

## **On-Site Homogenization and Analysis of Soil Samples for Energetic Residues**

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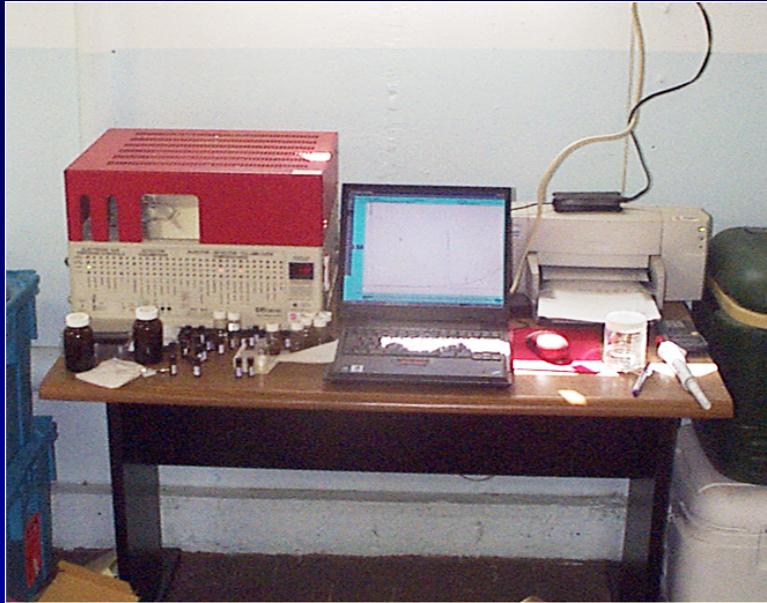
- \* U.S. Army Environmental Center,  
Martin H. Stutz, Project Monitor**
- \* U.S. Army Environmental Quality  
Technology Research Program Work  
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## Project Objectives

- \* On-site analysis of energetic residues
- \* On-site homogenization of composite and discrete soil samples for the analysis of energetic residues

## SRI / CRREL GC-TID Method

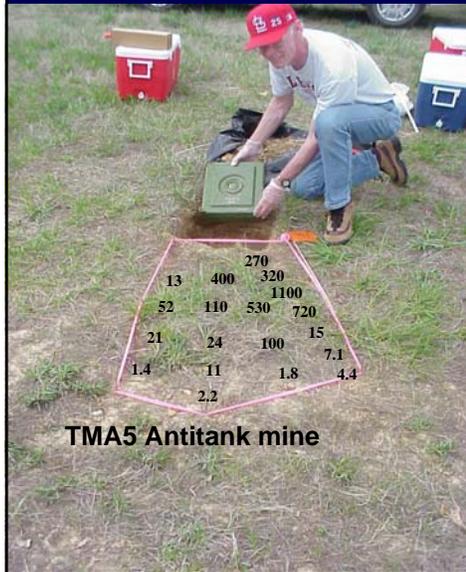
- GC-TID Instrument manufactured by SRI (Model 8610C)
- Method developed by Hewitt et al. 1999
- Allows on-site determination
  - Nitroaromatics: TNT, 2,4-DNT, TNB, 2&4-ADNT
  - Nitramines: RDX, HMX
  - Nitrate esters: PETN, NG



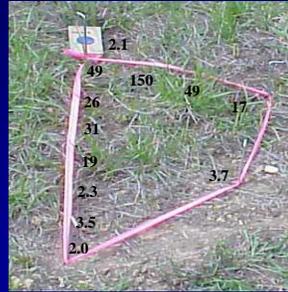
## **SRI / CRREL GC-TID ETV Results (soil)**

	<u>TNT</u>	<u>RDX</u>
Precision (%RSD)	17%	13%
Accuracy (mean recovery)	97%	91%
False positives	1%	0%
False negatives	3%	1%
Completeness	100%	100%

## Surface Concentration Distribution



2,4-DNT  $\mu\text{g}/\text{kg}$   
PMA-1A Antipersonnel mine



## Advantages / Disadvantages of GC-TID On-Site Analysis

### Advantages

- Provides excellent quantitative results for all major target analytes including **white phosphorous (NPD)**
- Low false positive / false negative rates
- Instrument cost only about \$9,000

### Disadvantages

- Requires chemist with GC experience
- May require compressed gasses
- New method; little track record at real sites

## **Characterization issues of high explosives and propellant residues at firing points and impact ranges**

- a. Surface - initial receptor
- b. Training range size (thousands of km<sup>2</sup>) and remoteness
- c. Residues are particles of various sizes





## **SERDP Program Objective**

Measure energetic residue concentrations associated with military training activities (source strengths ranking).

- a. Munitions firing
- b. High-order detonations
- c. Low-order detonations
- d. Blow-in-place operations and other disposal practices

# Sampling Strategies

Stratified random and judgmental sampling:

1. > 20 increment randomly collected composite samples

Area: grid, concentric rings, transects, etc.

Activity: firing point, target, impact crater, impact range

2. Discrete sampling

Activity: ruptured UXO, chunks (i.e., low-order detonation), burning tray, subsurface sampling





## Initial Site Characterization Study of an Active Training Range Where On-Site Analysis Was Taken to Help Guide the Sampling Activity.

Location: Ft. Greely, Alaska (Aug 2001)

Subsampling procedure: 10 to 15 randomly located increments removed from bags or aluminum pie pans containing large discrete or composite samples to build 15±5 g subsamples for on-site analysis. Subsamples removed within 24 hours of sample collection.

Samples ranged from highly vegetated to coarse beach sand.

### On-Site GC-TID vs. GC-ECD and HPLC (Methods 8095 and 8330) Results for subsamples from the same sandy soil composite sample

Sample ID	NG (mg/kg)		
	GC-ECD	GC-TID	HPLC
GI-003	5.1	4.7	6.5
GI-003-S1	16	25	23
GI-003-S2	19	27	23
GI-003-S3	4.8	11	10
GI-003-S4	<0.03	<0.1	<1
GI-003-S5	<0.03	<0.1	<1

## Comparison for NG in a vegetated matrix

Sample ID	NG (mg/kg)		
	GC-ECD	GC-TID	HPLC
Sally-23	32	32	33
Sally-23-S1	<0.03	<0.1	<1
Sally-23-S2	<0.03	<0.1	<1
Sally-23-S3	<0.03	<0.1	<1
Sally-23-S4	<0.03	<0.1	<1
Sally-23-S5	0.81	0.65	<1
Sally-23-S6	1.1	0.93	<1
Sally-23-S7	<0.03	<0.1	<1
Sally-23-S8	<0.03	<0.1	<1
Sally-23-S9	<0.03	<0.1	<1
Sally-23-S10	6.7	5.0	5.7

## On-Site Sample Homogenization

1. Air dry bulk sample.
2. Pass through #10 sieves (2 mm) and retain organic matter, removing only large twigs.
3. Screen for >1000 ppm explosives if necessary.
4. Grind sample in field-portable mill.
5. Thoroughly mix ground sample.
6. "Layered Bedding Subsampling"
7. Extract the entire subsample for analysis.

## Layered Bedding Subsampling

Slowly pour mixed sample onto a clean flat sheet of aluminum foil in a long rectangular pattern, maintaining a uniform shape (height and width) while making at least twenty passes. Remove an entire cross section of at least 1-cm width at the top of the pile.







## Homogenization, Subsampling, and GC-TID Analysis at Ft. Greely

Subsamples mg 2,4-DNT/kg

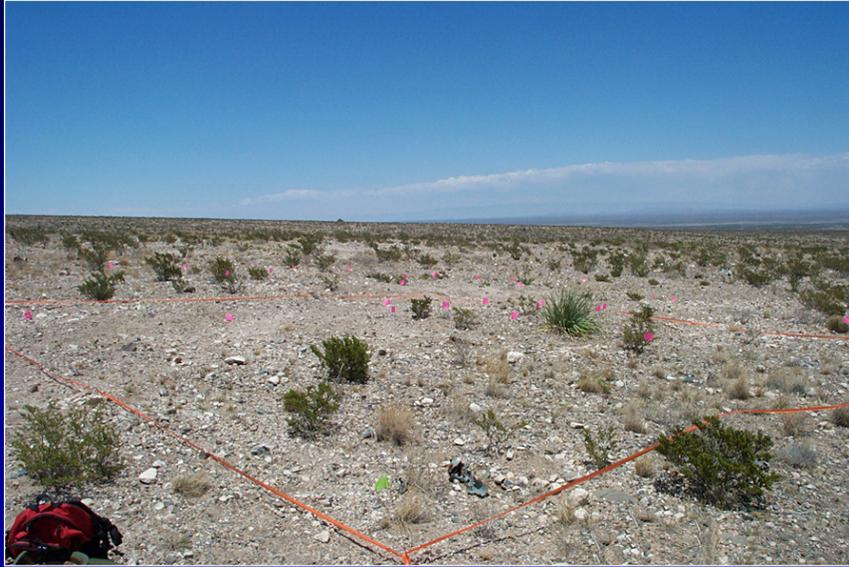
<u>Sample</u>	<u>A</u>	<u>B</u>	<u>%RPD</u>
<b>Low Vegetation Firing Point</b>			
FP Mark G#1	1.6	1.1	23
FP Mark G#2*	1.7	6.8	100
FP Audrey G#1	0.29	0.16	35
FP Audrey G#2	0.4	0.16	50
FP Audrey G#3	0.61	0.8	9.3
FP Audrey G#4	4.6	1.5	58
FP Audrey G#5	0.2	0.13	26
FP Audrey G#6	0.71	1.0	24
<b>High Vegetation Firing Point</b>			
FP Big Lake G#2	1.7	0.53	59
FP Sally G#5*	1.5	1.3	9.3
FP Sally G#2	0.95	0.91	2.8

The on-site sample homogenization procedure

## Homogenization, Subsampling, and Analysis at Ft. Greely

Subsamples (mg 2,4-DNT/kg)

<u>Sample</u>	<u>A</u>	<u>B</u>	<u>%RPD</u>
<b>Open Burning of Propellant (Sand)</b>			
OP-81	0.41	0.43	3.2
OP-7	12	12	0
<b>Grinder and Subsampling Blanks</b>			
Grinder Blank #1	<0.006		
Grinder Blank #2	<0.004		

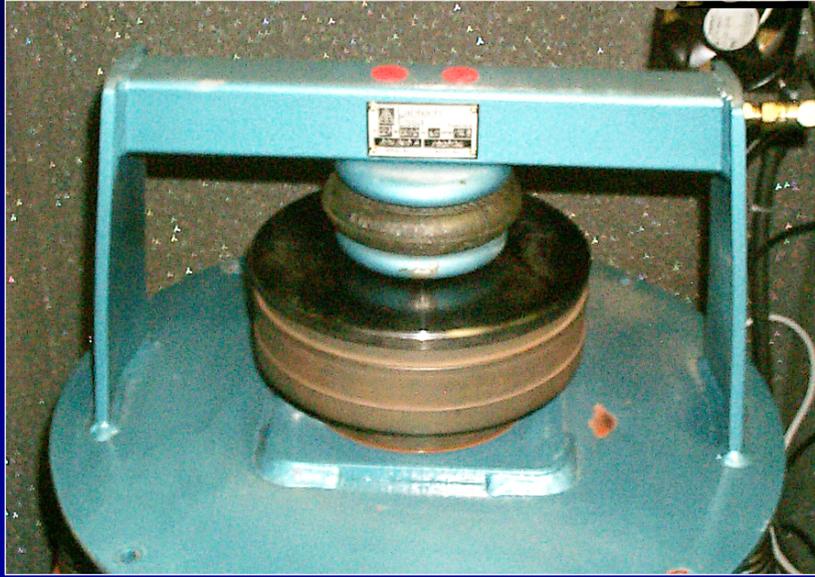


## Homogenization and Subsampling at Ft. Bliss

mg/kg

<u>Subsample</u>	<u>TNB</u>	<u>TNT</u>	<u>Tetryl</u>	<u>2A-DNT</u>	<u>4A-DNT</u>
BC-75A	0.099	2.00	1.45	0.152	0.140
BC-75B	0.109	1.97	0.950	0.146	0.148
BC-75C	0.095	1.98	2.90	0.142	0.133
BC-75D	0.103	1.99	1.84	0.141	0.135
BC-75E	0.092	1.91	0.958	0.140	0.123
BC-75F	0.093	1.85	0.503	0.142	0.135
BC-75G	0.095	1.87	2.75	0.140	0.136
<b>Mean</b>	<b>0.098</b>	<b>1.94</b>	<b>1.62</b>	<b>0.143</b>	<b>0.136</b>
<b>Std. Dev.</b>	<b>0.0063</b>	<b>0.063</b>	<b>0.925</b>	<b>0.0044</b>	<b>0.0075</b>
<b>Coef. Var.</b>	<b>6.4%</b>	<b>3.2%</b>	<b>57%</b>	<b>3.0%</b>	<b>5.5%</b>





- Subsampling error – effect of grinding on standard deviation in hand grenade range soil



Subsample	TNT Conc. mg/kg		RDX Conc. mg/kg	
	Not Ground	Ground	Not Ground	Ground
1	0.25	2.03	1.68	4.75
2	1.81	2.04	1.77	4.71
3	0.37	2.00	1.46	4.80
4	1.48	2.03	3.80	4.73
5	7.93	1.97	7.83	4.67
6	0.56	2.00	1.81	4.66
7	0.35	1.90	2.35	4.62
8	0.75	2.02	2.51	4.62
9	0.56	1.97	2.08	4.64
10	0.35	1.98	1.98	4.69
11	0.62	1.90	1.68	4.66
12	5.62	1.91	13.0	4.60
mean	1.72	1.98	3.50	4.68
std dev	2.46	0.051	3.47	0.057
RSD	143%	2.57%	99%	1.23%

## Homogenization, Subsampling and Analysis of Ft. Greely Samples On-site Vs. Off-site

Sample	On-site		Off-site	
	A	B	A	B
<b>Low Vegetation Firing Point</b>				
FP Mark G#1 (0°-25m)	1.6	1.1	1.3	1.2
FP Mark G#2* (0°-25m)	1.7	6.8	5.6	4.2
FP Mark G#2 (0°-50m)	0.98	0.37	0.17	0.35
FP Mark G#2 (60°L-25m)	0.98	1.5	1.4	1.4
FP Mark G#2 (60°L-50m)	0.015	0.010	0.14	0.10
FP Mark G#2 (60°R-25m)	0.63	0.91	0.96	2.5
FP Mark G#2 (60°R-50m)	1.8	0.67	0.21	0.14
<b>High Vegetation Firing Point</b>				
FP Sally G#5*	1.5	1.3	0.71	0.91
FP Sally G#2	0.95	0.91	0.25	0.21

## **Current on-site sample homogenization method**

- \* Effective for explosives residues (high explosives) in sandy soils.
- \* Not as effective for highly vegetative sample matrices. (Uncertainty can be managed by increasing the number of subsamples analyzed).

## **A Long Term Monitoring Challenge**

- Representative surface soil characterization
  - Analysis of large number discrete samples
  - Homogenize Composite samples

## **Potential LTM Program Initiatives**

- **Development of rapid on-site GC-TID analysis method for energetics in ground water and sediments.**
- **Technology Verification Program (Soil and Water).**
- **Demonstration of GC-TID analysis of energetics in soil.**
- **Field testing of on-line colorimetric detector for TNT, RDX, and perchlorate in ground water.**