Navy Energetics ManTech Center

NSWC IHEODTD
Flexible Manufacturing Capability

Presenter Patrick Greer, PhD

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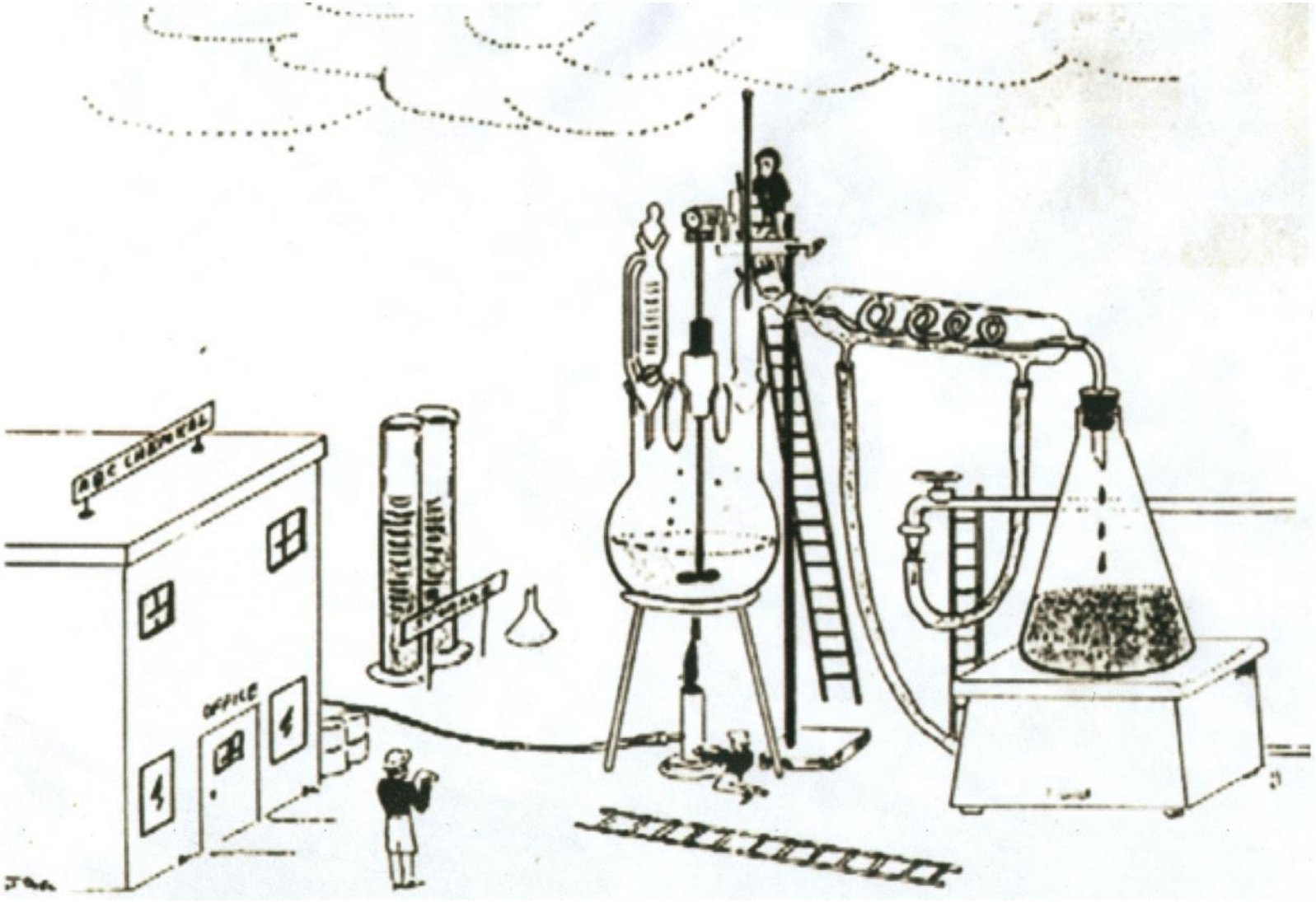
Event 2016 CAD/PAD Technical Exchange Workshop
Joint Base Andrews, Maryland

What is Process Scale-Up?



Fundamentals of Process Scale-Up

- Bench chemistry, gram scale
  - Performed by chemist, with many unknown factors of influence, high risk, an unclear process, and requirements that are not defined.
  - The goal is the science.
  - Typical glassware sizes range from 100mL to 5-L glass vessels.

- Automated laboratory reactor, 100 gram scale
- Pilot plant, kilogram scale
- Small manufacturing, 100 kilogram scale

Fundamentals of Process Scale-Up

- Bench chemistry, gram scale
- Automated laboratory reactor, 100 gram scale
  - Transition from chemist to chemical engineer, factors are becoming characterized, manufacturing process is being resolved, risks are identified, and requirements are more well defined.
  - The goal is safety and consistency.

- Pilot plant, kilogram scale
- Small manufacturing, 100 kilogram scale

Fundamentals of Process Scale-Up

- Bench chemistry, gram scale
- Automated laboratory reactor, 100 gram scale
- Pilot plant, kilogram scale
  - Performed by chemical engineer, factors of influence are well characterized, manufacturing process is set, risks are identified and mitigated, and requirements are defined.
  - The goal is production; a safe, robust and consistent process.
  - Glass jacketed vessels at 10, 20, 50 and 100-L size.

- Small manufacturing, 100 kilogram scale

Fundamentals of Process Scale-Up

- Bench chemistry, gram scale
- Automated laboratory reactor, 100 gram scale
- Pilot plant, kilogram scale
- Small manufacturing, 10-100 kilogram scale
  - Performed by chemical engineer and operators, factors of influence are well characterized, manufacturing process is set, risks are identified and mitigated, and requirements are defined.
  - The goal is production; safe, robust consistent, and economical process.

Chemical Scale-Up Capabilities

Code M24 Scale-Up: A group of chemists and chemical engineers

Laboratory Research
- Synthesize new energetic molecules of interest
- Provide consultation in areas of expertise
- Optimization of energetic chemical precursors

Manufacture small quantities of rare materials for the energetic community
- Materials that are not available in the market due to small demand but are needed by the energetic community
- Provide a CONUS source for critical chemicals (e.g. DDNP, LMNR, XU-238)

Manufacture large quantities of energetics
- Scale-up of energetics only produced previously in laboratory quantities
- Quantities necessary for end-item testing

Chemical Scale-up Facilities

<u>Laboratory</u>

- Laboratory scale, 100mL to 5-L size glassware
- Laboratory vacuum oven, computer controlled
- In-house analytical tools (DSC, HPLC, FTIR, NMR, UV-Vis)
- Reaction calorimeter systems (used for collecting safety data)
  - Mettler-Toledo EasyMax™ (100mL) and RC1e™ (2-L)
  - Analytical tools (FBRM, ReactIR, PVM)

<u>Bays 3 and 4 (intermediate)</u>

- Reaction calorimeter system (RC1e with FBRM, ReactIR capability)
- Remote operations up through 100-L glass vessels

<u>Bay 1(pilot plant) – (under construction)</u>

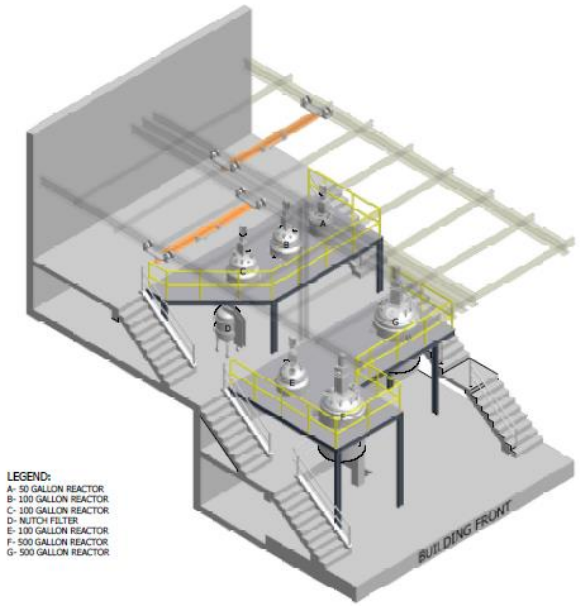
- New 50, 100, and 500-gallon reactors
  - FBRM/MonARC-capable vessels
  - New temperature control units
  - Integrated Dehumidification System
  - Two 3 ton cranes

<u>Vacuum Oven – (currently being upgraded)</u>

- Heated glycol shelf vacuum system

Flexible Manufacturing Facility

- Pfaudler glass lined and jacketed reactors (50, 100, and 500-gallon reactors)
- 800-gallon conical tank on load cells
- 100-ton chiller and steam temperature control units
- Integrated dehumidification system and HVAC
- Currently under construction; estimated to begin an inert process in late 2018

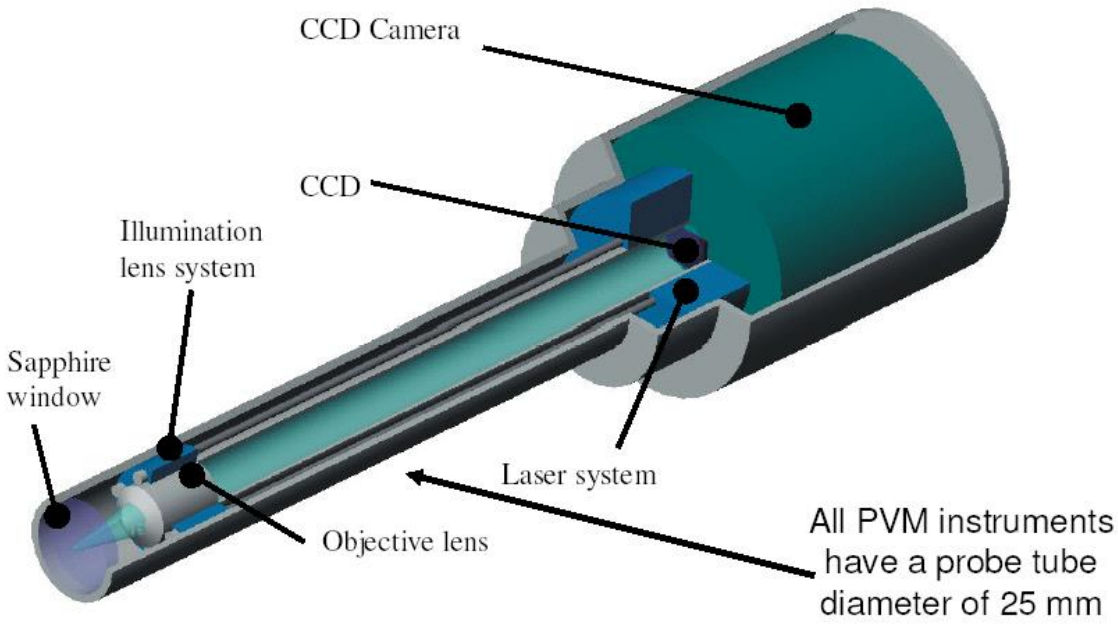


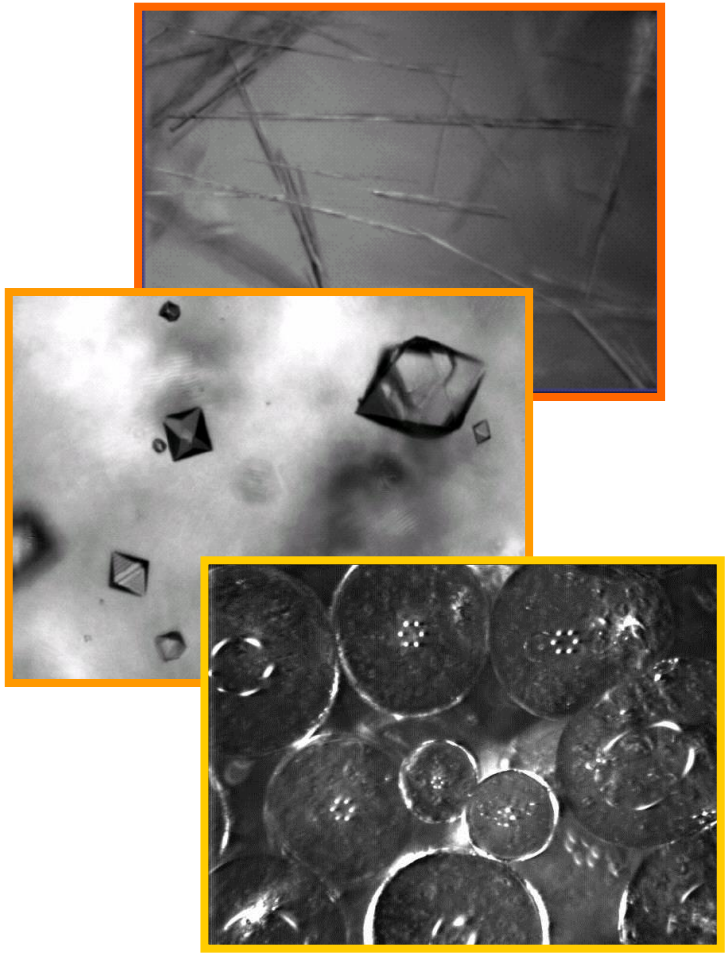
Process Development Tools
Heat Flow Calorimetry

Mettler-Toledo RC1
Reaction Calorimeter

- Measure heat generated during reactions
- Evaluate how heat is released (accumulation?)
- Identify reaction endpoints
- Determine heat evolved/cooling required upon scale-up
- Perform repeatable, programmed experiments

Real-time Process Analytical Tools: Particle Video Microscope (PVM)





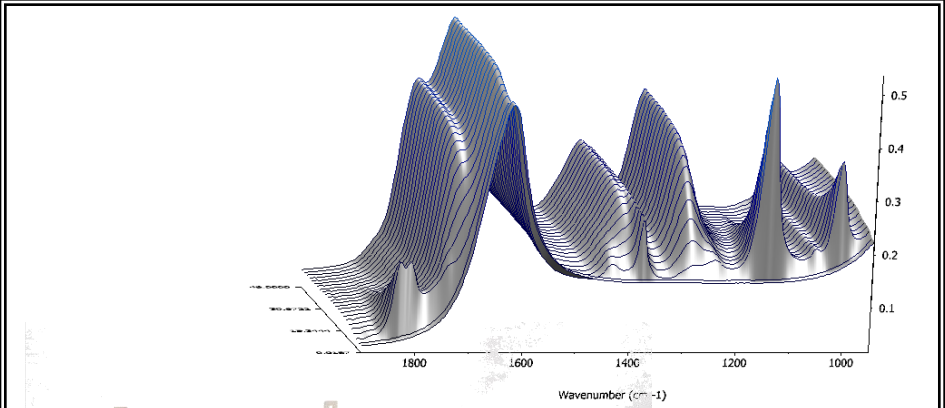
Real-time Process Analytical Tools: Focused Beam Reflectance Measurement

In-process determinations of:

- particle size distribution
- morphology information (needles, spheres, cubes)
- particle count (tracks appearance & disappearance of particles of a particular size)

FBRM probes

Real-time Process Analytical Tools: ReactIR

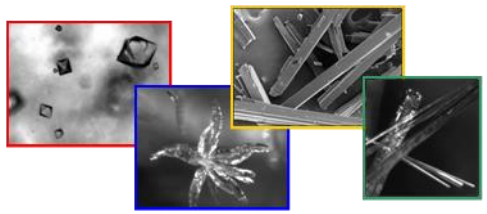


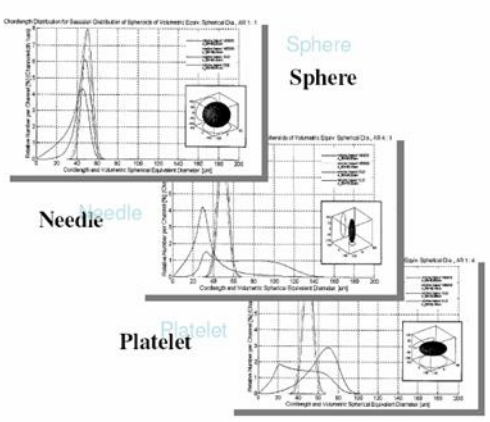
Provides in-process mid-IR spectra of reaction mixture at specified intervals throughout reaction

Used to identify relative concentrations

- starting materials
- intermediates
- byproducts
- products

Multi-Cell Crystallization System (EasyMax™)





- Allows real time, simultaneous collection of crystallization and reaction data in multiple reaction vessels.
- Provides particle size distribution and count as well as providing mid-IR spectra.
- Provides critical data during the evaluation of crystallization of energetic materials and quantifying the effect of process variables on the particle system.

Laboratory Analytical Tools

Differential Scanning Calorimeter
- TA Q20 with Autosampler

Fourier Transform Infrared Spectrophotometer
- Cary 630

Nuclear Magnetic Resonance Spectrometer
- Anasazi 90 MHz

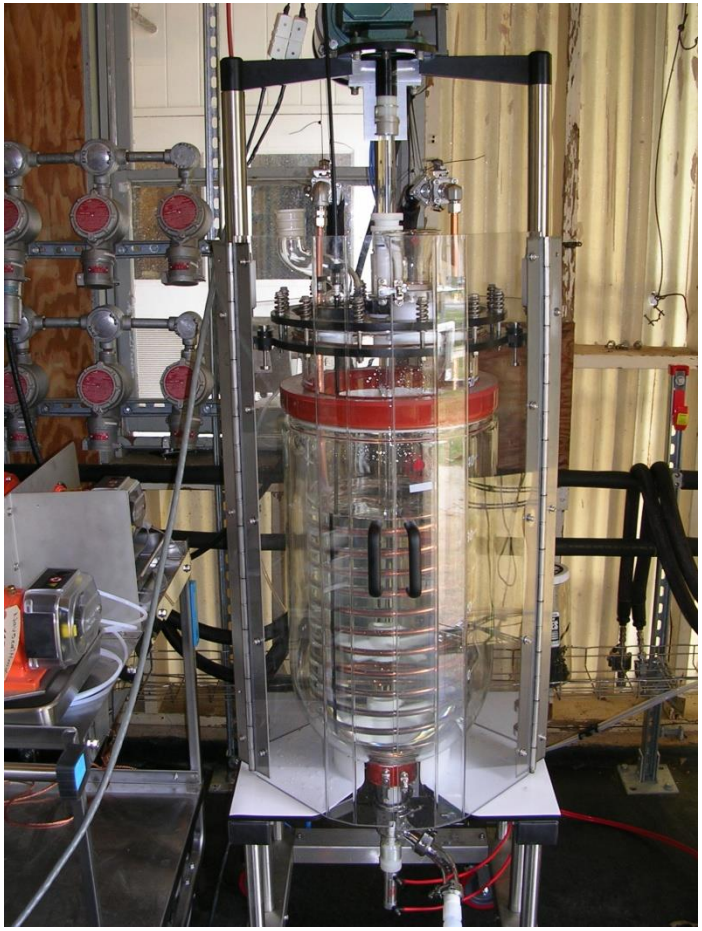
Laboratory Analytical Tools

High Performance Liquid Chromatography
- Agilent Technologies 1200 Series

Digital Microscope
- Keyence Model VHX-600

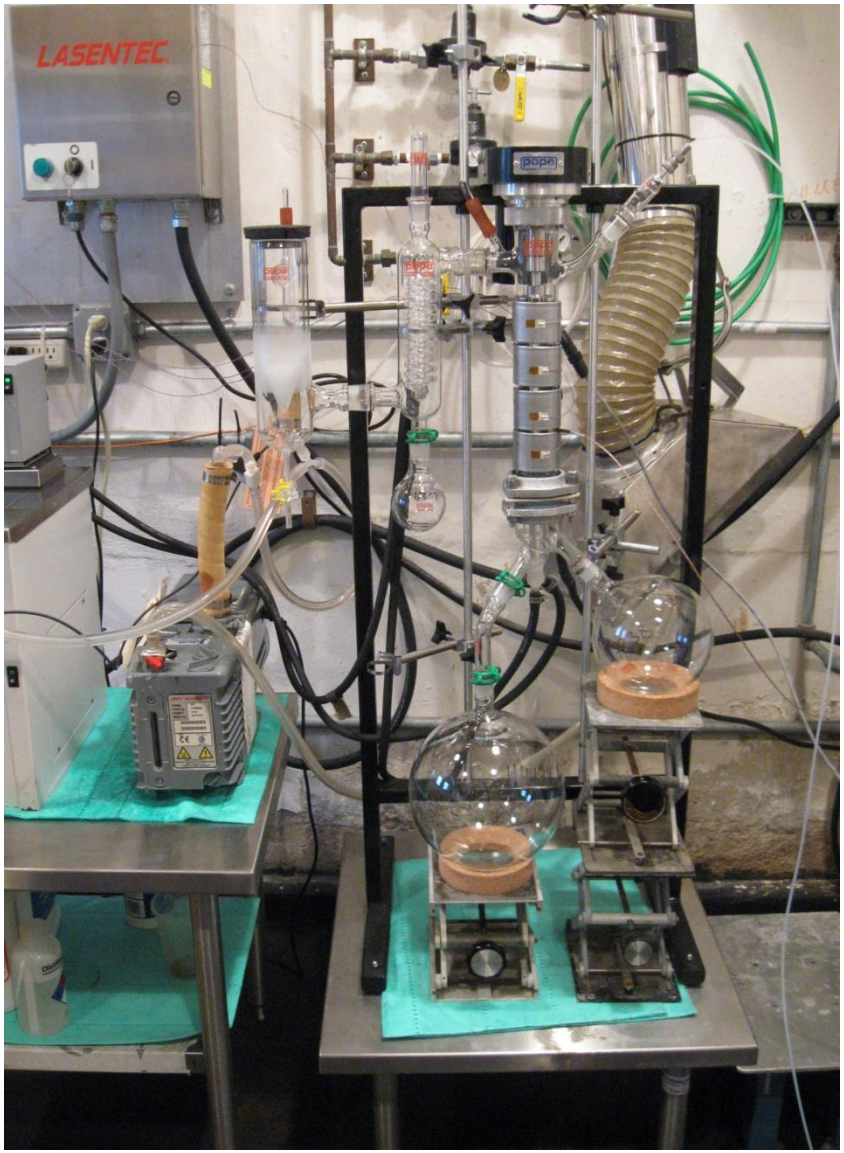
Intermediate-scale Synthesis

- Scale up glassware
  - 1L, 2L, 5L, 10L, 50L, 100L cylindrical glass reactors
  - Various portable and fixed temperature control units
  - Remote operation and monitoring of larger glass vessels with data logging, video recording



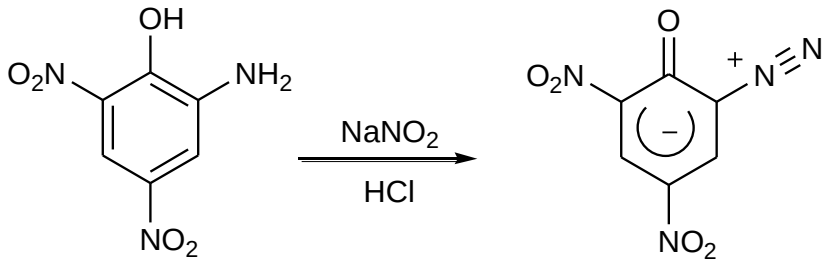
NAVSEA
WARFARE CENTERS
Indian Head EOD Technology Division

Evaporation/Purification



Serving the CAD/PAD Community:

2-diazo-4,6-dinitrophenol (DDNP)



picramic acid

(commerically available)

DDNP

$C_6H_2N_4O_5$

MW= 215.14

- Appearance: Crystals typically are yellow but range from drk. yellow to green. Photosensitive to light by turning dark.
- Density: Often reported 1.63 g/cm^3, 1.719 (X-ray)
- ΔH_f = 321 kJ/mol
- Melting Point = 157-158^{o}C (decomp.)
- Readily soluble in acetone and acetic acid, less soluble in alcohols, ethyl acetate. Slightly soluble in water.

- DDNP is used in a variety of Electro Explosive Devices (EEDs).
- IHEODTD's current process is at the 10 gram scale for DDNP with crude yields greater than 90%.
- Currently the process is being reviewed and future work is planned for 30 gram scale. Full analytical characterization is also planned (e.g. IR, DSC).
- Working with the Analytical Department at IHEODTD to fully test lots of DDNP to Mil. Spec. JAN-D-552.

Source: Matyas, R., Pachman, J. "Chapter 6 - Diazodinitrophenol", *Primary Explosives*, Springer Publisher, 2013.

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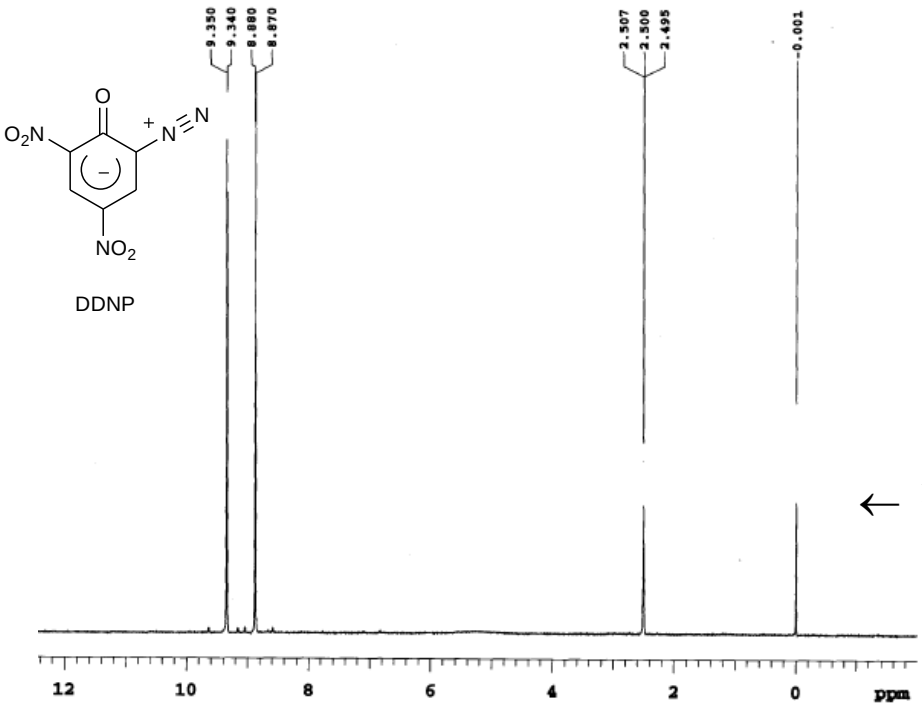
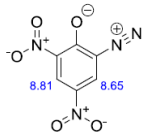
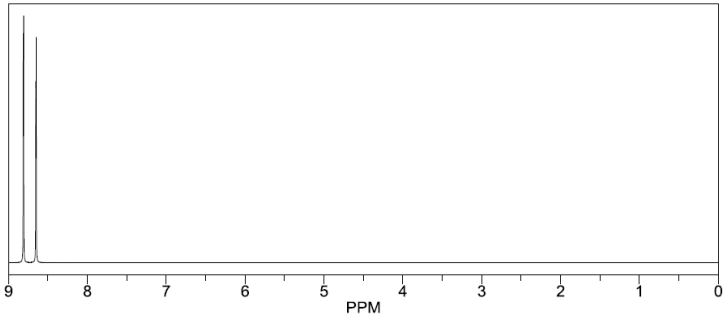


DDNP



Estimation quality is indicated by color: good, medium, rough



← ^{1}HNMR lab data matches well with theoretical data (ChemDraw™ software).

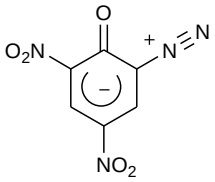
Sensitivity data performed at IHEODTD

Sample	ERL Impact 50% hgt. (cm)	BAM Friction 10 TIL (newtons)	ABL ESD 20 TIL (joules)
DDNP, IHM16BDNP-054	18 (M)	8 (H)	0.010 (H)
RDX class 5	22 (M)	108 (M)	0.037 (M)

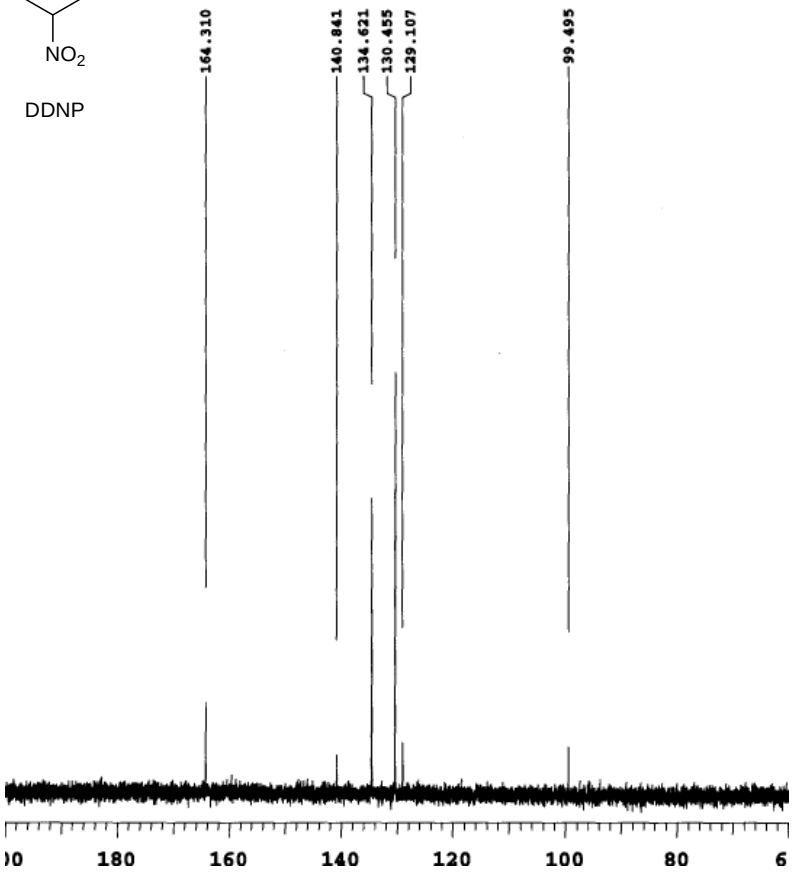
L = low sensitivity M = medium sensitivity H = high sensitivity

Serving the CAD/PAD Community:

2-diazo-4,6-dinitrophenol (DDNP)



DDNP



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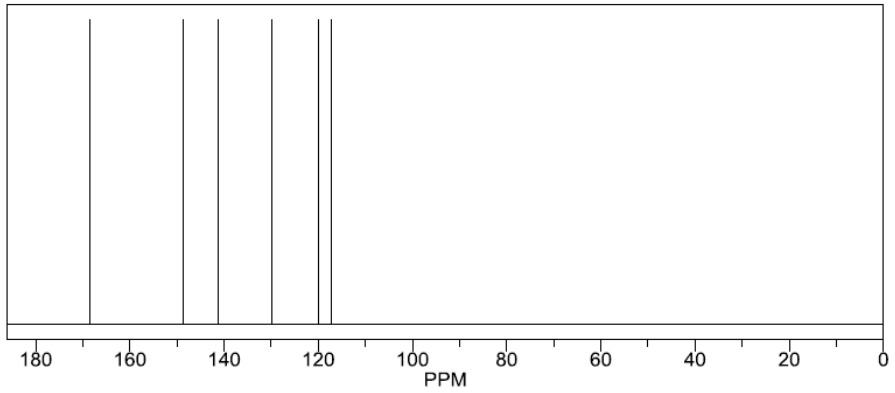
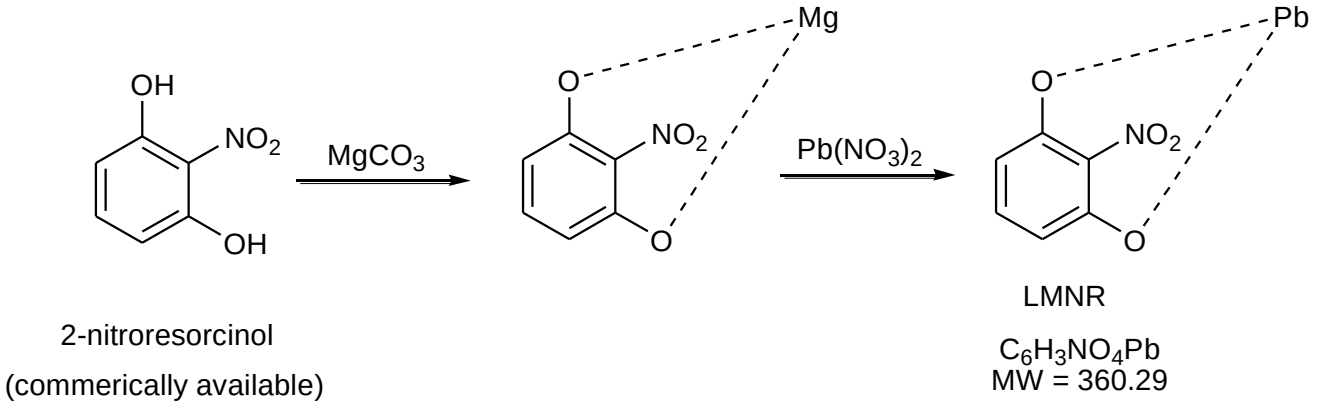


← ^{13}C NMR shows 6 peaks, data matches with theoretical data

Serving the CAD/PAD Community:

Lead Mononitroresorcinate (LMNR)



2-nitroresorcinol

(commerically available)

LMNR

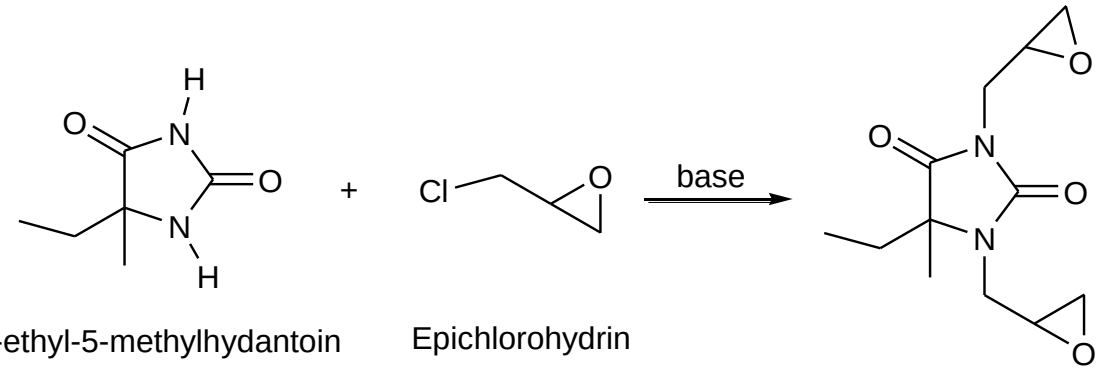
$C_6H_3NO_4Pb$

MW = 360.29

- LMNR is used in the MK 112 squib actuated switch for the AN/BST-1 emergency communication buoy for submarines.
- Current CONUS supplier is considering whether they will continue making the LMNR anymore.
- IHEODTD is reviewing the synthesize of LMNR. Working with the Analytical Department to perform Mil. Spec. testing under MIL-L-46496.
- The CAD/PAD community requirement would be for 100-200 grams/months over the next 2-4 years totaling 4000 grams LMNR.

Serving the CAD/PAD Community:

1,3-diglycidyl-5-ethyl-5-methylhydantoin (XU-238)



5-ethyl-5-methylhydantoin

Epichlorohydrin

XU-238

$C_{12}H_{18}N_2O_4$
MW = 254.28

Base: Triethylamine or Benzyltrimethylammonium chloride

- XU-238 is an epoxy resin used as a bonding agent in EC-08 propellant.
- EC-08 is used in MK 109 Canopy Jettison Rocket Motor (CJRM) and F-16 CJRM.
- CONUS supplier is currently producing XU-238 and indicated disinterest in future production.
- CAD/PAD's annual requirement is 8-lb/year.
- IHEODTD was asked to produce a 50g lot for suitability testing in propellant formulation.
- An overview of the synthetic work completed will be presented in a talk on Thursday May 26, 2016 titled, "Evaluation of a Manufacturing Capability for XU-238 at IHEODTD"