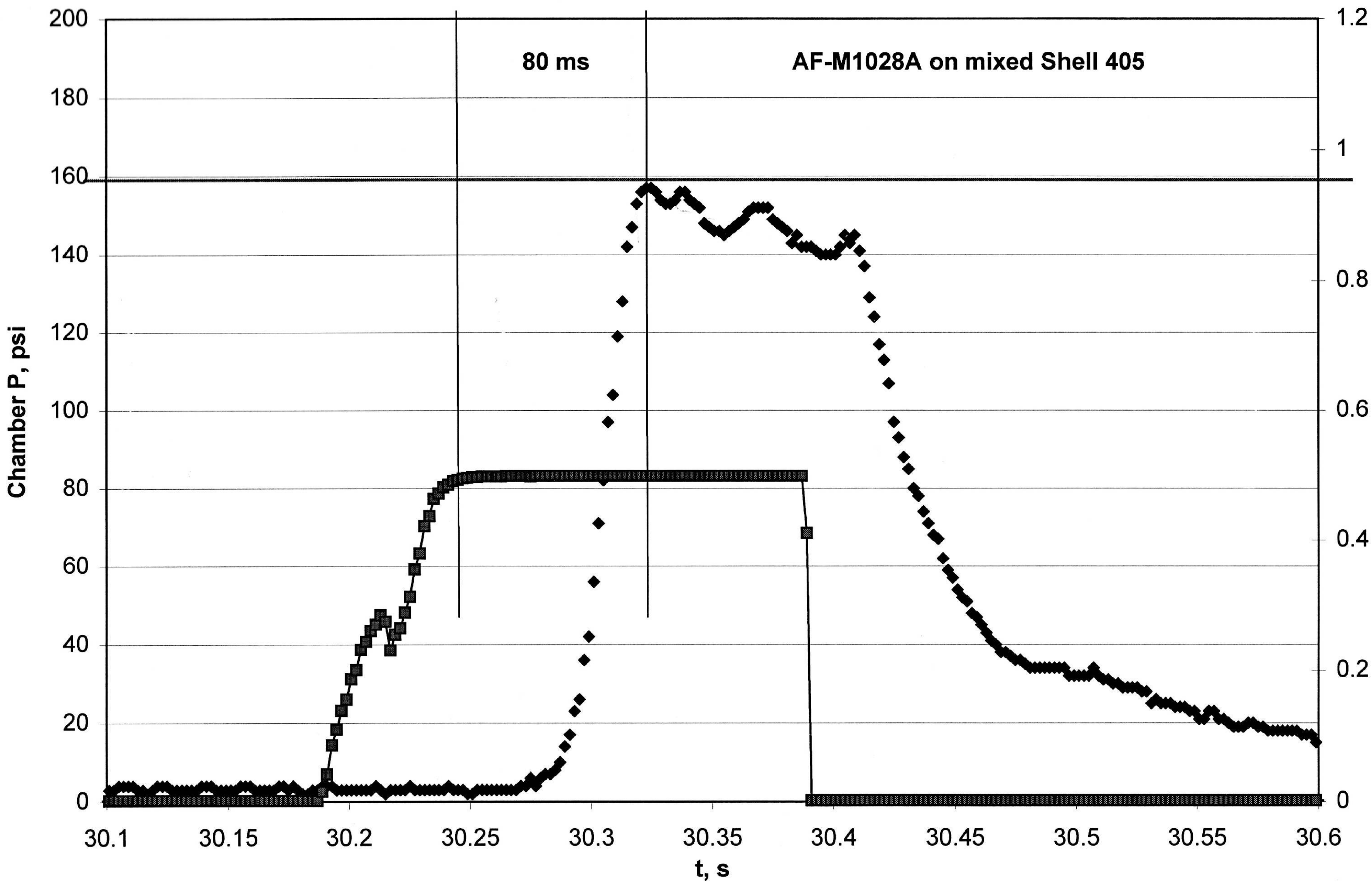
- Satellites
- F16 EPUs
- Gas Generators

Thruster Test Pulse Characterization



Good, repeatable propellant injection & flow through catalyst bed

Thruster Test Pulse Characterization



Good pulse ignition and repeatable shape

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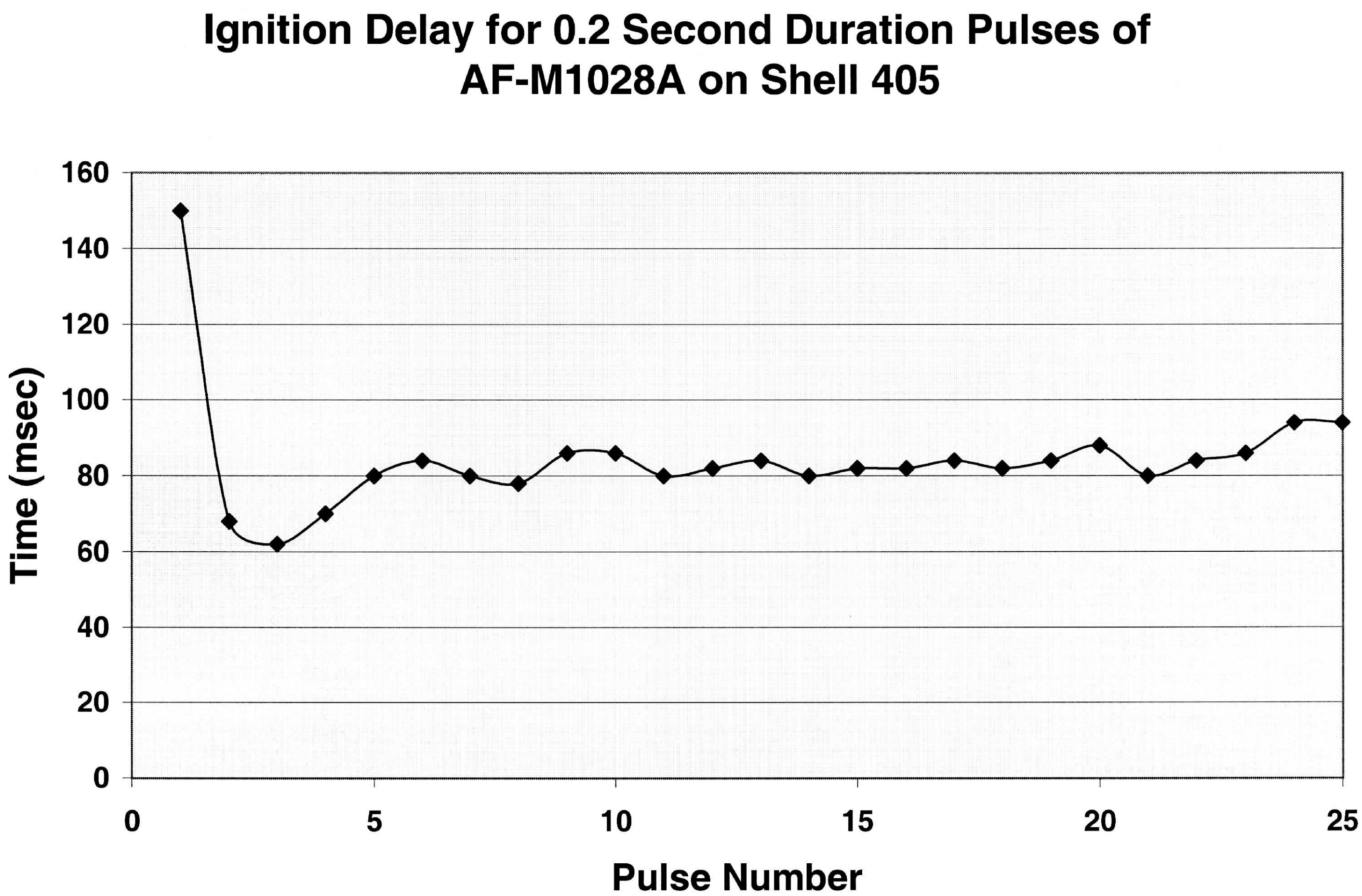
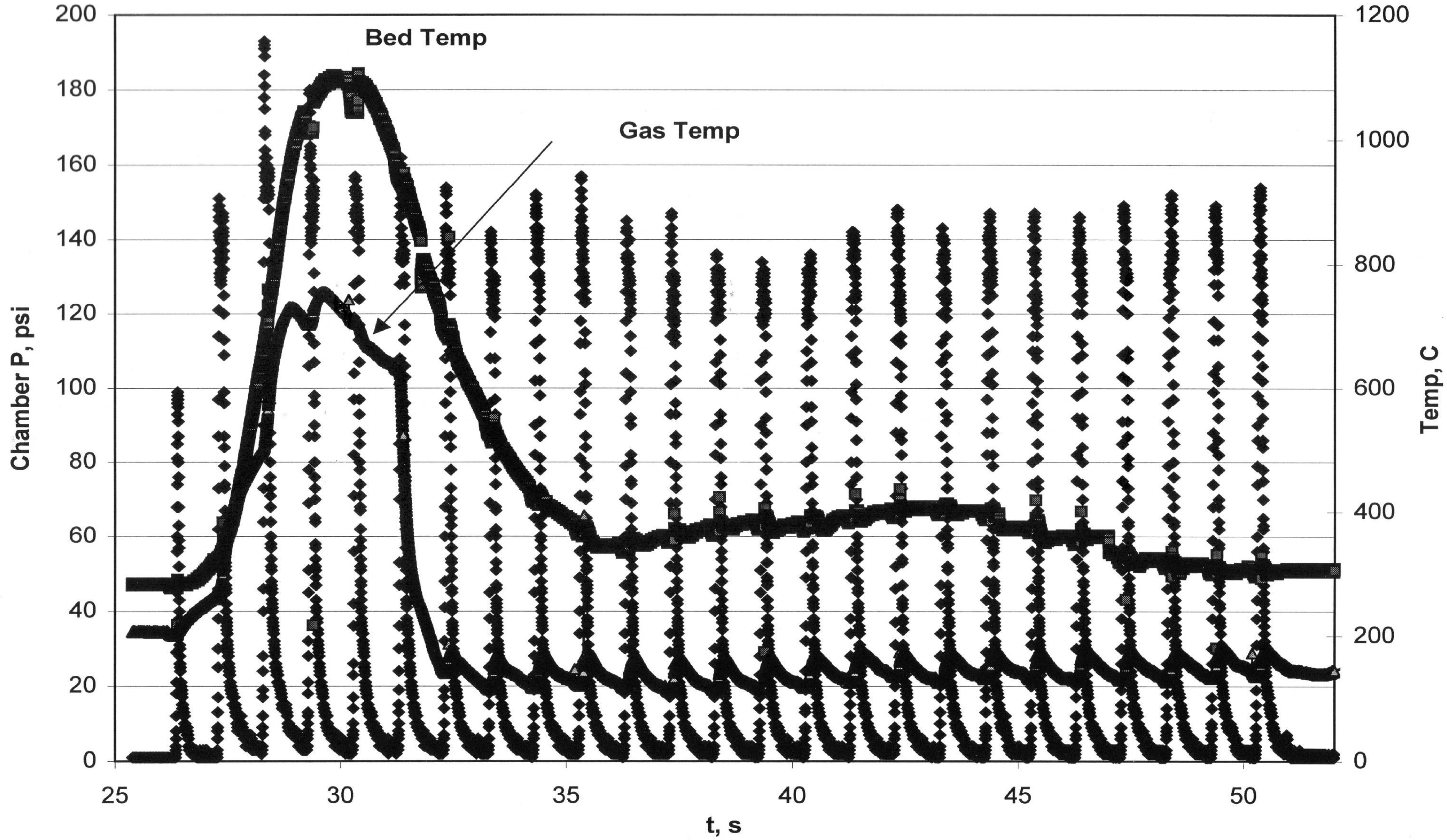
Thruster Test Pulse Characterization



Good, repeatable ignition delay for pulse train

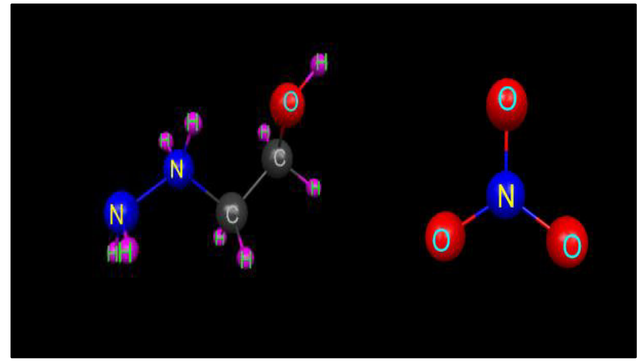
Thruster Combustion



- Catalyst bed temperature > 1400K
- Exhaust gas temperature ≈ 1000K

Ionic Liquids as Explosives

IL-Based Explosive DetonabilityTest (2-kg)



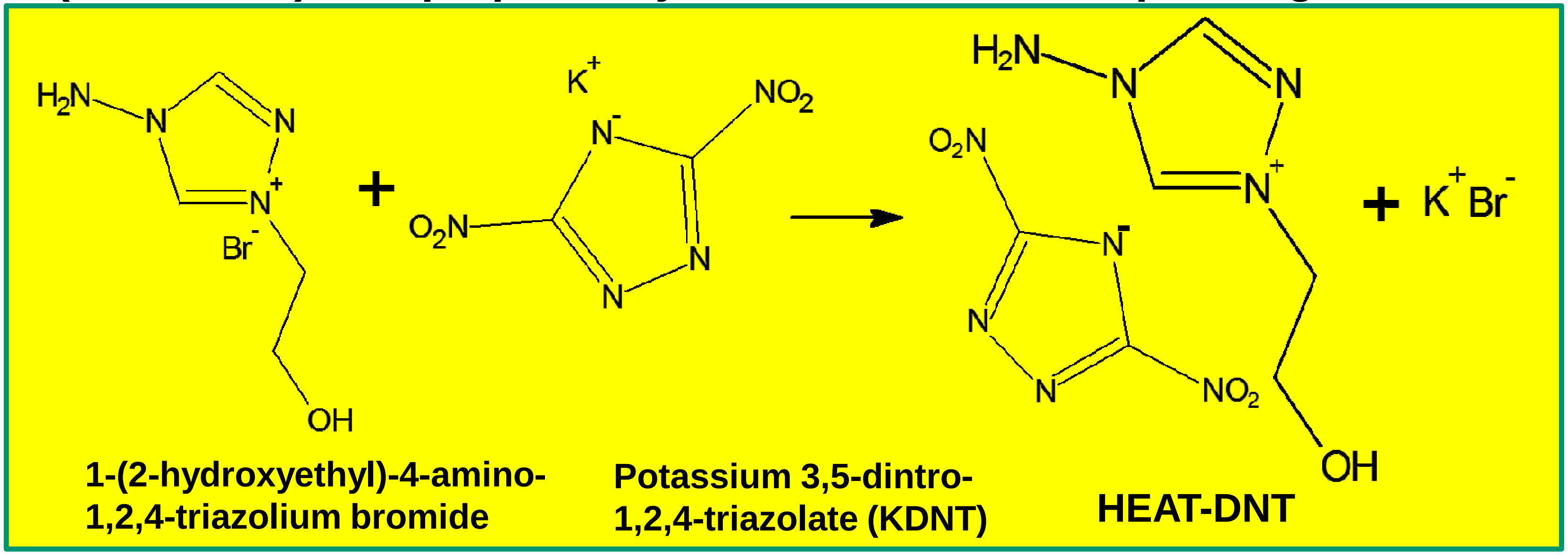
- **Initial USAF work on energetic RTILs over 15-years ago**
- **Recognized potential for advanced explosives**
- **Navy encouraged R&D on melt cast explosives**

HEAT-DNT

- Azolium Azolates incorporating 3,5-dinitro-1,2,4-triazolates known
  - Katritzki, Rogers, Holbrey et.al. ,Chem. Commun., 2005, 2–5
    - BMIM-DNT found to be an IL with T_m = 35C & T_{decomp} = 239°C
  - Shreeve & Xue, Adv. Materials. 2005, *17*, 2142-2146
    - 1-(2-azidoethyl)-1,2,4-triazolium 3,5-dinitro-1,2,4-triazolate; T_m = 85C & T_{decomp} = 140°C

AFRL effort aimed at high T_m & high T_{decomp} ILs using triazolium cations

1-(2-hydroxyethyl)-4-amino-1,2,4-triazolium 3,5-dinitro-1,2,4-triazolate (HEAT-DNT) was prepared by metathesis of corresponding salts



HEAT-DNT

Safety & Performance Properties	
Impact sensitivity	5 no go @ 70 kg*cm
Friction	5 no go @ 117 newtons
Melting point	107 C *
Decomposition onset	>200 C
Heat of formation	0 kcal/mol (est.)
Density	1.61 g/cc (measured)
Shock velocity	7160 m/s (calcd.)
P c-j	20.46 GPa (calcd.)
E detonation	5.985 KJ/cc (calcd.)

- Higher T_m & T_{decomp} certainly achieved
- Performance near TNT
- Synthesis undertaken seeking IL with higher energy cation, AMT (1-amino-3-methyl-1,2,3 triazolium)

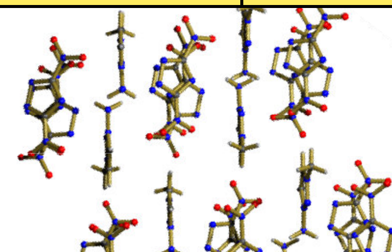
AMT-DNT Properties

Properties of AMT-DNT <u>improvement over HEAT-DNT</u>

1-amino-3-methyl-1,2,3-triazolium 3,5-dinitro-1,2,4-triazolate	M.P.	Decomp. Temp.	Density (g/cc)	Heat of Form. (est)
	84^o C	235^{o}C	1.6037(m)	+76 kcal/mol

<u>X-ray crystal structure of AMT-DNT</u>

- Note association of anions & near perpendicular arrangement of cation rings to anion rings



Ingredients	Total Detonation Energy (KJ/cc)	Shock Velocity (mm/μs)	C-J Pressure (GPa)
TNT	6.94	7.06	19.7
AMT-DNT	6.96	7.39	22.3
HEAT-DNT	5.99	7.16	20.5
1-AMTN	7.92	8.12	23.6

*** CHEETAH 4.0 product library exp6.2**

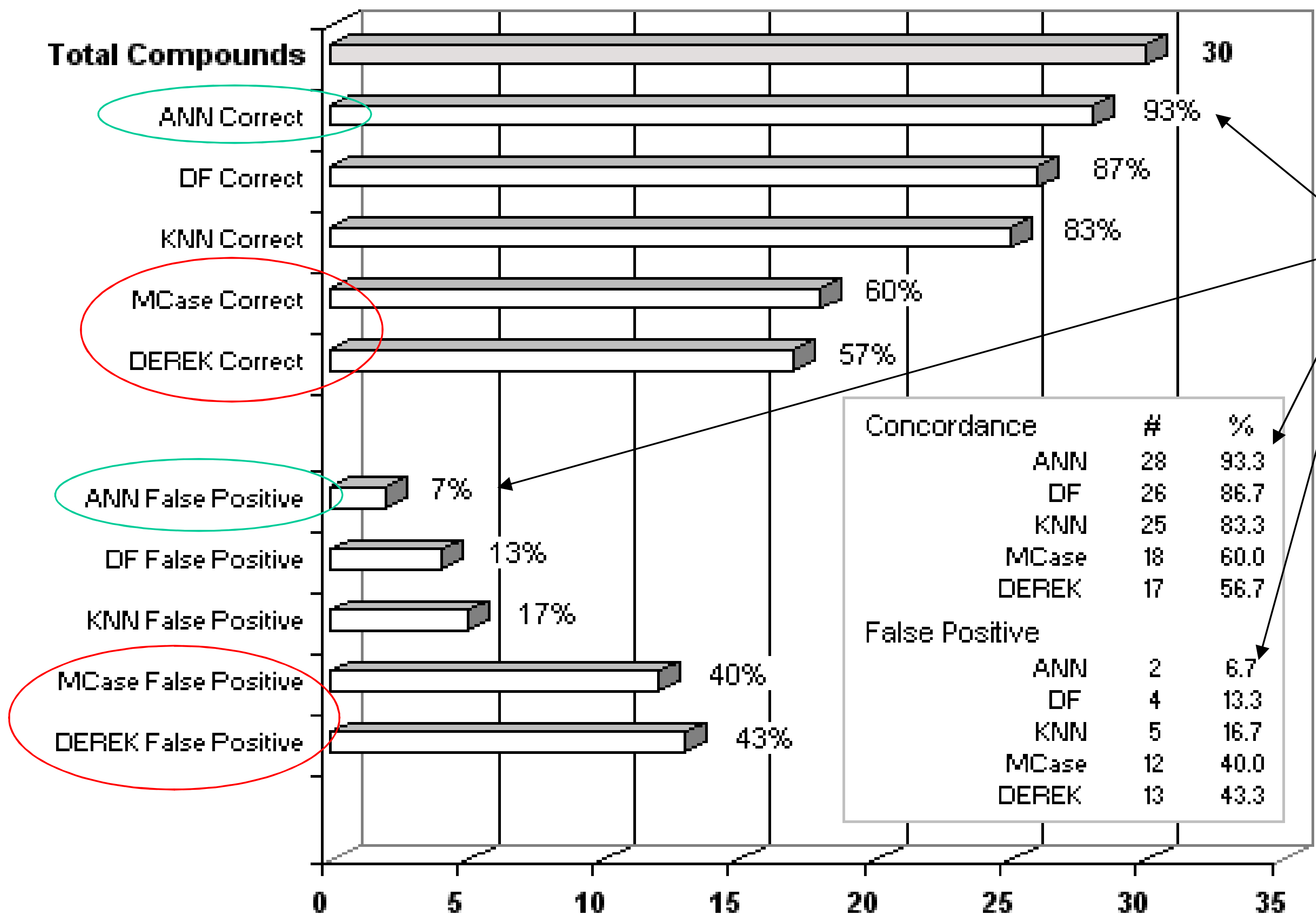
Another Challenge: Predictive Toxicology

- **Background**
  - – **<u>Next generation propellants & explosives are emerging</u> with many programs championed by US Army, Navy and USAF involvement**
    - **Environmentally benign impact initiated devices (DOE)**
    - **Lead-free electrical & percussion primers (Navy/Army)**
    - **Chlorine-free pyrotechnics (Navy)**
    - **Chlorine-free (AP-free) solid propellant (Army/Navy/AF)**
  - – **USAF AF-M315E**
    - **Propellant uses ionic liquids to yield low vapor toxicity**
  - – **Sweden/ECAPS LMP-103S**
    - **Propellant uses ADN-based formulation**

New PEP materials are likely to employ advanced energetic molecules

***<u>Issue</u>*: Currently available, predictive toxicology models (e.g. TopKat, EPI Suite, ADMET) do not comprehensively handle EMs, particularly salts**

Comparison of prediction methods for general toxicity of 30 drugs in external test set

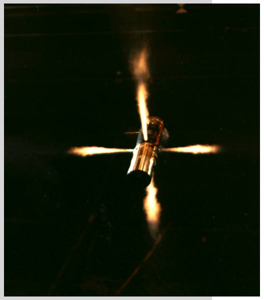


Artificial neural networks outperformed other methods

(Golbraikh, A. & Tropsha A., *J. Mol. Graphics Mod*. 2002, 20, 269-276.)

Predictive Methods Expected Payoff

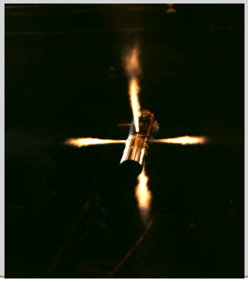
- Well-functioning, predictive toxicological methods for EM development can significantly affect life cycle costs for new systems
- DoD will be able to make more informed program decisions
- ESOH risks will be mitigated early in Acquisition/RDT&E process



- DoD will save $$$ in clean-up, compliance and restoration costs

Summary

- **AFRL continues efforts in energetic ionic liquids research**
  - **IL-based propellants can convey unique capabilities**
  - **Energetic ILs have intriguing explosive properties**
- **IL material properties promise *significantly improved performance* & *reduced toxicity* compared to hydrazine fuels**
  - **Moving to lower testing/operations costs, improved operational responsiveness (as propellant candidates emerge, cost analysis will determine overall system benefits)**
  - **Leading to next generation systems with increased payload, range, and lifetime**



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– Cliff Bedford, ONR, Energetic ILs for Melt Castable Explosives