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Explosives Analysis Using Porapak® RDX Solid Phase Extraction Cartridges

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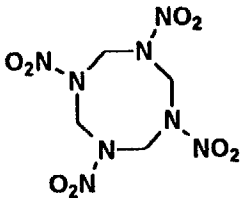
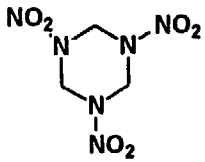
Outline

- Introduction
- Preconcentration by Solid Phase Extraction
- HPLC Optimization
- Confirmation by Photodiode Array Detection
- Conclusion

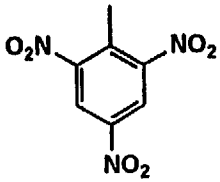
Structures of Nitroaromatic and Nitramine Explosives, By-Products and Degradation Products



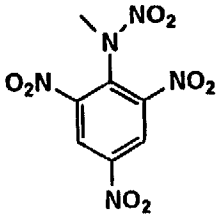
HMX



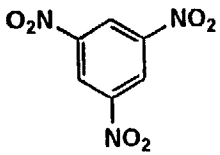
RDX



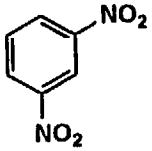
TNT



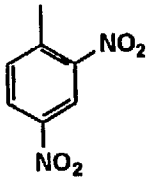
TETRYL



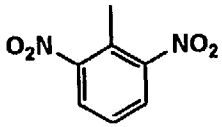
1,3,5-TNB



1,3-DNB

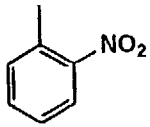


2,4-DNT

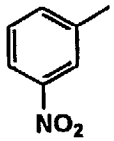


2,6-DNT

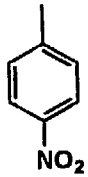
NB



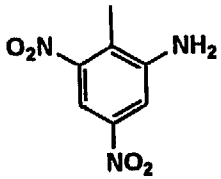
2-NT



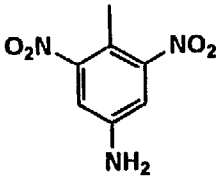
3-NT



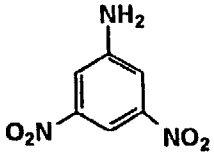
4-NT



2-Am-4,6-DNT



4-Am-2,6-DNT



3,5-DNA

Introduction

- Over 10,000 Identified Contaminated Sites
  - Munitions Manufacturing
  - Storage Depots
  - Demolition Sites
  - Artillery Ranges
- Remediation
  - USATHAMA
  - EPA - Office of Solid Waste

EPA Toxicity Guidelines

Compound	Proposed Drinking Water Limits (ppb)
HMX	400
RDX	2
TNT	2
2,4-DNT	50
2,6-DNT	40
1,3-DNB	1

Overview of Analytical Methods

- Chemical Methods
- Immunoassay
- Gas Chromatography
- HPLC
- Capillary Electrophoresis

Preconcentration Methods

- Liquid-Liquid Extraction
  - Toluene Extraction

    F Belkin, RW Bishop and MV Sheely, J Chromatogr. Sci 24 (1985) 532.

    » Excellent Extraction Efficiency for Nitroaromatics (~100% Recovery)

    » Poor Nitramine Extraction (~15% Recovery)
  - Salting-out Extraction

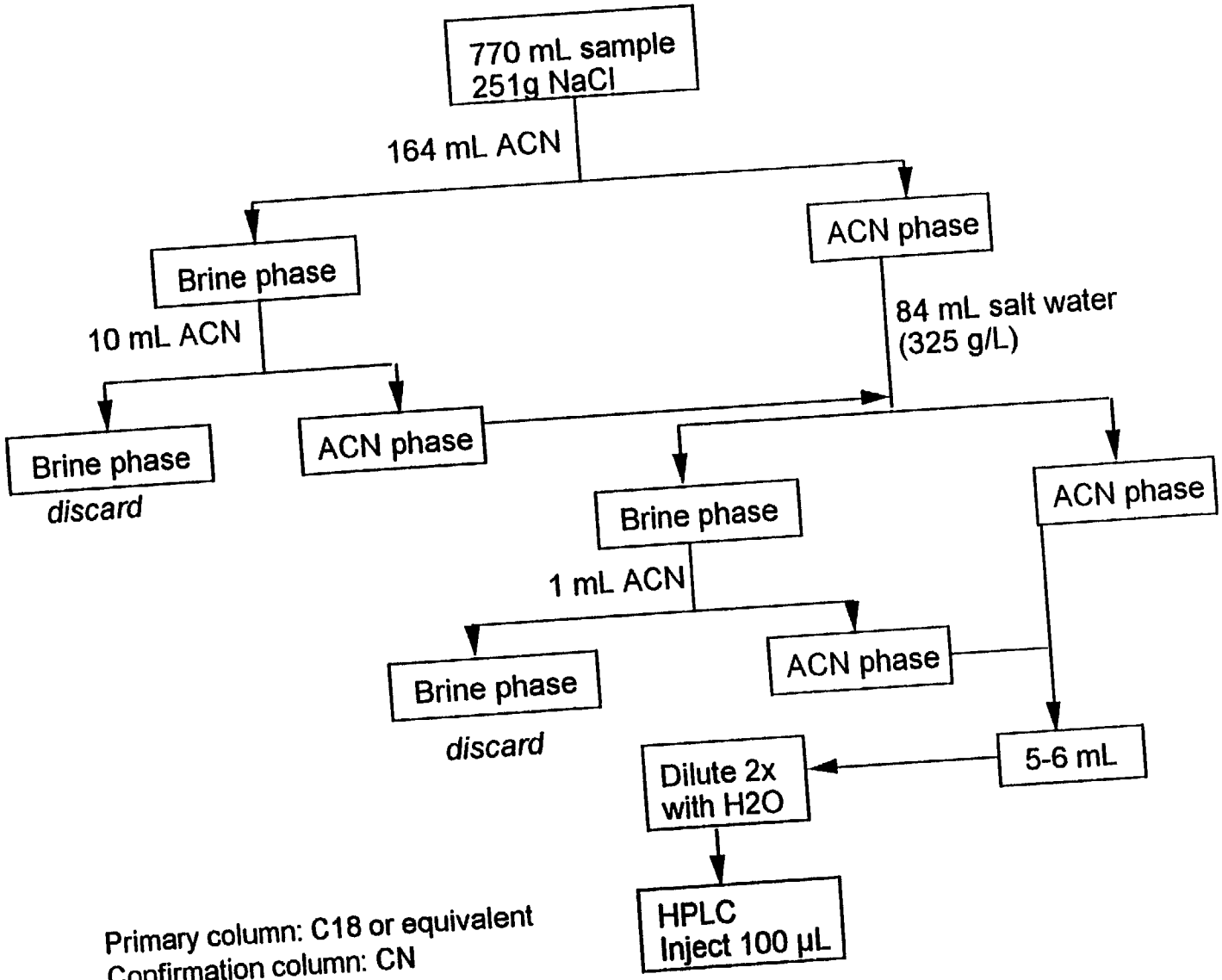
    PH Miyares and TF Jenkins, CRREL Special Report 90-30 (1990).

    » 5M NaCl, Two Phases with Acetonitrile

    » Excellent Extraction Efficiency for Nitroaromatics and Nitramines (90% recovery)

    » Currently Used in EPA SW846/Method 8330

Method 8330 Flow Sheet



Primary column: C18 or equivalent
Confirmation column: CN

Problems with LLE

- Time Consuming, Labor Intensive
- Large Solvent Consumption per Analysis
- Cross-contamination

Compare to Liquid-Solid Extraction (i.e. Solid Phase Extraction)

SPE Protocol

- Condition Cartridge
- Load Sample (concentrate)
- Elute Concentrated Sample (100-fold concentration)

SPE vs. LLE

- 10-fold Reduction in Solvent Consumption
- Significant Reduction in Time
  - multiple samples on vacuum manifold
  - ease of automation
- Similar Concentration Factors Compared to LLE

Preconcentration - SPE

– Polar Explosives Poorly Retained on C18 and PS/DVB

1976 - Strong Adsorption of Polar HMX on Polyvinylpyrrolidone

1984 - Porapak R (DVB/NVP copolymer) shown to give Excellent Recoveries of Explosives

1991 - Porapak R Used for Routine Preconcentration of Explosives in Water Samples

1994 - Porapak® RDX Introduced

References:

1) DH Freeman et al, *J Chromatogr. 118* (1976) 157

2) MP Maskarinec et al *J Chromatogr.302(1984)51*

3)MG Winslow et al, *Proceedings of the EPA 7th Annual Waste Testing and Quality Assurance Symposium*, 1991