Preparation of Common Nitrate Esters by Mild Nitration of Polyols

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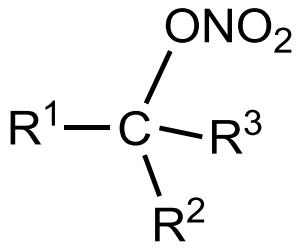
Outline

- Background
- Targeted Nitrate Esters
- Synthesis Optimization and Results
- Summary

Background



- Nitrate esters are common explosives widely used in both commercial and military applications – typically as plasticizers.
- Nitroglycerine (NG) was first discovered in 1846 by Italian chemist Ascanio Sobrero who warned against using it as an explosive due to sensitivity issues.
- Alfred Nobel developed useful NG based explosives after discovering that it can be absorbed onto porous materials.
- The high oxygen content of the $–NO_3$ group offers easily overoxidized potential. Nitrate esters can be mixed with carbonaceous (oxygen deficient) explosives like nitrocellulose.
- Facile preparation by nitration of alcohols.

For a thorough review of nitrate esters see: Agrawal, J. P.; Hodgson, R. D. *Organic Chemistry of Explosives*; John Wiley & Sons, Ltd.: West Sussex, 2007, p. 87; and references therein.

Nitrate Ester Applications

General Nitrate Ester Usage

- Widely used in production of gun propellants, rocket propellants, and explosives
- These materials provide the ability to manipulate key formulation parameters:
  - Density
  - Oxygen balance
  - Sensitivity
- Techniques and procedures have been developed allowing nitrate esters to be safely processed and handled

<u>Examples</u>

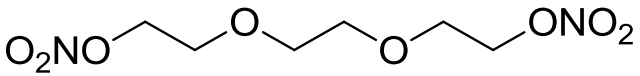
PETN

- Most stable and least reactive of the common nitrate ester explosives
- Mixed with phlegmatizers for use in detonation cord
- Can be mixed with synthetic polymers to form PBXs
- Pentolite = 1:1 PETN and TNT; used as a military explosive and in booster charges

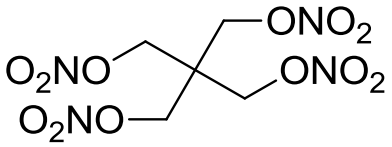
TMETN, TEGDN, BTTN

- Investigated near the time of NG discovery for use as a freezing point depressant and desensitizer for NG.

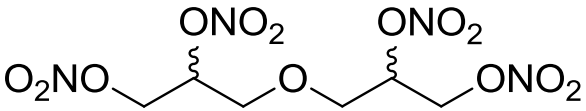
Synthetic Targets



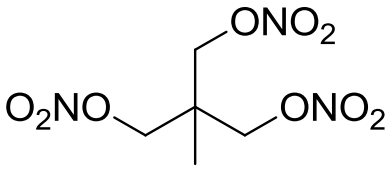
Triethylene Glycol Dinitrate (TEGDN)



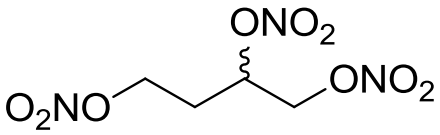
Pentaerythritol Tetranitrate (PETN)



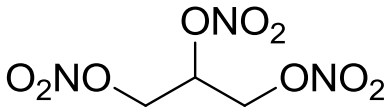
Diglycerol Tetranitrate (DGTN)



1,1,1-(Trimethylol)ethane Trinitrate (TMETN)



1,2,4-Butanetriol Trinitrate (BTTN)



Nitroglycerin (NG)

Nitration Conditions - Generalizations

Drawbacks

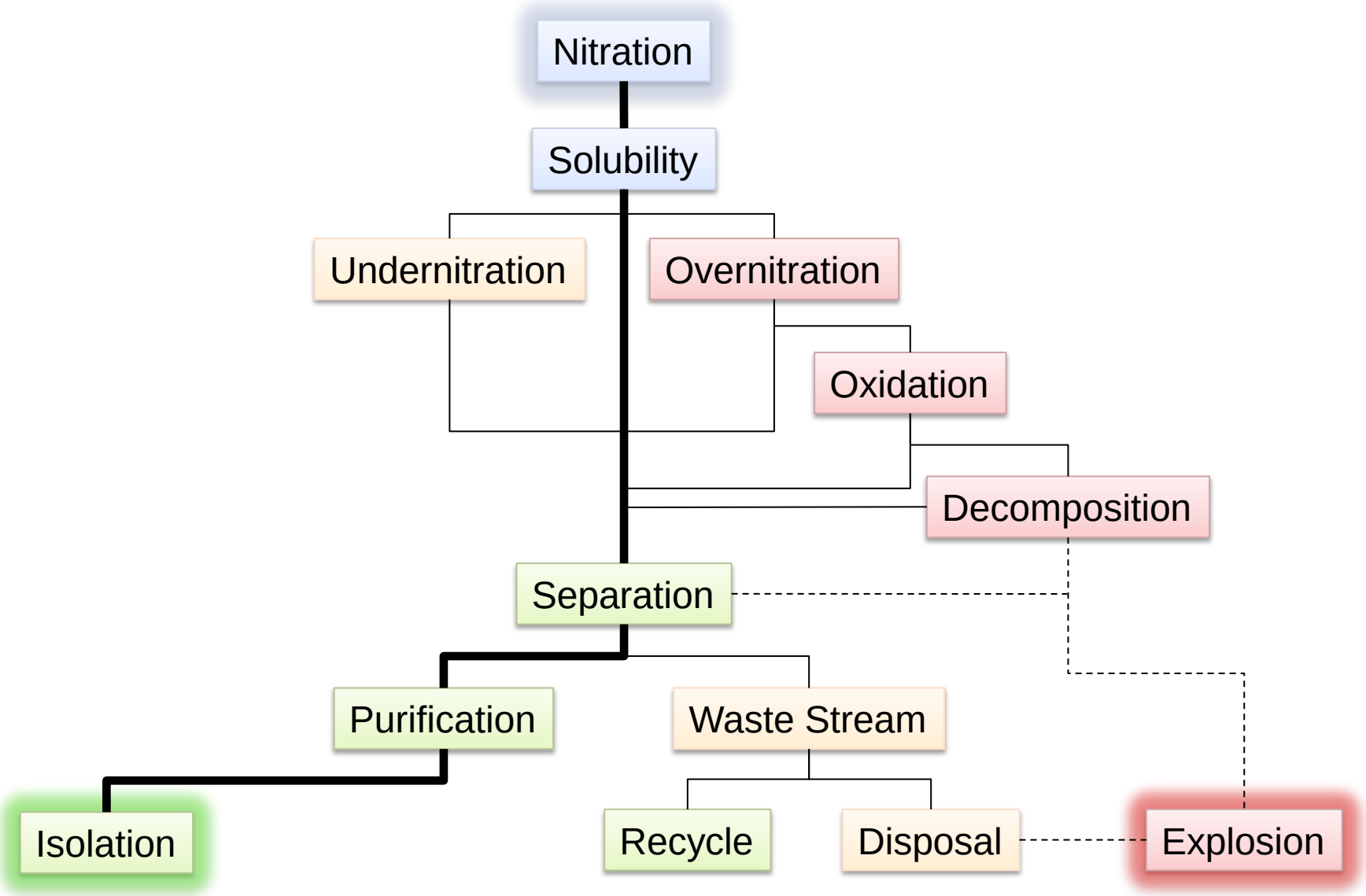
- Strongly acidic
- Oxidizing
- Selectivity
- Exothermic
  - Thermal runaway
  - Explosions
- ***Product separation – Hazardous waste streams***

Countermeasures

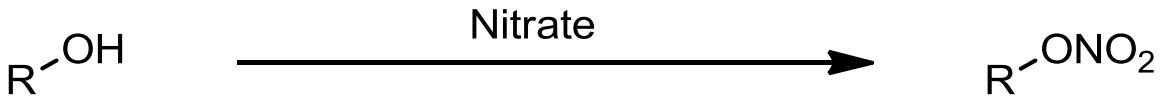
- Remote operations
- Strict control
- Elaborate equipment
- Blast/explosion proof shielding and buildings
- Multiple extractions and washings

Albright, L. F.; Hanson, C. *Industrial and Laboratory Nitrations* (ACS Symposium Series 22); American Chemical Society: Washington, DC, 1976; (a) Ross, D. S.; Kirshen, N. A. Chapter 7, 114–131; (b) Hanson, C.; Kaghazchi, T.; Pratt, M. W. T. Chapter 8, 132–155; (c) Deno, N. C. Chapter 9, 156–159.

Nitration Considerations

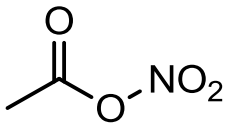
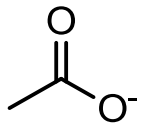


Typical *O*-Nitrating Agents



Nitric Acid (HNO_3)
- Fuming (86-95% HNO_3)
- Commercial (68-70% HNO_3)

Mixed Acid (H_2SO_4/HNO_3) $H_2SO_4 + HNO_3 \longrightarrow NO_2^+ + HSO_4^- + H_2O$
- Mixed acid/CH_2Cl_2

Nitric Acid/Acetic Anhydride $HNO_3 + AcOAc \longrightarrow$  $\longrightarrow$  $+ NO_2^+$

N_2O_4

$R-OH + N_2O_4 \longrightarrow R-ONO_2 + HNO_2$

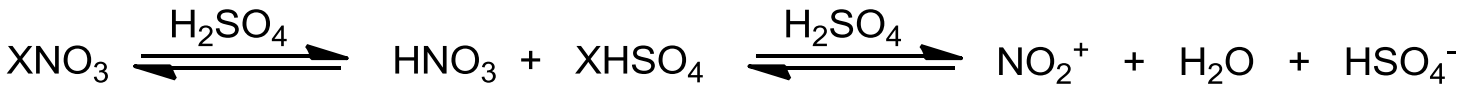
$R-O^-Na^+ + N_2O_4 \longrightarrow R-ONO_2 + NaNO_2$

N_2O_5 $R-OH + N_2O_5 \longrightarrow R-ONO_2 + HNO_3$

Many others….

For a review of nitrations see: Olah, G. A.; Malhotra, R.; Narang, S. C. *Nitration: Methods and Mechanisms*; VCH: New York, 1989.

Mild Nitrating Mixture – Nitrate Salt/H_2SO_4

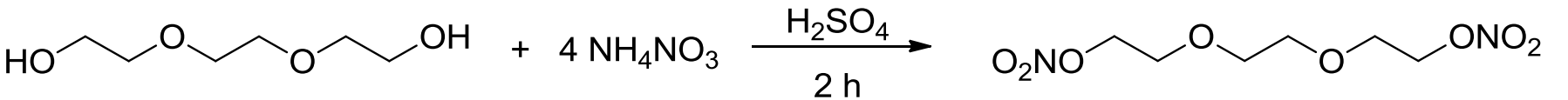


X = K^+, Na^+, **NH_4^+**

Advantages Over Mixed Acid

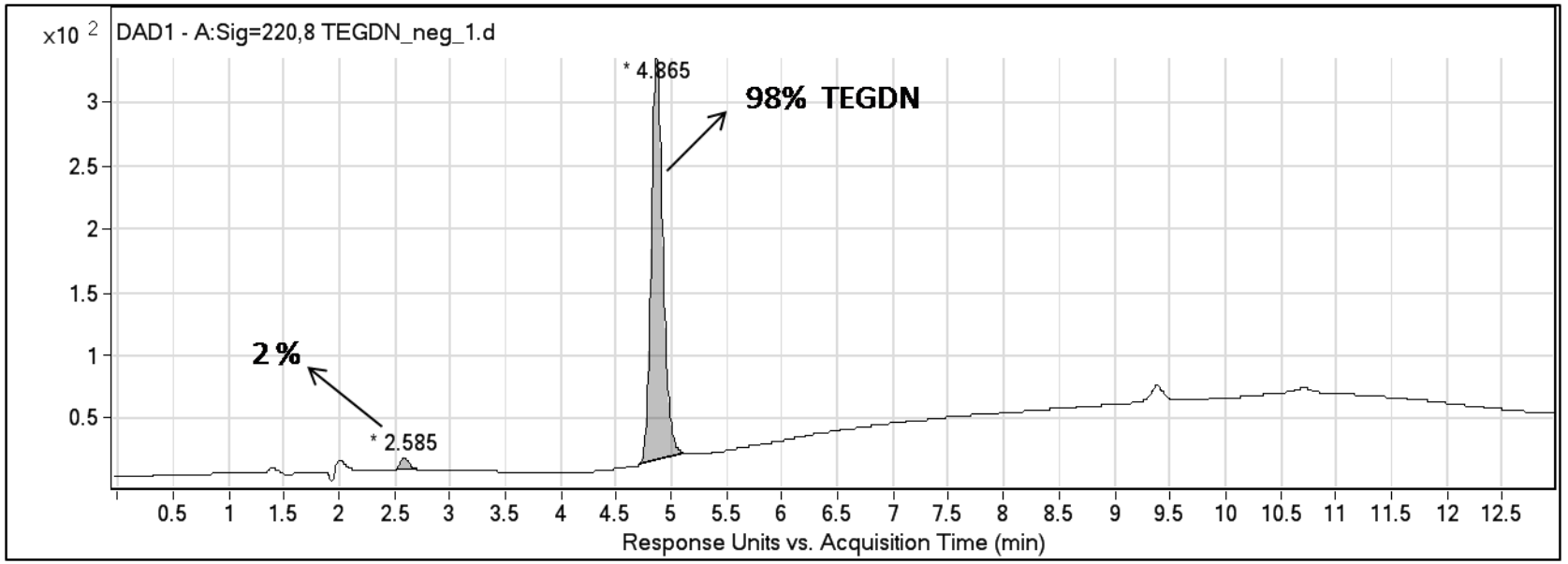
- Nitrate salts are stable with long shelf lives
- Nitrate salts are less hazardous than HNO_3
- Mild exotherm of mixing nitrate salts with H_2SO_4
- Simple stoichiometric control of NO_2^+ group
- Limits NO_x vapors
- Partial neutralization of H_2SO_4 in the nitration process
- Limits the amount of nitric acid in the waste stream
    - Limits the amount of nitrate esters in the waste stream

Triethylene Glycol Dinitrate (TEGDN)

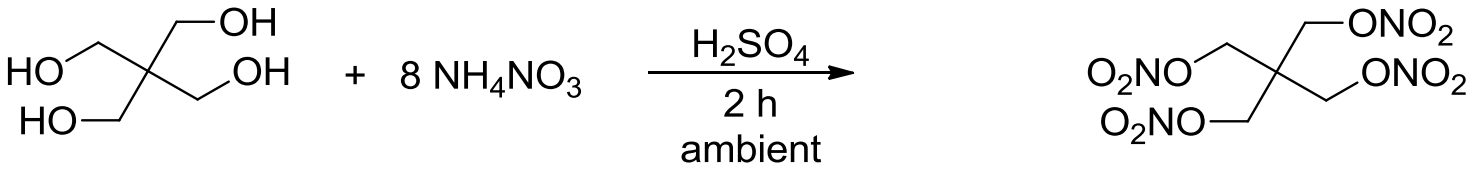


Triethylene Glycol

Triethylene Glycol Dinitrate (TEGDN)
64% yield

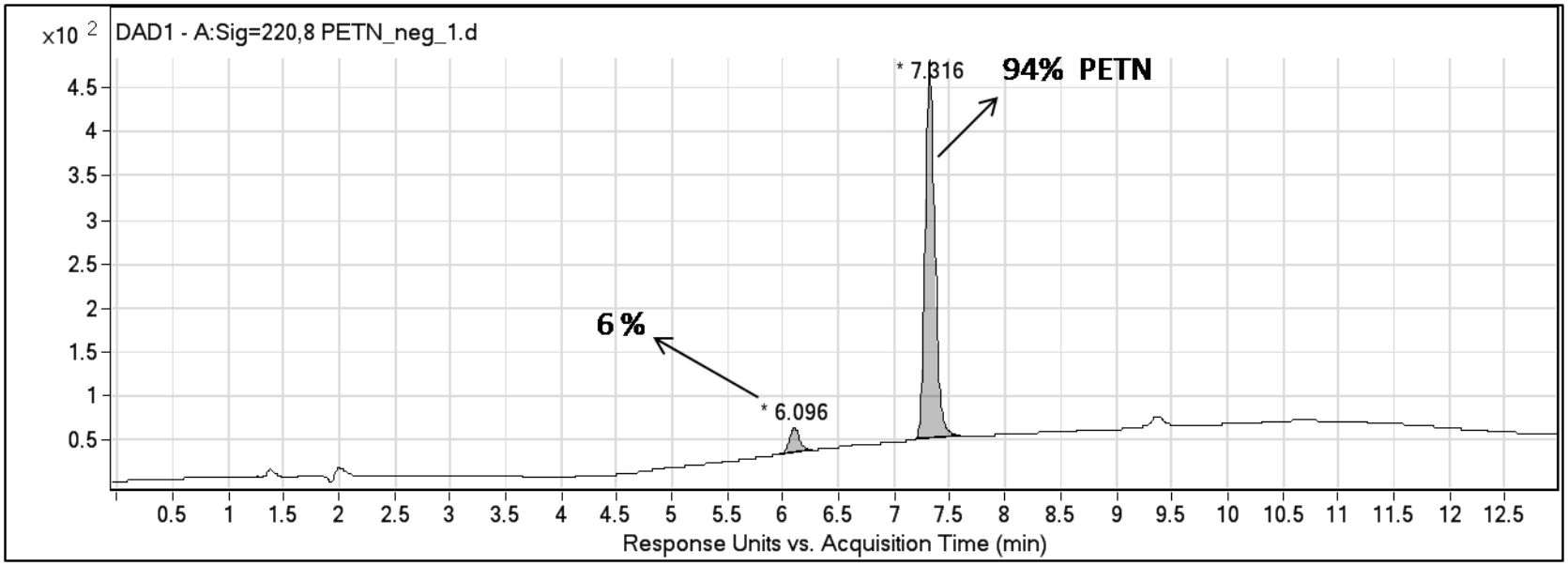


Pentaerythritol Tetranitrate (PETN)

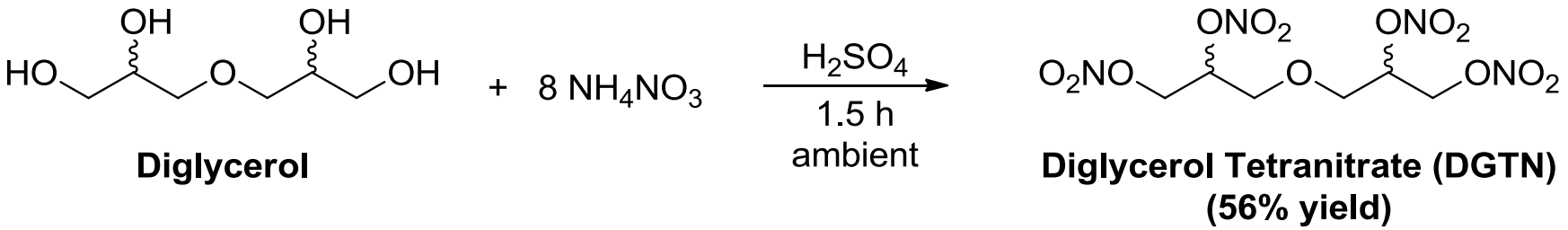


Pentaerythritol

Pentaerythritol Tetranitrate (PETN)
62% yield

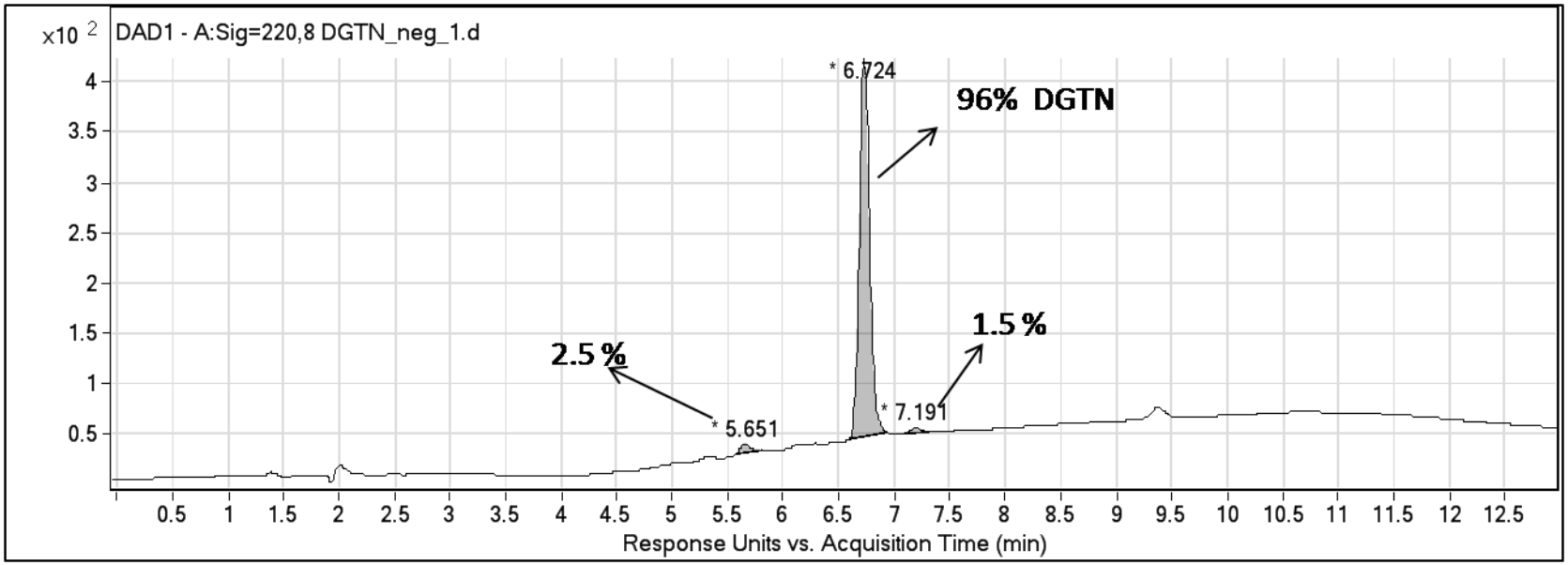


Diglycerol Tetranitrate (DGTN)

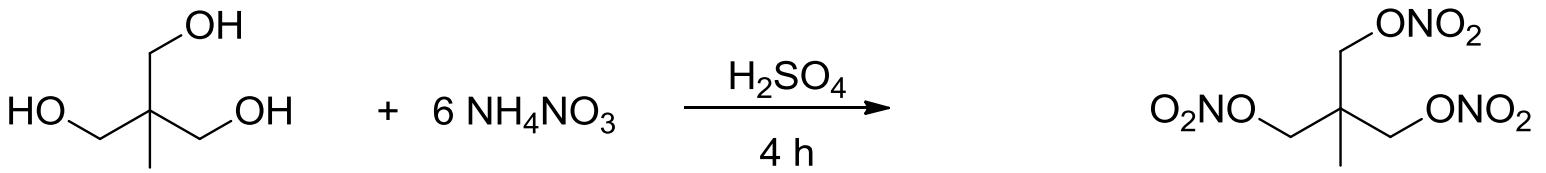


Diglycerol

Diglycerol Tetranitrate (DGTN)
(56% yield)

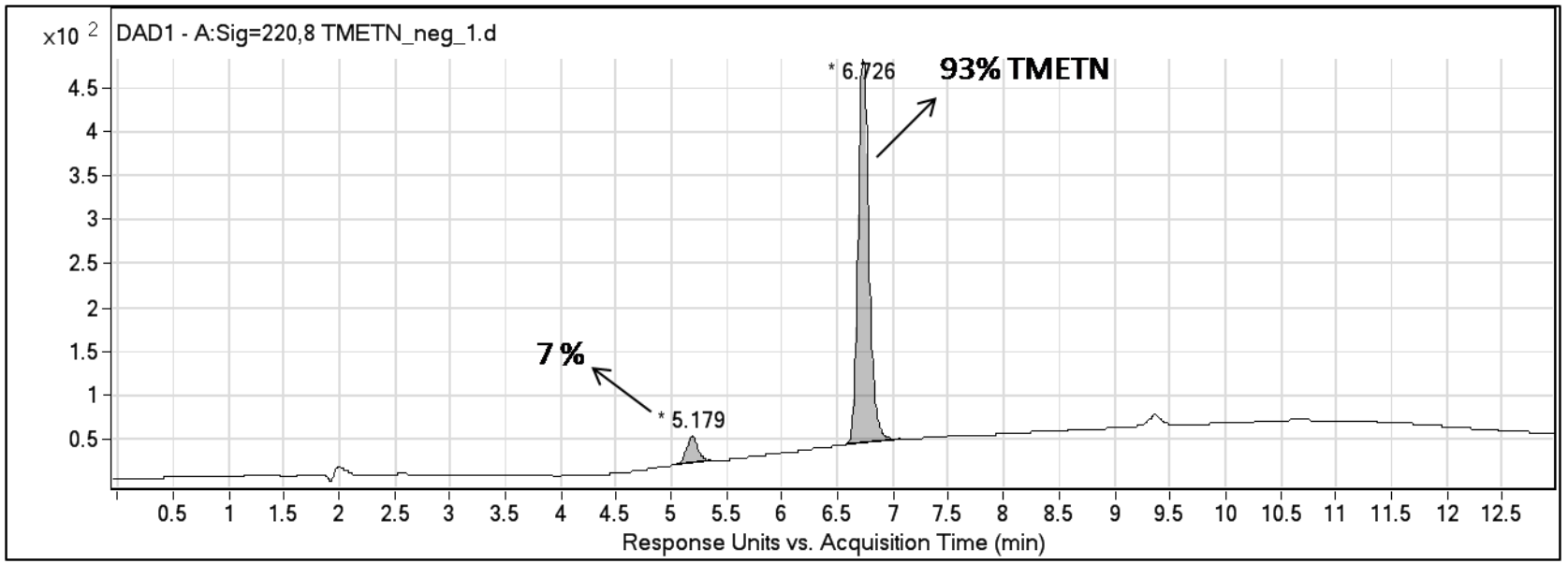


1,1,1-Tris(methylol)ethane Trinitrate (TMETN)



Trimethylol Ethane

1,1,1-Tris(methylol) Ethane Trinitrate (TMETN)
51% yield



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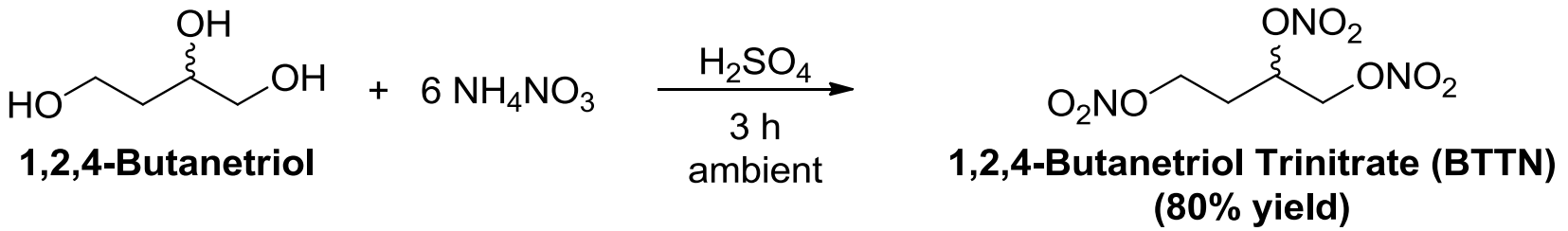
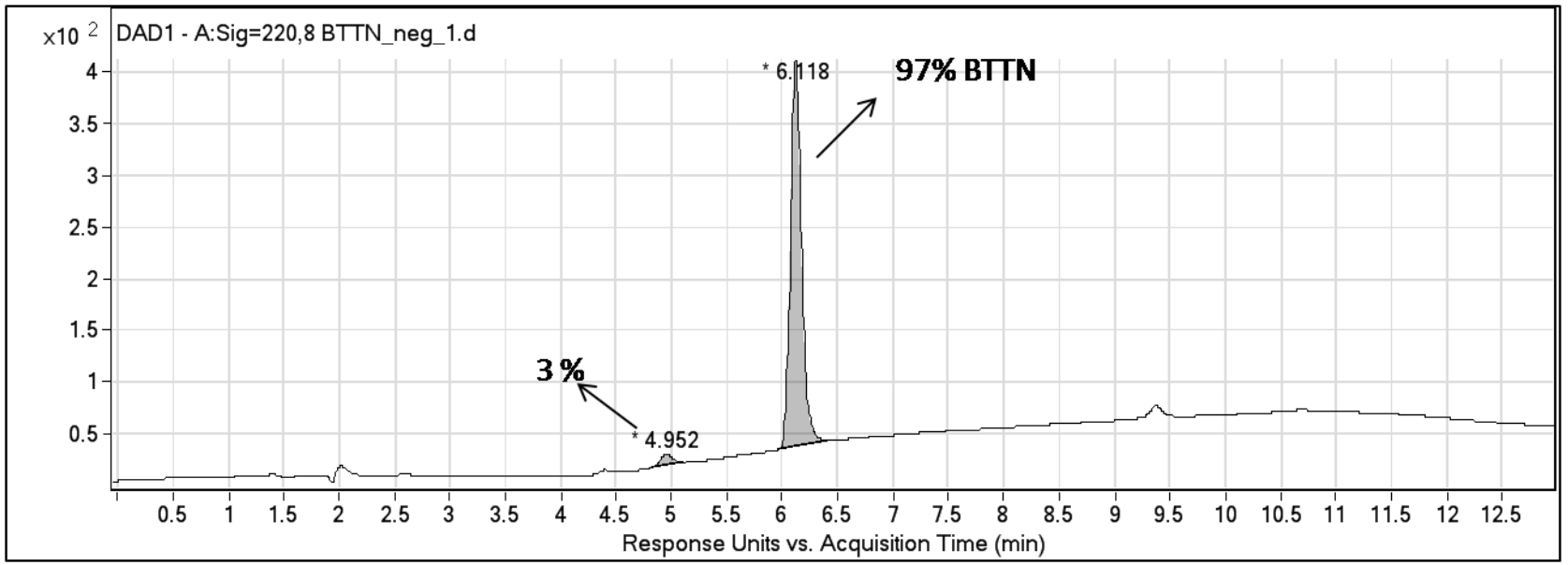
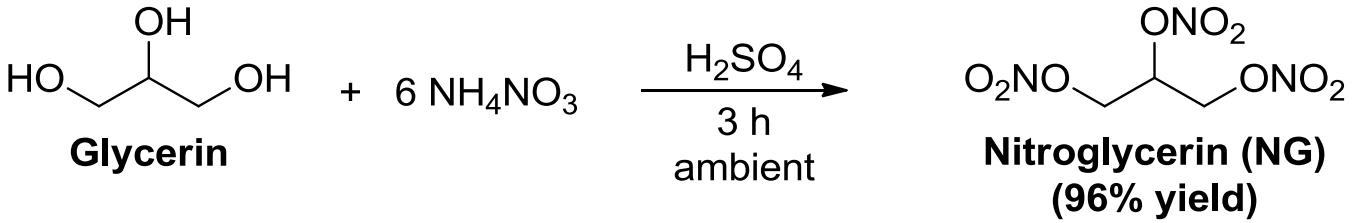


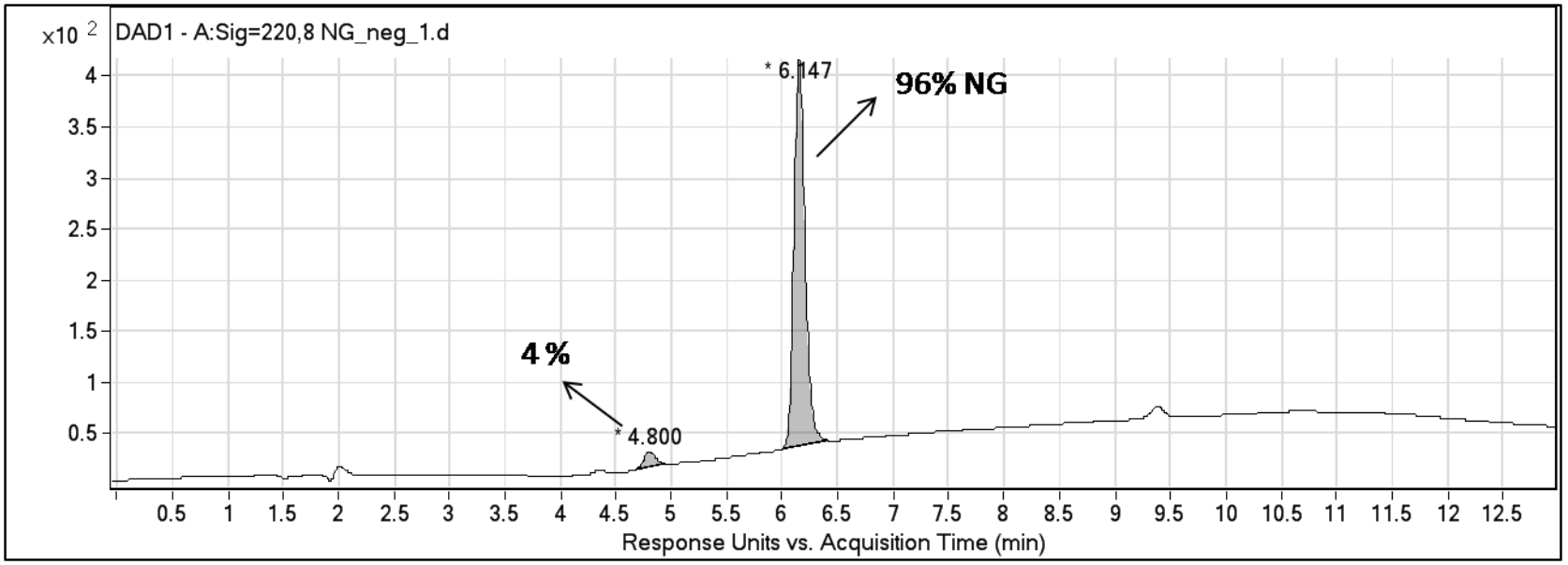
1,2,4-Butanetriol

1,2,4-Butanetriol Trinitrate (BTTN) (80% yield)



Nitroglycerine (NG)





Summary

- 6 Common nitrate esters prepared by mild nitration method
- Preliminary results suggest that nitrate salt/H_2SO_4 is:
  - Equally effective as mixed acid
  - Less hazardous than mixed acid
  - More controllable than mixed acid
  - Practical for lab- or large-scale batch synthesis of nitrate esters
  - Potentially adaptable to continuous processing
  - Worthy of additional investigation as nitrating agent for other energetic materials

Nitrate Ester	Crude % Yield (unoptimized)	% Purity (HPLC/UV)
TEGDN	64	98
PETN	62	94
DGTN	56	96
TMETN	51	93
BTTN	80	97
NG	96	96

Acknowledgments
Dr. Shawn Parry, HPLC analysis
PM - Nathan Seidner
Paul Braithwaite