

July 13, 2015

# Reducing False Positives When Monitoring for Low Concentrations of Airborne Organic Chemicals in the Workplace

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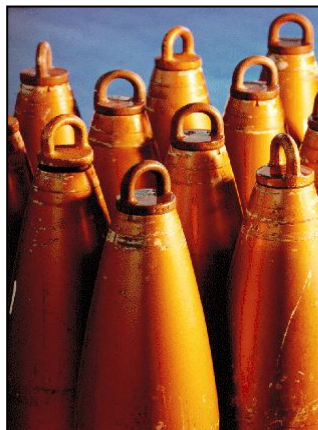
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# Acronyms

ABCDF	Aberdeen Chemical Agent-Disposal Pilot Plant
ACAMS	Automatic Continuous Air Monitoring System
BGCAPP	Blue Grass Chemical Agent-Disposal Pilot Plant
CAMDS	Chemical Agent Munitions Disposal System
CSD	Chlorine Selective Detector
FPD	Flame Photometric Detector
GC	Gas Chromatography; Gas Chromatographic
LMF	Linear Mass Flow Meter
LMFC	Linear Mass Flow Controller
MINICAMS®	Miniature Automatic Continuous Air Monitoring System
NRT	Near Real Time
PCAPP	Pueblo Chemical Agent-Disposal Pilot Plant
PCT	PreConcentrator Tube —glass tube packed with a solid adsorbent
PM	Preventive Maintenance
PPE	Personal Protective Equipment
STEL	Short Term Exposure Limit
TOCDF	Tooele Chemical-Agent Disposal Facility
WPL	Worker Protection Limit
XSD	Halogen Specific Detector

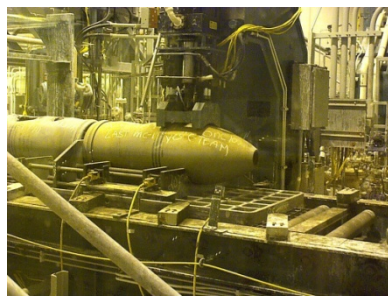
# U.S. Stockpile of Chemical Weapons

- In 1994, the US stockpile of chemical weapons was formally declared in response to the U.S. signing the Chemical Weapons Convention in 1993.
- The declared US stockpile consisted of a total of 31,000 tons of sarin (GB), mustard (HD), and agent VX and small quantities of Lewisite (L) and tabun (GA).
- As of 2015, only about 3,135 tons of the US stockpile remains to be destroyed
  - 2,611 tons of HD at Pueblo Chemical Depot
  - 306 tons of GB, 127 tons of VX, and 91 tons of HD at Bluegrass Army Depot





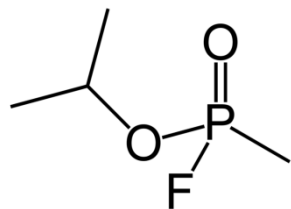
## Examples of activities at disposal sites requiring the protection of workers, the general public, and the environment



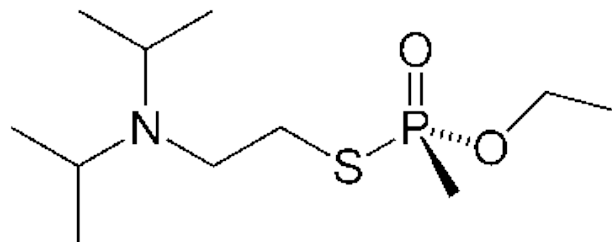
# Airborne Exposure Limits (AELs)

mg/m<sup>3</sup>

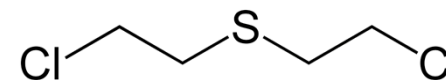
	GPL	WPL	STEL	SEL	IDLH
<b>GB</b>	0.000001	0.00003	0.0001	0.0003	0.1
<b>VX</b>	0.0000006	0.000001	0.00001	0.0003	0.003
<b>HD</b>	0.00002	0.0004	0.003	0.03	0.7



**GB (Sarin)**



**VX**



**HD (Mustard)**

# NRT Monitoring Systems for Chemical Agents

## ACAMS



- Historically used to monitor at the 15-min Short-Term Exposure Limit (STEL) but, lately, the 8-hr Worker Protection Limit (WPL) also
- Operating principles
  - collection of agent vapors using a solid adsorbent bed
  - thermal desorption and “injection” into a GC column
  - separation by temperature-programmed capillary GC
  - detection using a highly selective GC detector (e.g., an FPD)

## MINICAMS®



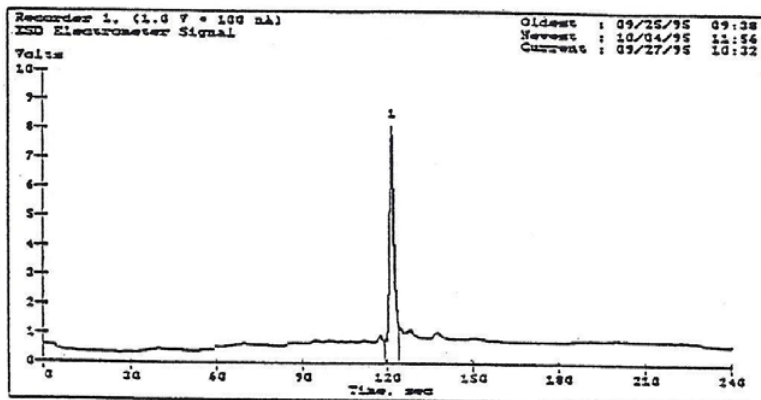
MINICAMS® is a registered trademark of CMS Research Corporation, Pelham, Alabama

## AirAlert™ by Battelle



# A Chemical Is Reported as Agent If

- It results in a change in the signal from the GC detector (i.e., a peak in the gas chromatogram) and
- It has a retention time that falls within the selected (preset) retention-time window



Chromatogram courtesy of Sandra Macon, CMS Field Products (OICO)

## False Positives

- A false positive occurs if the GC peak observed is not caused by chemical agent
- A false positive may be caused by
  - operator error and instrument artifacts
  - electronic noise (internal or external to the monitor)
  - pressure fluctuations in supplied compressed gases
  - other chemicals present in the area sampled**
- False positives introduce additional risks, such as
  - unnecessary donning of PPE
  - reduced confidence in the monitoring system
  - potential disruption of agent operations



# Chemical Agent Munitions Disposal System (CAMDS)

Pilot-Scale Test Facility: Operated 1979 – 2011

## A Case Study of False Positives





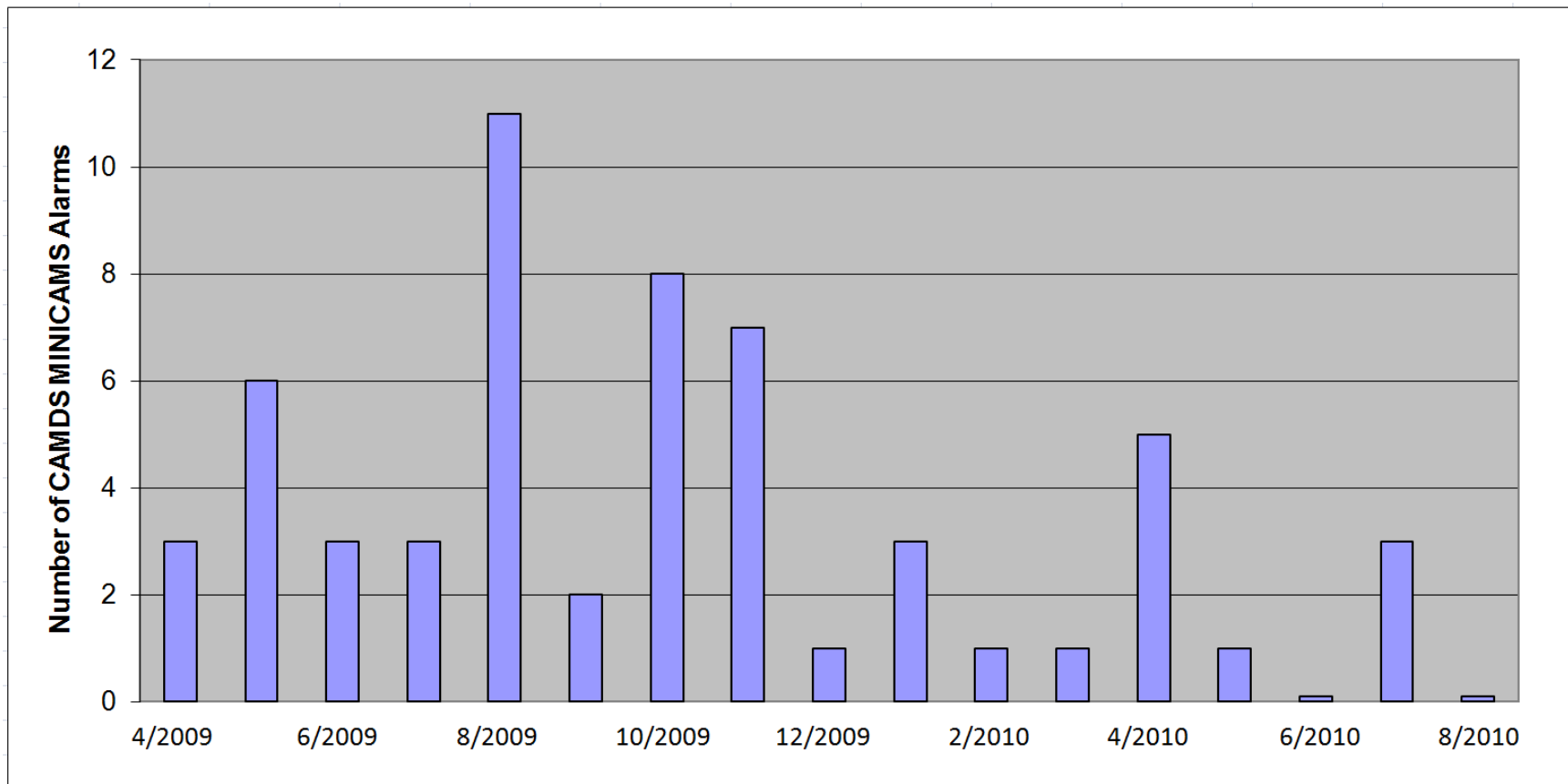
# Monitoring at CAMDS (as of June 2009)

About 20 XSD MINICAMS units, 24/7 HD monitoring at the STEL



About 20 FPD MINICAMS units,  
24/7 simultaneous VX/GB  
monitoring at the STEL

## 58 False Positives at CAMDS (2009-2010)



# False Positives\* at CAMDS by Agent

4/1/2009 – 8/31/2010

Agent	TOTAL	Operator Error	Other Causes
<b>VX</b>	<b>46</b>	<b>3</b>	<b>43</b>
<b>GB</b>	1	0	1 (equipment failure)
<b>VX/GB</b>	7	5	2 (equipment failure)
<b>HD</b>	4	3	1 (chemical interference)

\*MINICAMS concentration reports greater than or equal to 0.5 STEL, the alarm level, that were not confirmed

# Causes of VX False Positives at CAMDS

- |                           |    |
|---------------------------|----|
| • Chemical interferences? | 16 |
| • Confirmed               | 2  |
| • Operator error          | 3  |

## Corrective Actions

Improved training & aids

## Result of Low Mass On-Column for VX\*

- |                      |   |
|----------------------|---|
| • Baseline shift     | 7 |
| • Electrical noise   | 5 |
| • Equipment failure? | 4 |
| • New PCT burnoff    | 4 |
| • FPD light leak     | 3 |
| • New V-to-G pad?    | 2 |

## Corrective Actions

Air compressor adjustment

Adjusted peak width limit

Too frequent preventive maintenance

Preconditioned PCTs

Light leak tests on FPDs

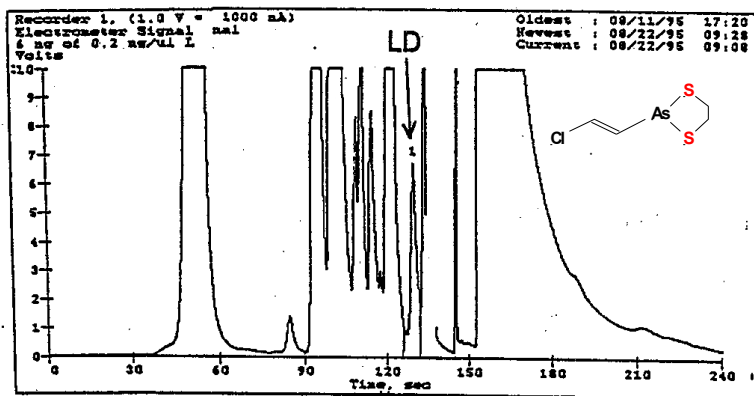
Preconditioned V-to-G pads?

\*About 3.5 pg of analyte on column at the alarm level (0.5 STEL)



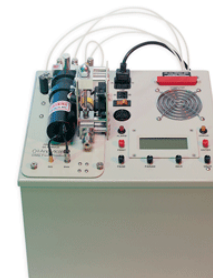
# Approaches to Eliminating False Positives Caused by Chemical Interferences

# Chemical False Positives May Sometimes Be Eliminated by Using a Different Detector

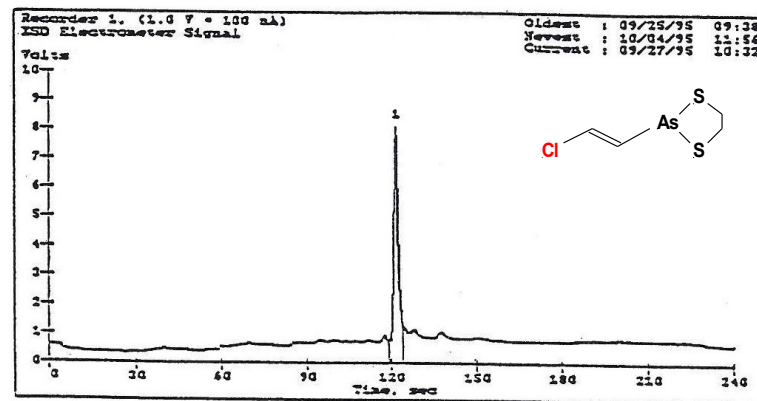


Chromatograms courtesy of Sandra Macon, CMS Field Products (OICO)

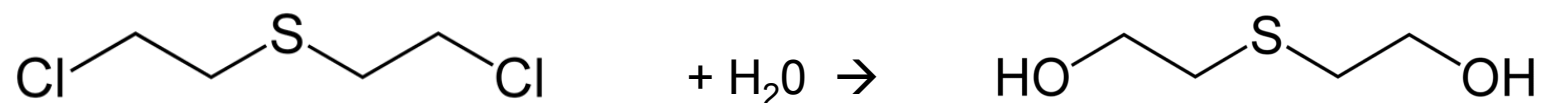
Detection of Derivatized  
Lewisite 1 Using an  
FPD (sulfur mode)



Detection of Derivatized  
Lewisite 1 Using an XSD  
(halogen specific detector)



## Another Example: HD in the Presence of Thiodiglycol



Hydrolysis of agent mustard (HD) at ABCDF, BGCAPP and PCAPP



FPD MINICAMS — S

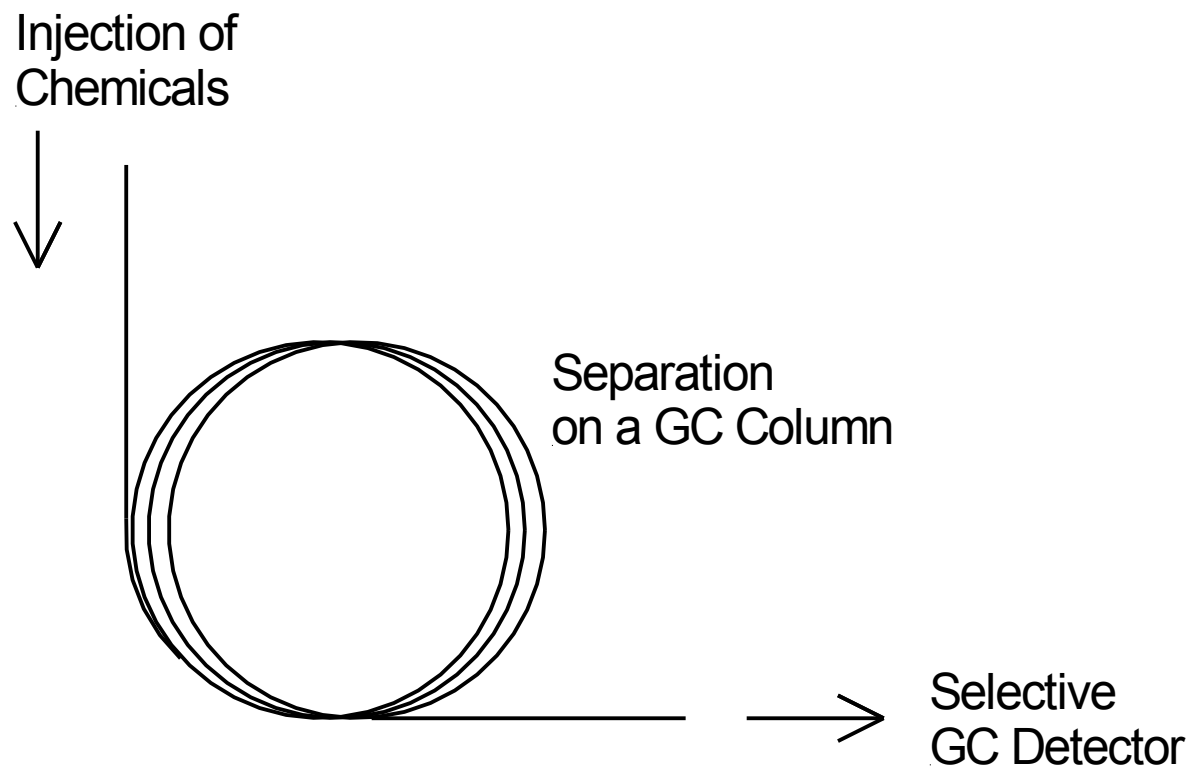


XSD MINICAMS — CI

# Adding Heart Cut Capability to NRT Monitoring Systems

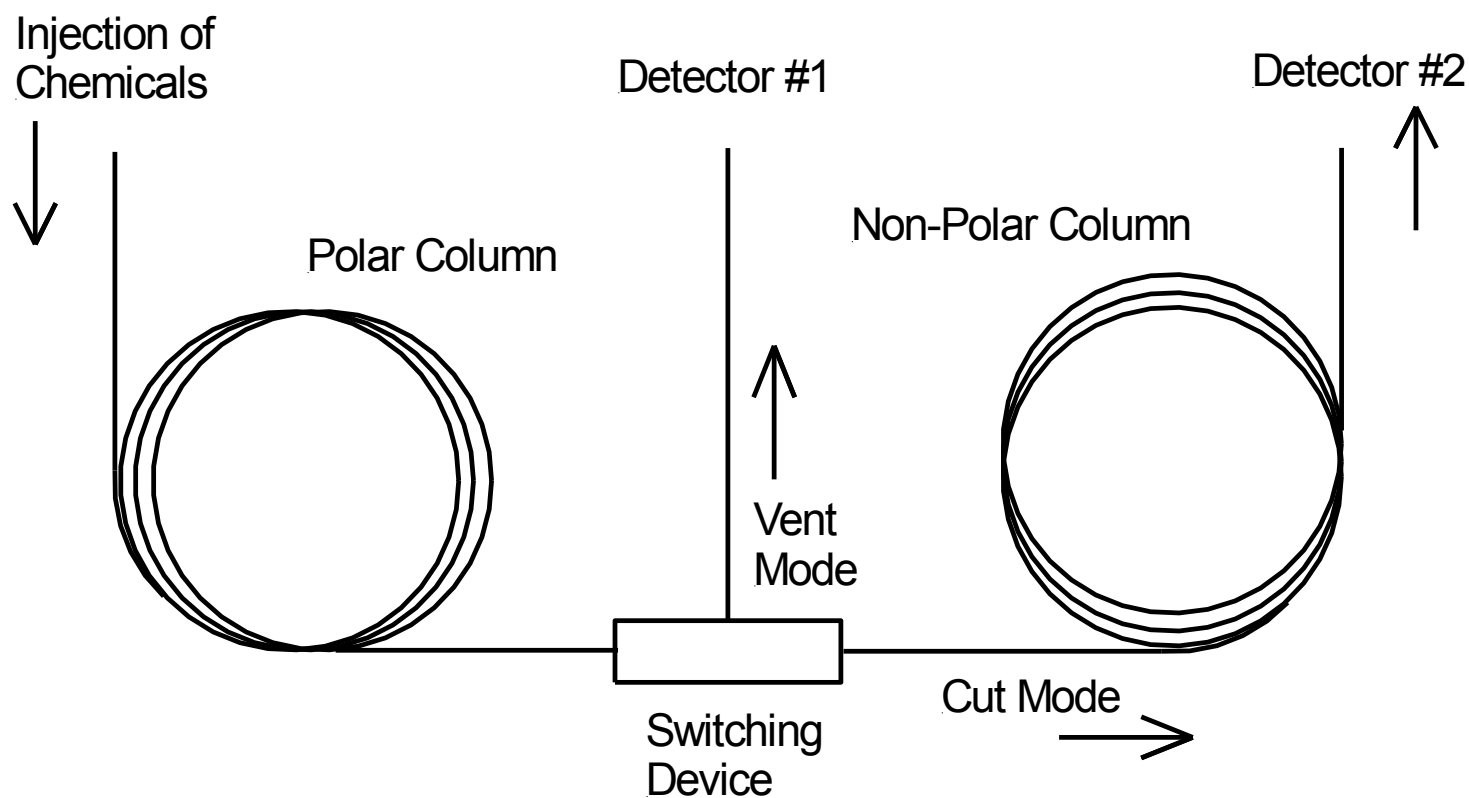


# Separation of Chemicals on a Single GC Column



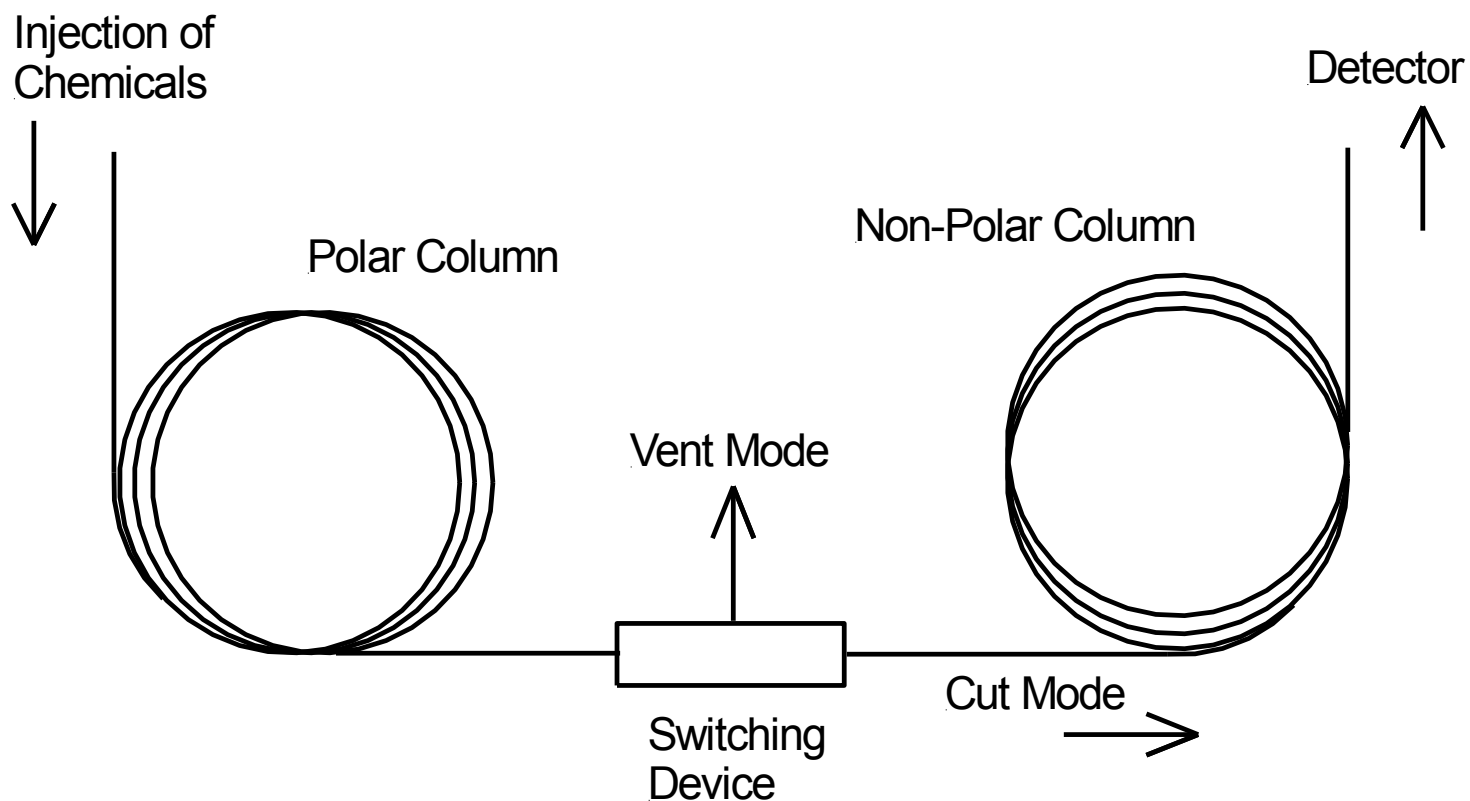
# Conventional Heart Cut Configuration

Typical for a Laboratory Gas Chromatograph



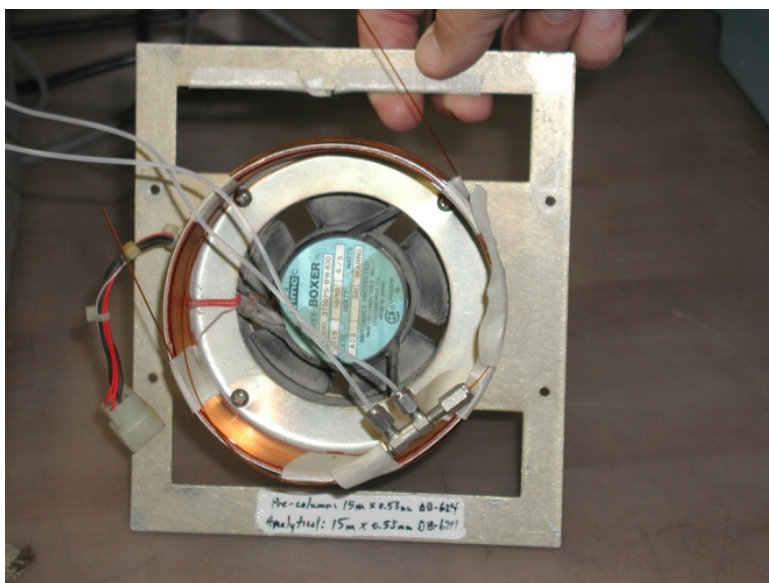
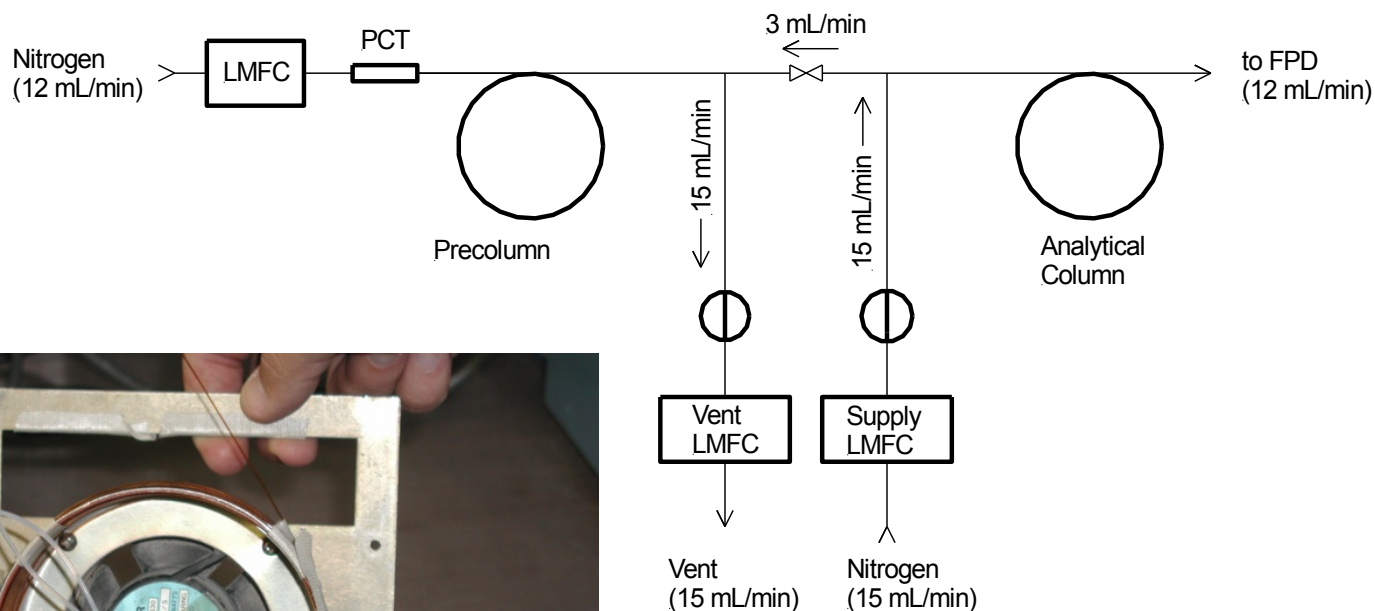
# Heart Cut without a Second Detector

NRT Monitors Typically Cannot Support a “Mid Point” Detector



# Implementation of Heart Cut in the ACAMS

Mid-Point Restrictor Approach—effective during the VX mine drum campaign at TOCDF

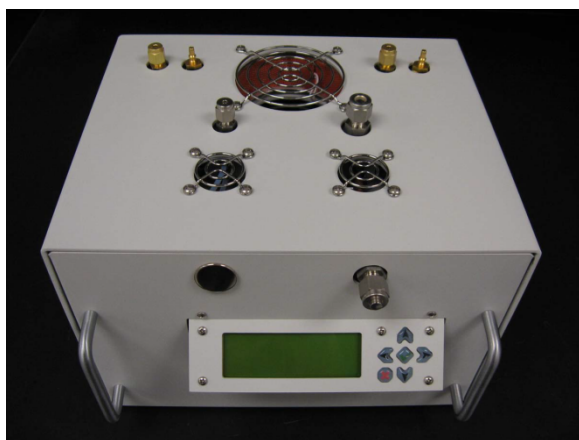




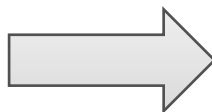
# Implementation of Heart Cut for the MINICAMS

Use of an External Selective Sampler—available from NRT Methodologies, Inc. (Tooele, Utah)

**Selective Sampler**—simple interface to the MINICAMS

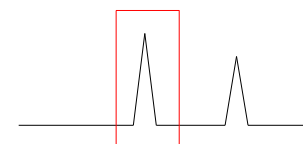
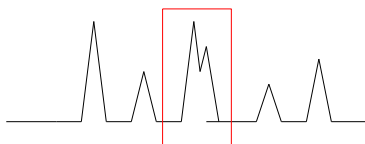


Or any other vacuum-based sampling system



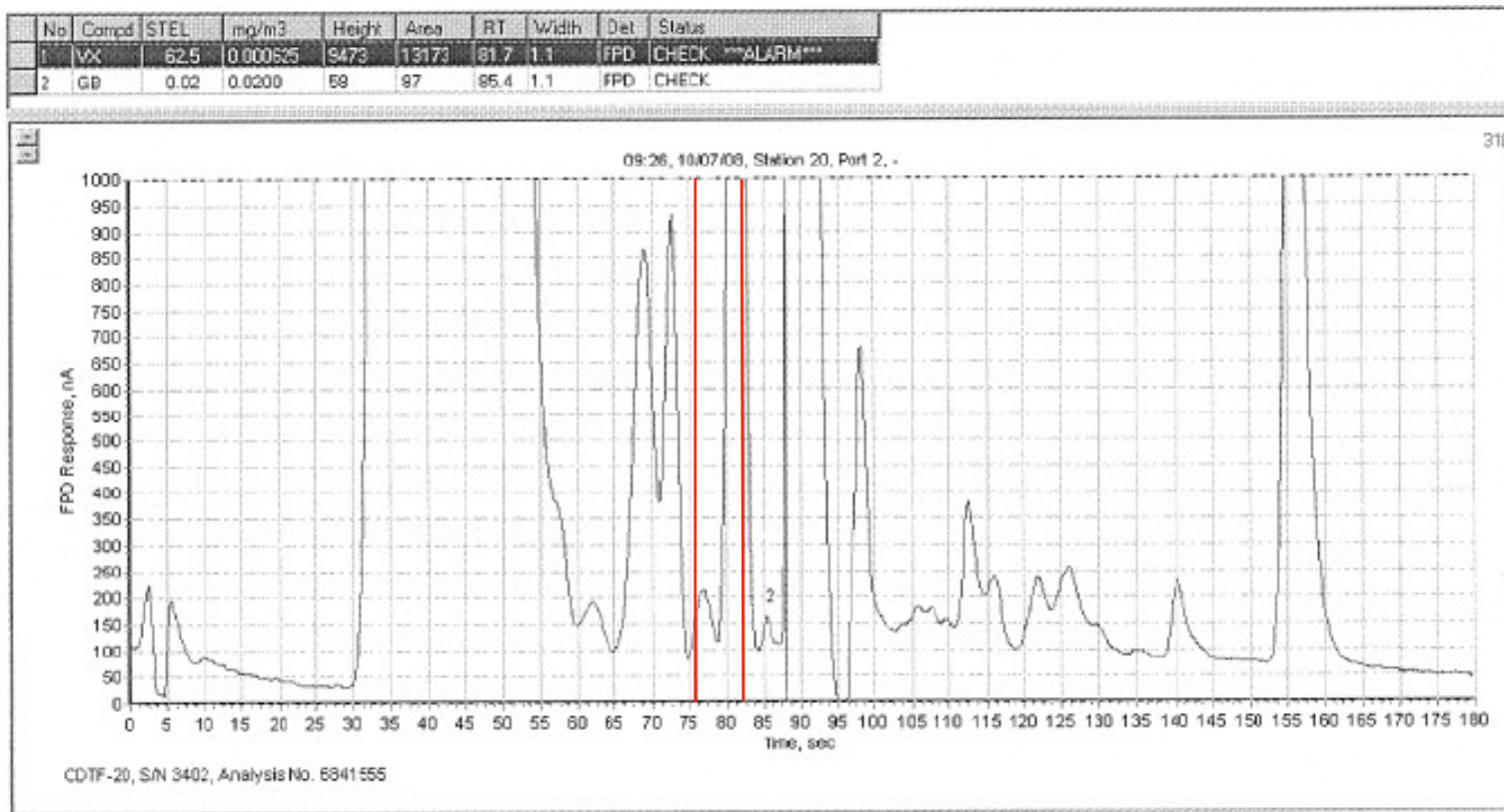
**FPD MINICAMS**

- Sampling on a solid adsorbent bed
- Separation on a polar GC column
- Transfer of chemicals eluting the column only during the heart-cut retention time window



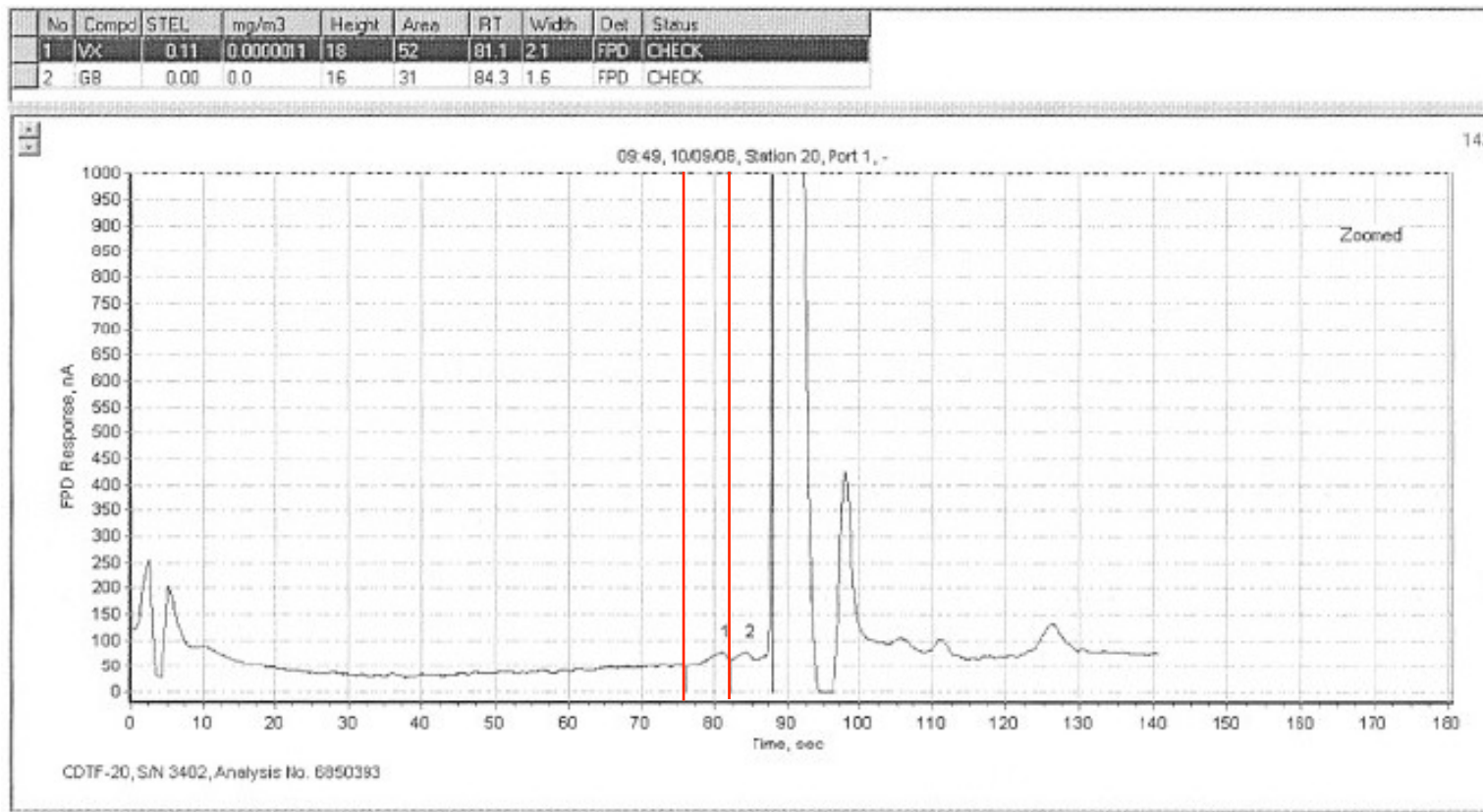
# MINICAMS Chromatogram—without the Selective Sampler

## 62.5 STEL reported for VX—a false positive



# MINICAMS Chromatogram—with the Selective Sampler

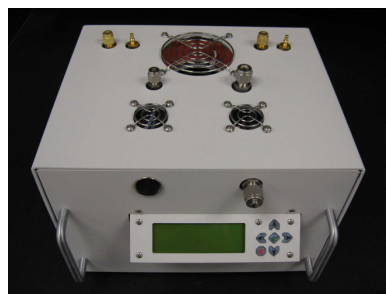
VX concentration report for the same sample matrix only 0.11 STEL



# MINICAMS—heart-cut capability with the Selective Sampler

- Simple interface between the MINICAMS and the Selective Sampler
- Selective Sampler is a slave to the MINICAMS cycle
- Requires two MINICAMS instrument cycles for sampling and analysis of a given matrix
  - one for the Selective Sampler followed by one for the MINICAMS
- Applicable primarily
  - where false positives create public concern (e.g., stack emissions)
  - for sampling complex matrices (e.g., decontaminated waste)
  - clearing contaminated areas through “air washing”

**NRT Methodologies, Inc.**  
(Tooele, Utah)





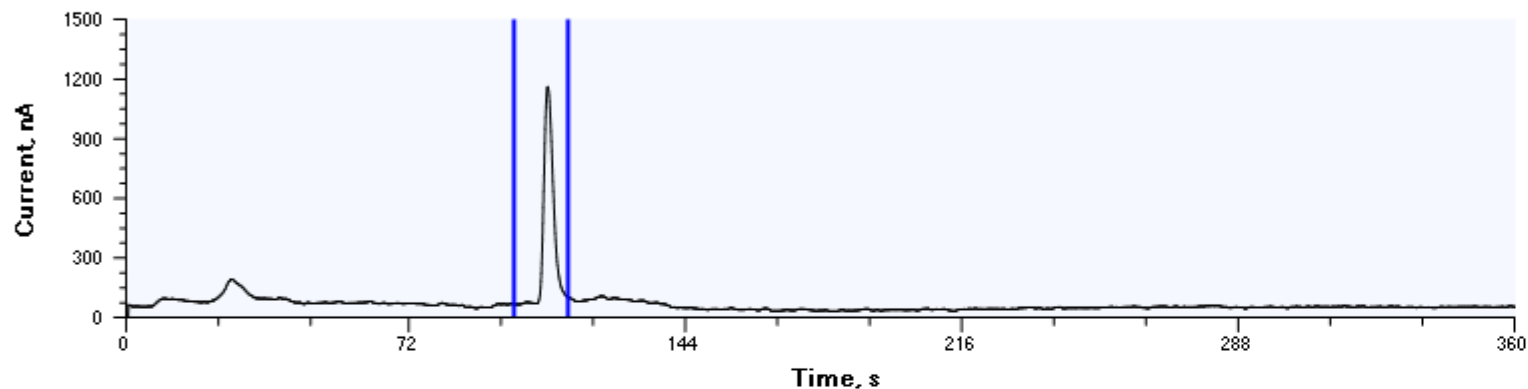
# Battelle's AirAlert™

- Flexible sampling and analytical platform with internal space for expansion
- All sampling and analytical components plug-in for ease of replacement
- Readily reconfigured for various applications (removable module)
- Only two surface-mount circuit boards
- Only six simple wiring harnesses
- Lower cost of manufacturing
- Reduced weight (13 pounds)
- 0.7 cubic feet



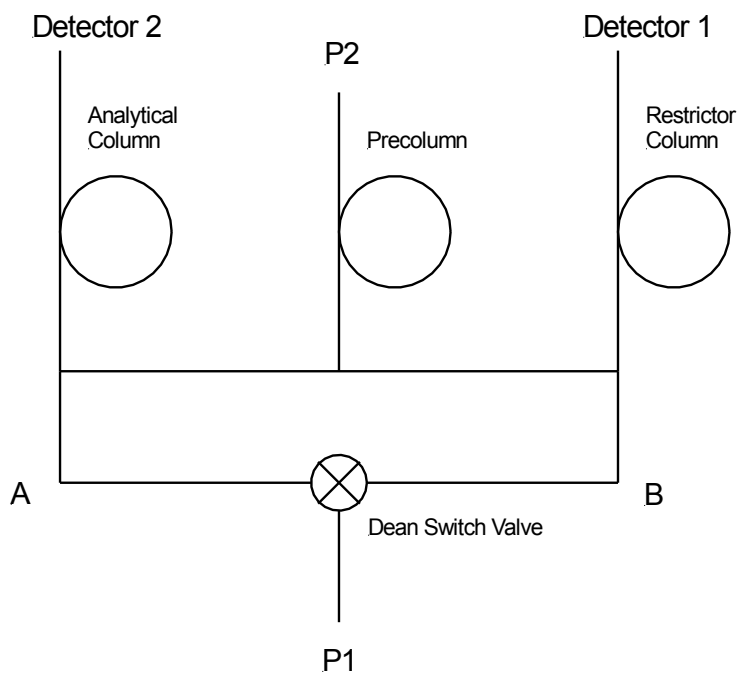
## AirAlert—sampling and analytical capabilities

- Spare sampling and analytical modules to minimize down time  
—replaceable in 5 minutes without the use of any tools
- Sampling and analytical module with a chlorine selective detector (CSD)
- Sampling and analytical module with a flame photometric detector (FPD)



# Adding Heart Cut Capability to the AirAlert

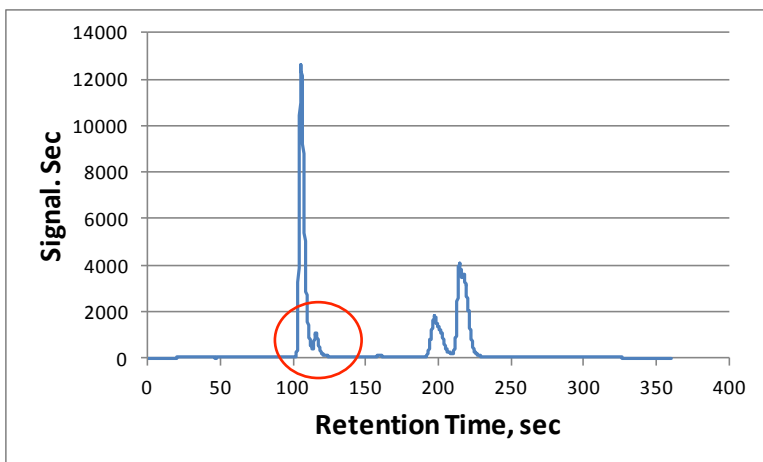
## Traditional Dean Switch Approach



## AirAlert Dean Switch Approach

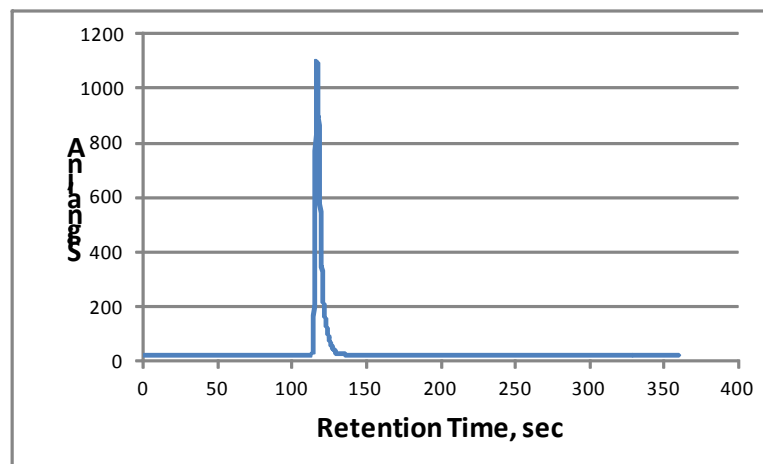
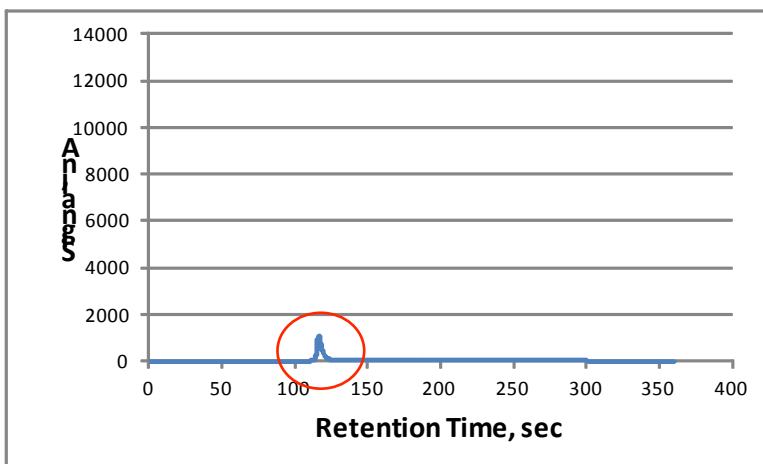
Awaiting approval  
from Battelle's patent  
attorney's  
before releasing  
additional technical  
details

# Performance of the Heart Cut for the AirAlert



←No heart cut:

Small analyte peak on  
the trailing edge of a much larger peak



Chromatograms for same sample matrix with heart cut enabled-----

# Reduction of False Positives

- Improved operator training—on causes of false positives
- Proper equipment set up—to minimize false positives
- Operator aids (e.g., check lists)—to avoid errors that cause false positives
- Preconditioning of key expendables (e.g., solid adsorbents in PCTs)
- Increased mass on column (e.g., longer sample period)
- Proper set up and control of compressed gases and other utilities
- Integration of heart-cut capability into NRT equipment



# Questions?

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