Detection of Explosives at a Formerly Used Defense Site with a Portable SPME/GC-CIT Mass Spectrometer

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US Army and the Environment

The Army's Environmental Vision and Mission

The Vision:

The Army will integrate environmental values into its Mission to sustain readiness, improve the soldier's quality of life, strengthen community relationships, and provide sound stewardship of resources.

The Mission:

The Army will develop and implement cost-effective measures to protect and sustain the environment in support of the military operations, installation management, and materiel development.

Long Term Monitoring Research

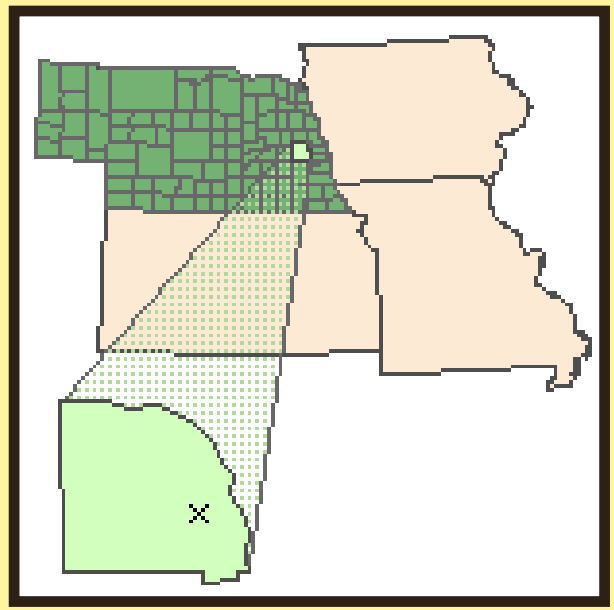
- Reduce costs associated with long term monitoring of groundwater
- Develop field analytical methods for explosives and other semi-volatile analytes
- Use portable instrumentation
- Perform solvent-free extractions
- Obtain results in near real time
- Generate quality data acceptable to regulators

Long Term Monitoring Research

- Solid phase micro-extraction fibers
  - Small sample volume
  - Several different coatings available
  - Low cost
- Portable mass spectrometer
  - SPME inlet
  - Wide mass range
  - Fast chromatographic separation
  - Remote operation
  - Positive and negative ion detection

Nebraska Ordnance Plant

- 17,000 acre Superfund site near Mead, NE
- Load, assemble and pack facility
- Finished munitions storage
- In use by DoD 1942 - 1964
- TNT, RDX, TCE contaminants
- Final NPL status
- Clean-up by granular activated carbon and advanced oxidation processes



Nebraska Ordnance Plant

Field Conditions at NOP

Detection of Explosives

EPA SW-846 Method 8330

- 14 Explosives
- Solid phase extraction of 500 mL sample
- Primary analysis by RP-HPLC
- Second HPLC run required for confirmation of identity
- Typical detection limits - low ug/L
- Acceptance ranges for blanks, surrogates, standards, and calibration

Portable GC/CIT

Resolution:	Unit
Analyzer:	Cylindrical Ion Trap
Size:	18.7 in x 18.7 in x 18.7 in
Weight:	60 lbs
Mass Range:	400 amu

Griffin Analytical

Minotaur 400 Cylindrical Ion Trap MS

SPME Considerations

SPME is based on multiphase equilibrium distribution

Extracted amount is proportional to concentration if sample volume is large compared to fiber volume

$$n = K_{fs} V_f C_i$$

- n = amount extracted
- K_{fs} = fiber/sample distribution constant
- V_f = fiber volume
- C_i = initial analyte concentration

SPME Considerations

SPME extraction time based on mass transfer

$$t_e = t_{95\%e} = \delta_f^2 / 2D_f$$

t_e = Equilibration time = ∞

$t_{95\%e}$ = Equilibration time for 95% of equilibrium amount of analyte extracted

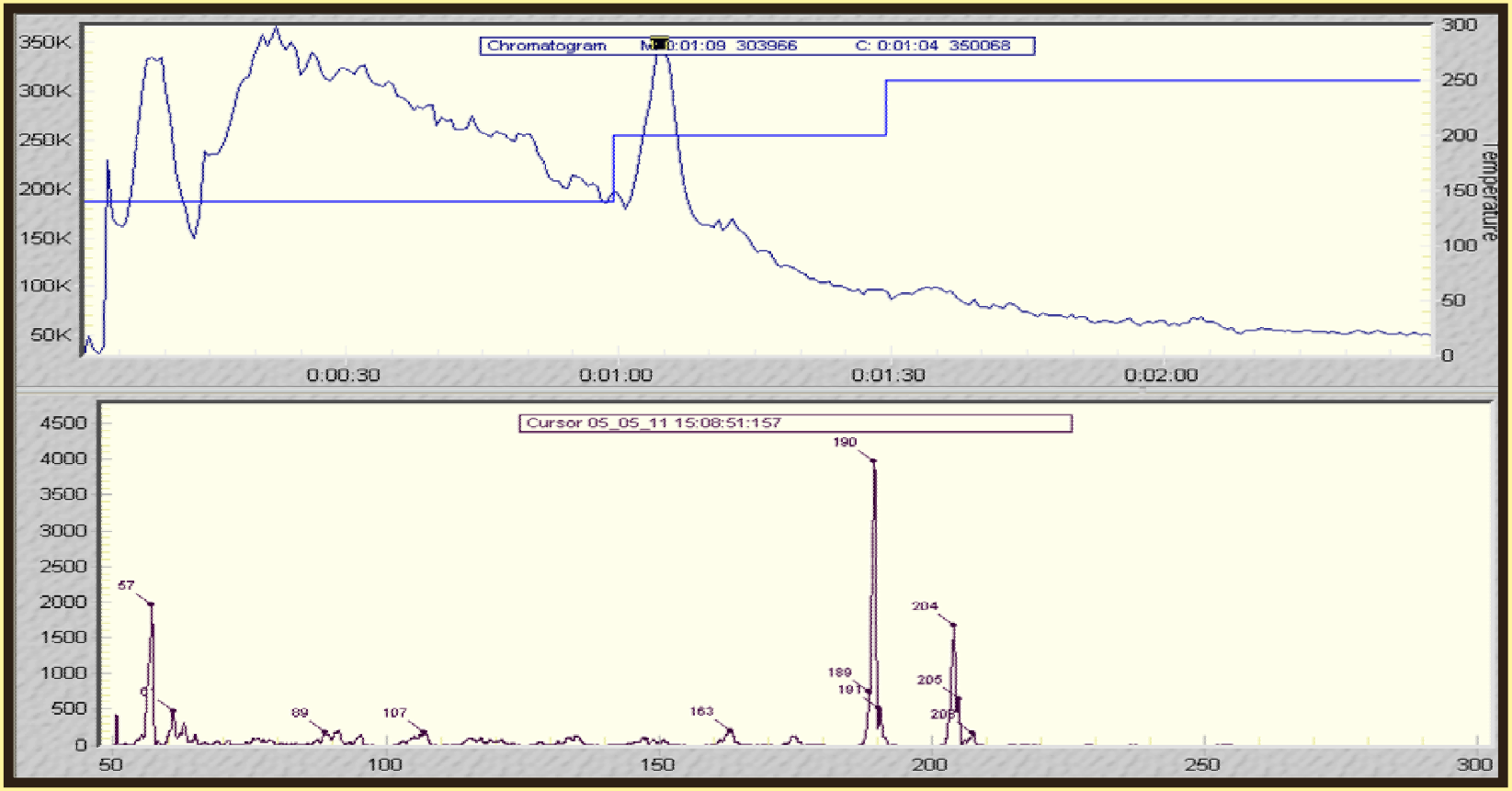
δ_f = Fiber coating thickness

D_f = Diffusion coefficient of analyte in the coating

SPME Considerations

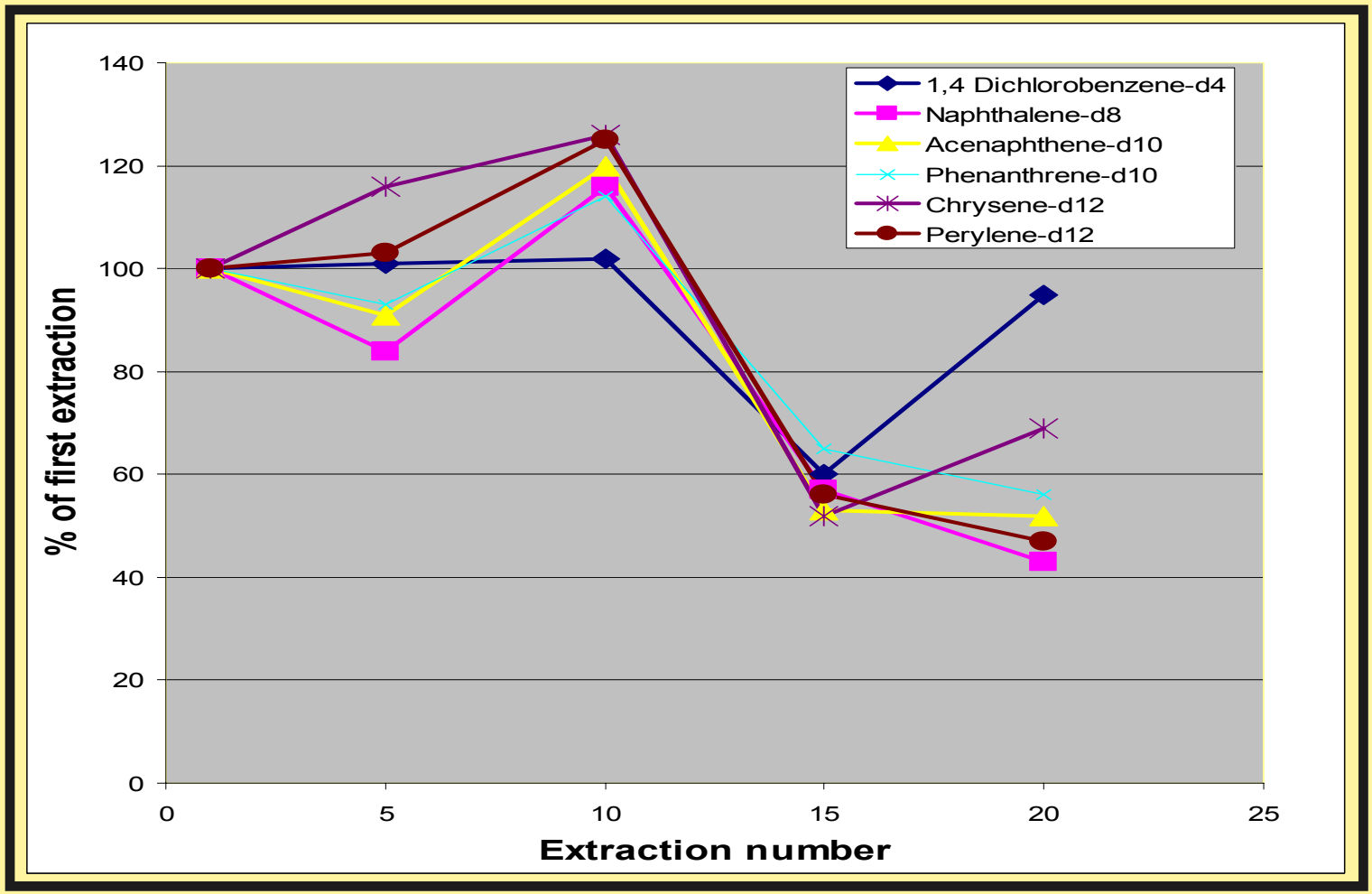
- Coating type
- Coating thickness
- Extraction time, temperature
- Analyte solubility
- Agitation speed
- Desorption temperature, rate
- Number of uses
- Coating bleed

SPME Considerations



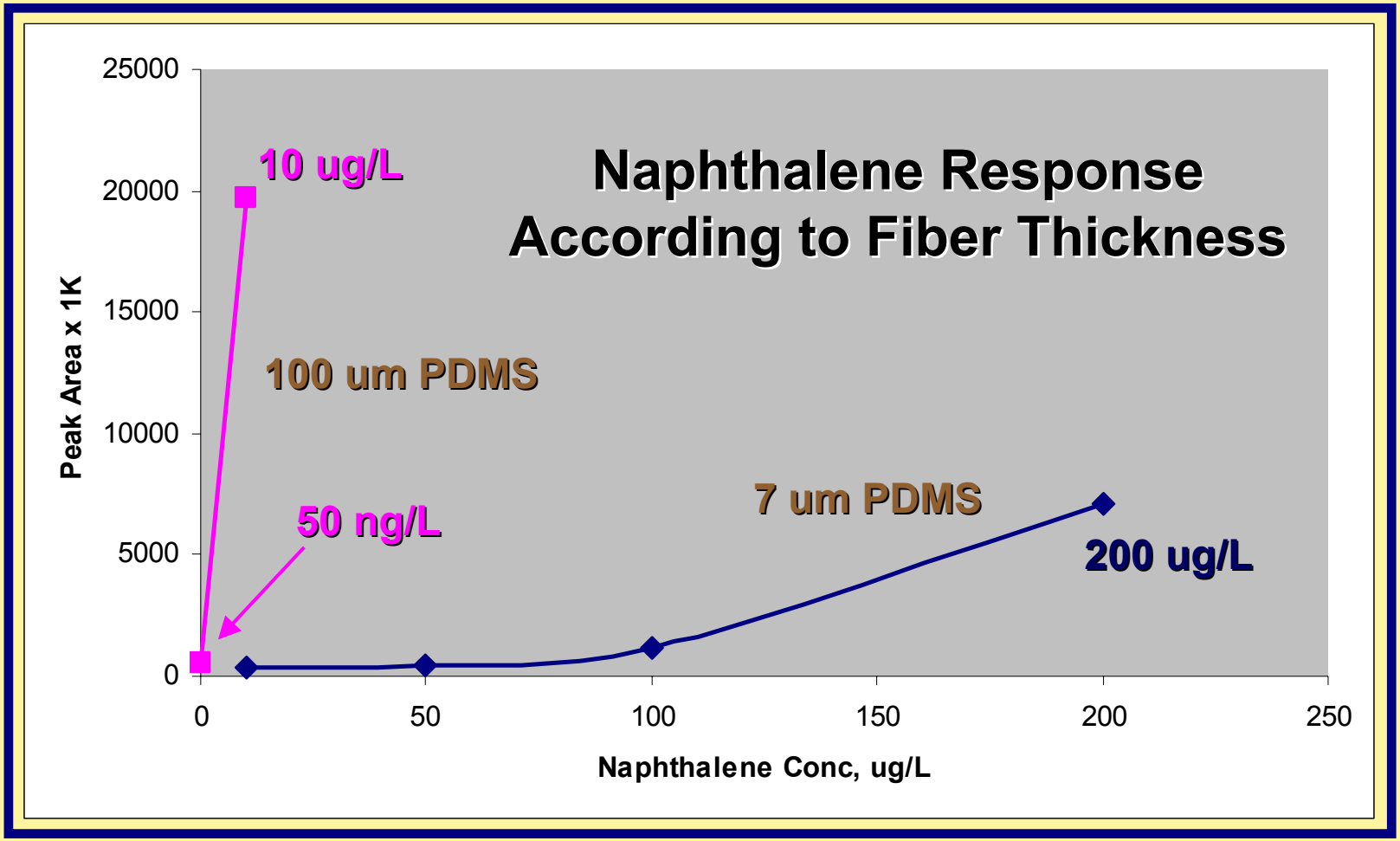
Ions observed during pre-conditioning and use with samples

SPME Considerations

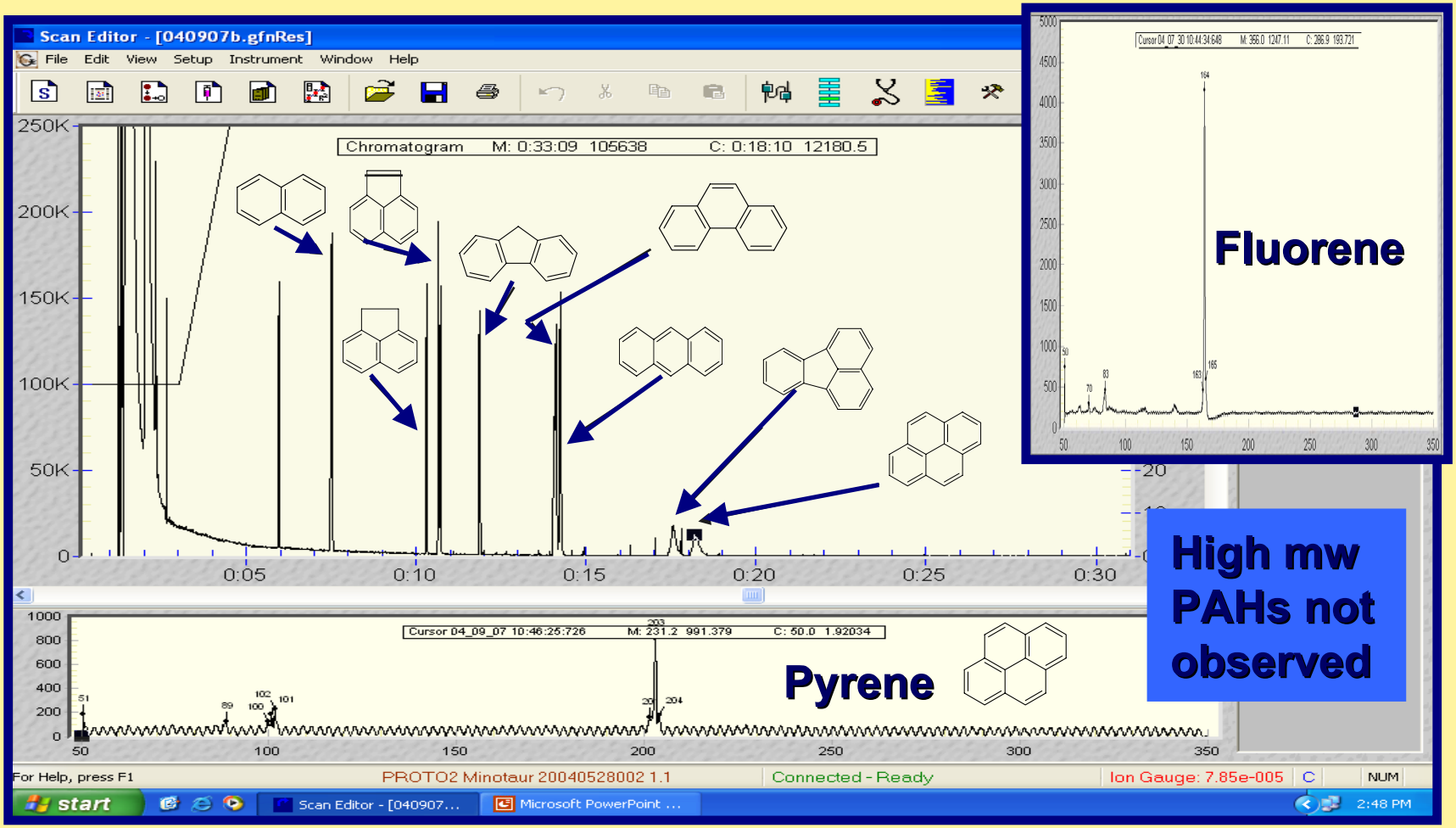


Internal Standard areas were outside acceptance limits after 15 uses

SPME Considerations



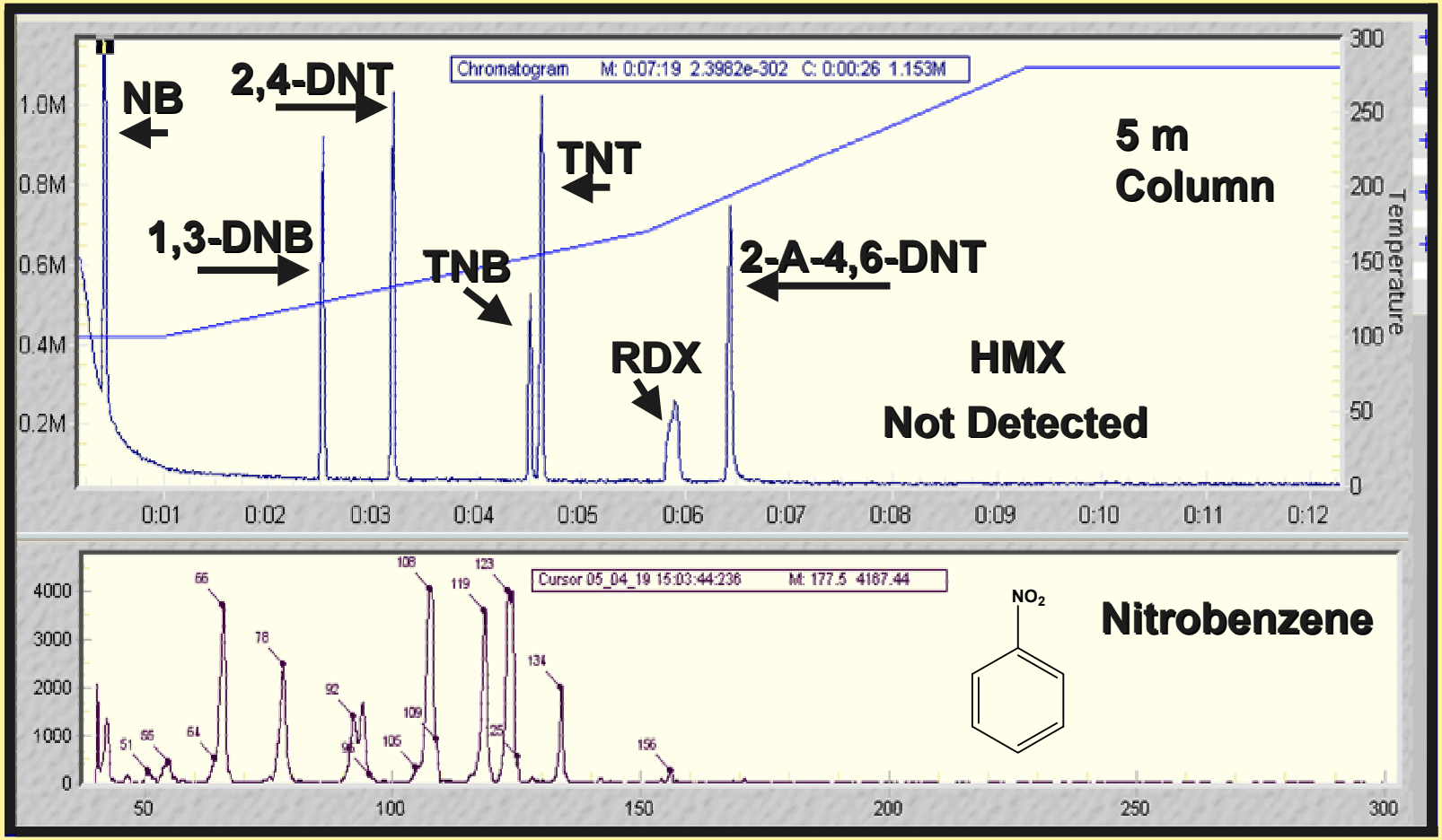
SPME Considerations



65 um PDMS/DVB Fiber, 15 m Column

Portable Operations

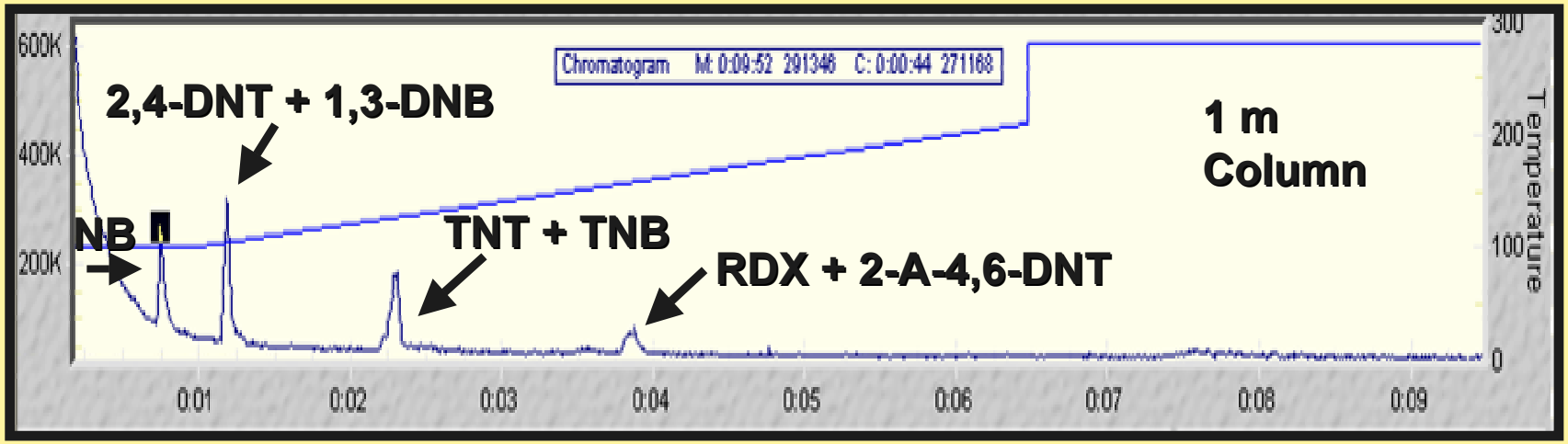
GC/CIT of Explosives

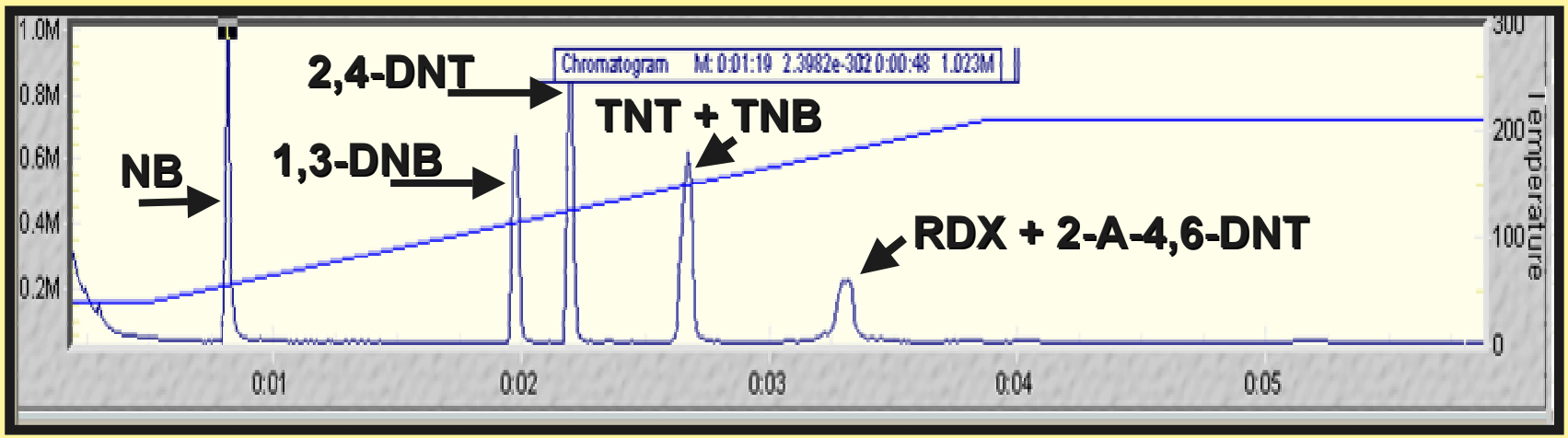


GC/CIT of 8 Component Explosives Mixture - 100 ng each

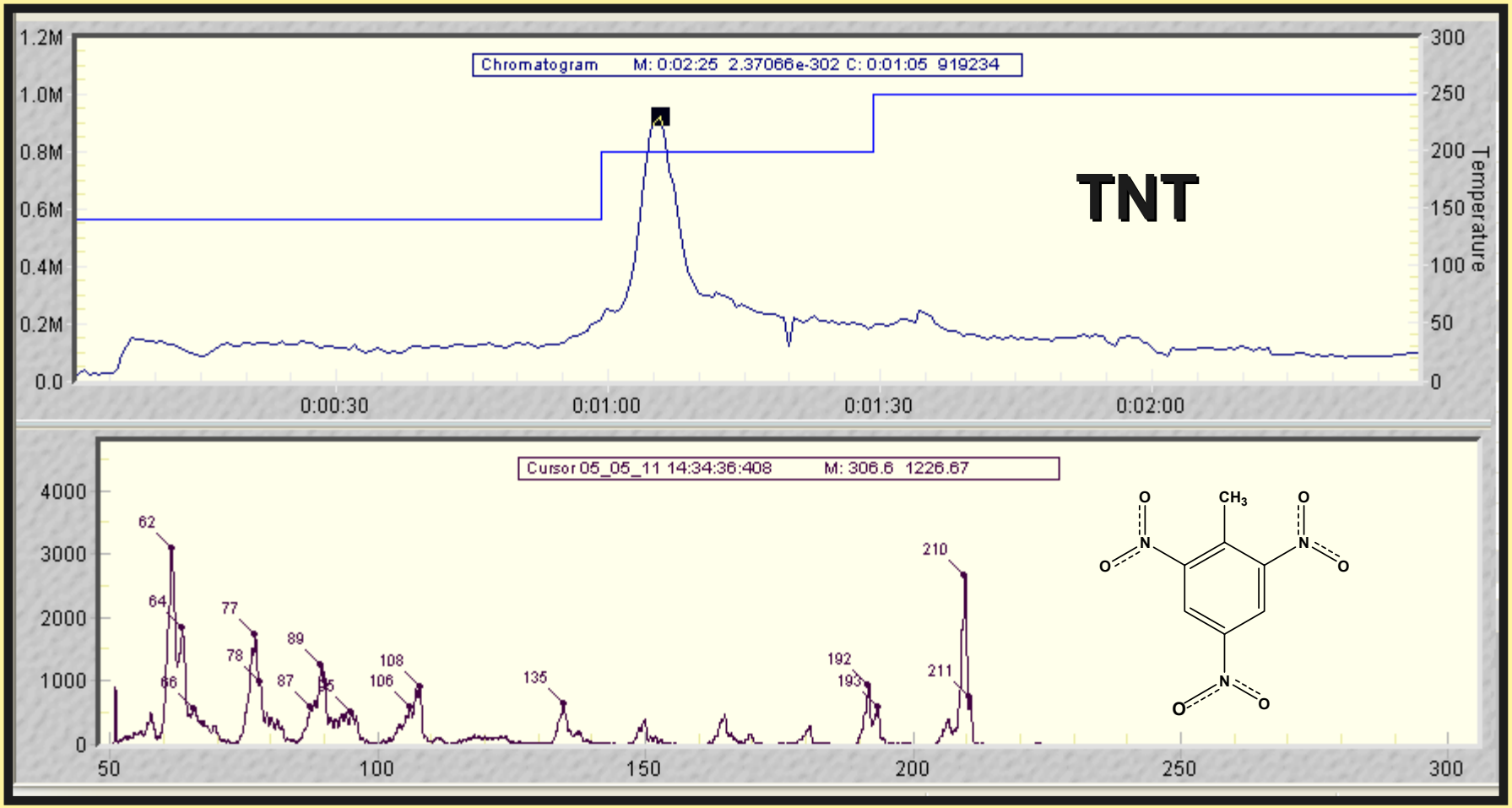
GC/CIT of Explosives

100 ng each explosives mixture on column





SPME-GC/CIT of Explosives



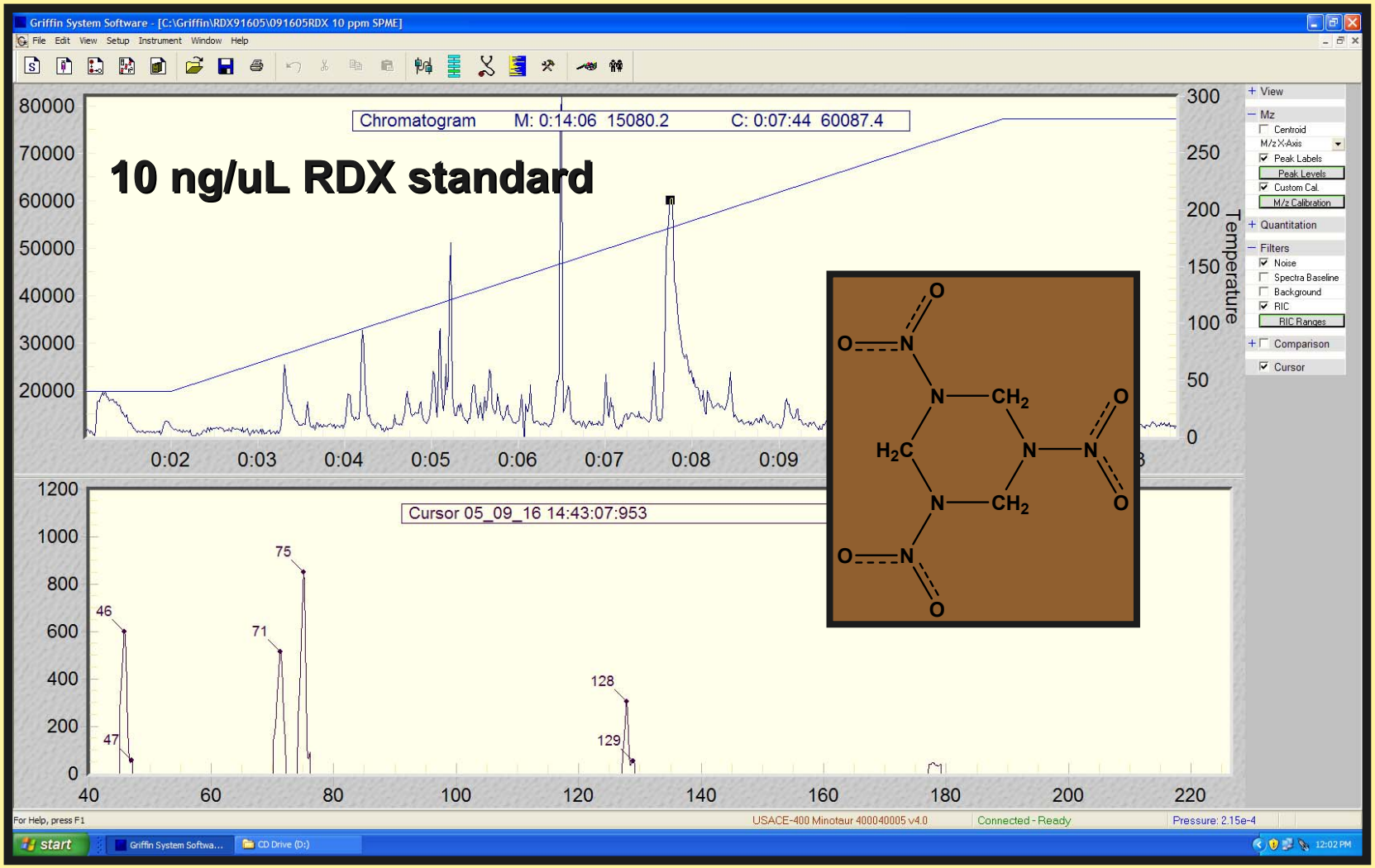
SPME-GC/MS of 1 ng/mL TNT

Portable Operations

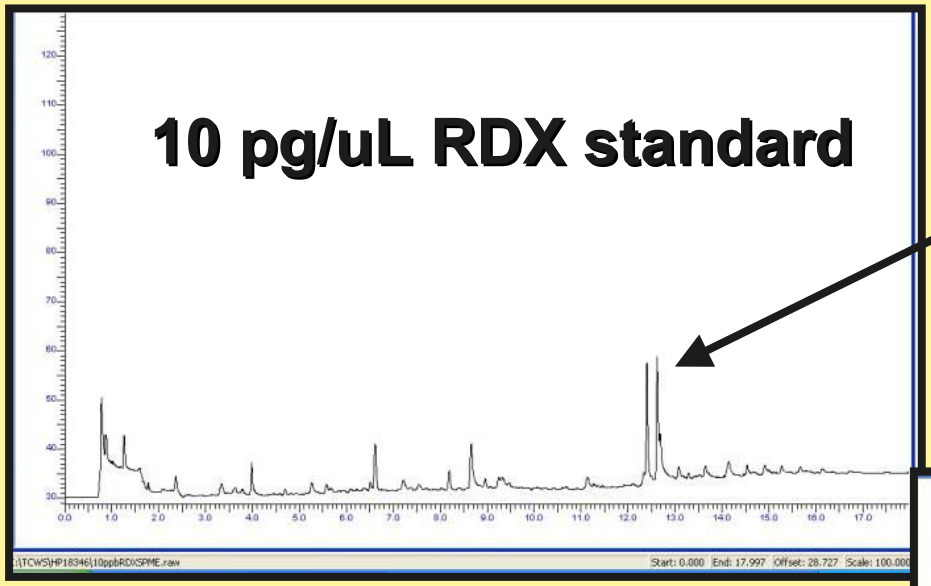
Portable Operations

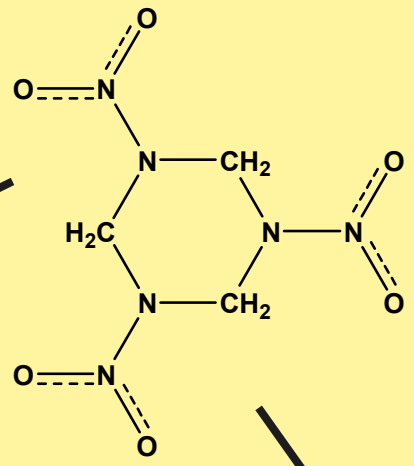
- Minotaur 400
  - 60 lbs
- Honda generator
  - 3.5 HP
  - 120 V, 2000W
  - 1.1 gal gas (8 hrs)
  - 46 lbs
- UHP He
  - Q cylinder
  - 16 L
  - 63 lbs

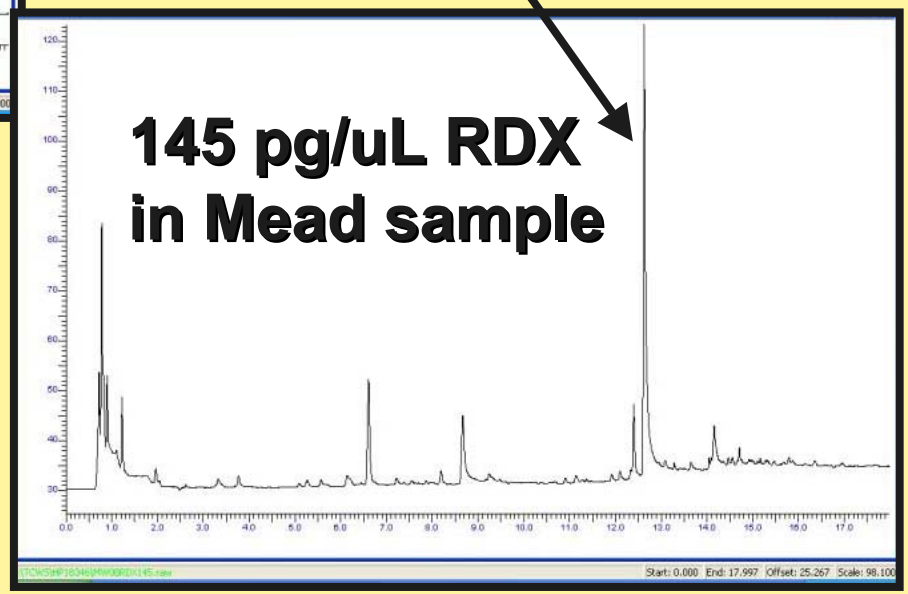
SPME-GC/CIT of RDX



SPME-GC/ECD of RDX







RDX <u>can</u> be detected at low levels after extraction on SPME with electron capture detection

Acknowledgements

Randy Laubscher

John Shannon

Griffin Analytical

Environmental Quality Technology Program
Technical Director John Cullinane

Long Term Monitoring Focus Area