Evaluation of Field Analytical Technologies for Explosives Detection

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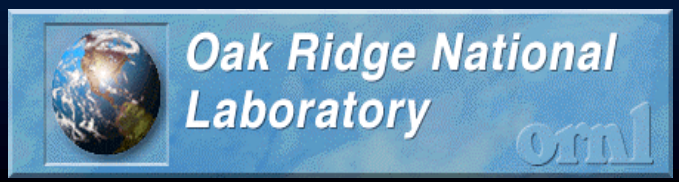

Co-Authors

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Chuck Bayne

Eric Koglin

Tom Jenkins

Overview of Environmental Technology Verification Process

Statisticians

Project Officers

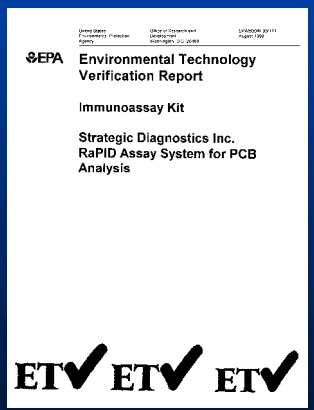
Developers

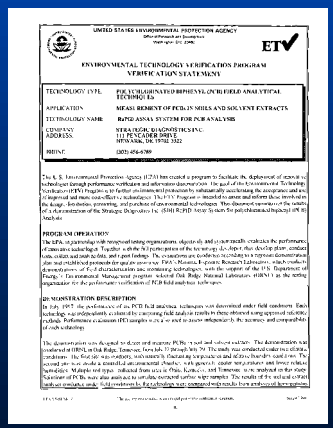
Chemists

Stakeholders

Experimental Plan

Samples are collected, homogenized, labeled, and assembled for distribution.





Product is report and verification statement.

Technology developers analyze randomized samples under field conditions.

Examples of the Contamination Problem

Contaminated soil requires protection from the weather following excavation at Milan Army Ammunition Plant.

Leaking process water pipes and contaminated groundwater at Volunteer Army Ammunition Plant.

Experimental Design Drivers

- Field conditions comparable to real world.
- Wide range of sample matrices, both soil and water, wider than typically acquired from a single site.
- Wide range of target analyte concentrations.
- Replicates imbedded in design requires homogenous samples.

Samples Acquired from Multiple Facilities

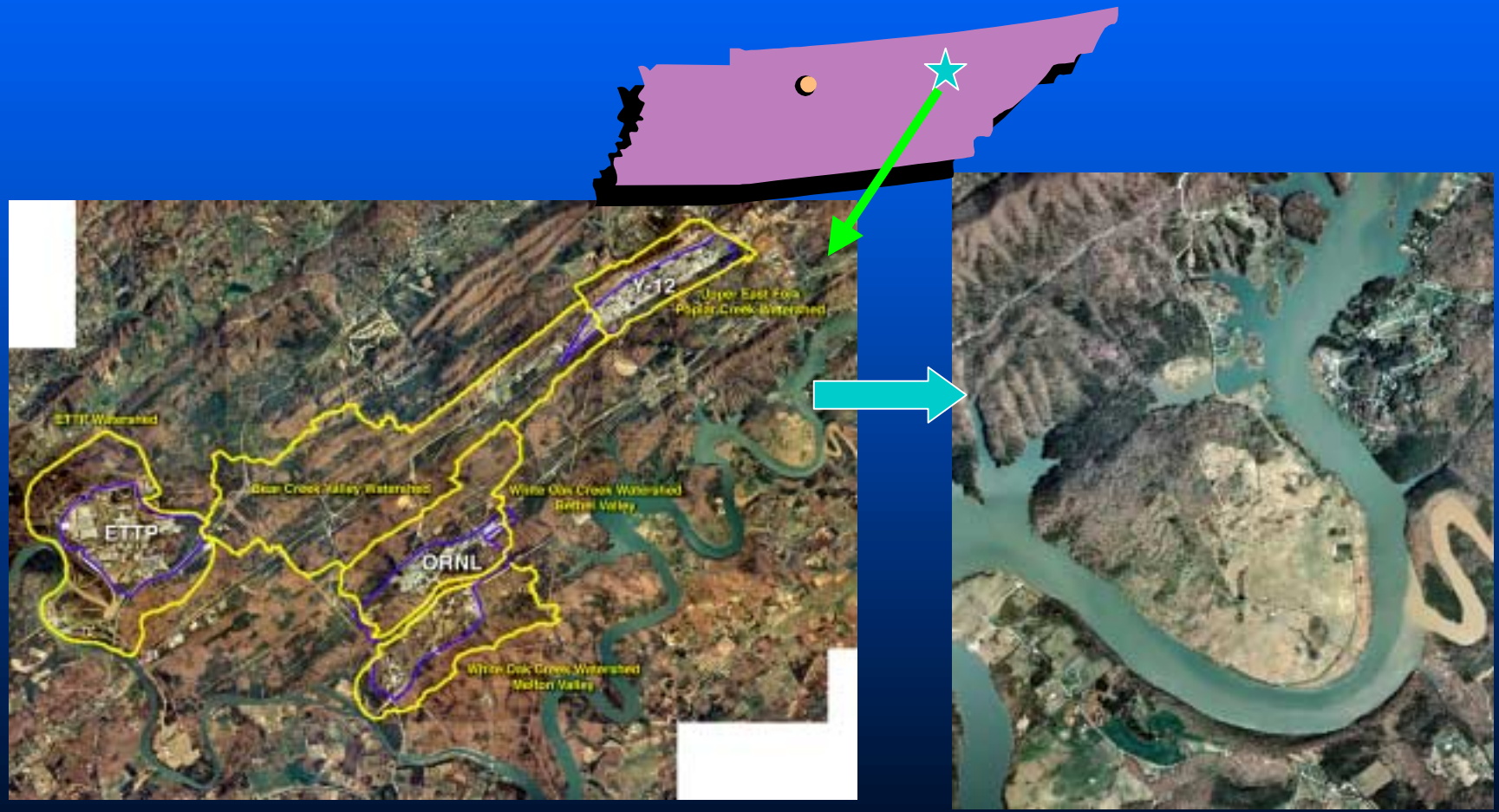
Part of Design Team Meets in Orlando Prior to Developer's Conference

Developers' Conference Orlando, March '99

Field Sample Acquisition

Sort, Process, Homogenize, Randomize, and Label 2000 Samples

Verification Site Location: East End of Oak Ridge Reservation



Actual Verification Test Site

Freels Bend Cabin Area

Developers Receive Site-Specific Safety Training Prior to Start of Verification Testing

EPA and ORNL Conduct QA Audits During the Verification Testing

FAST 2000
Research International

- Continuous flow immunosensor developed by Naval Research Laboratory and licensed to RI.
- Antibodies for target analyte are immobilized within membrane.
- Molecules similar to target are labeled with a fluorophore (Cyanine-based dye).
- Natural water contaminated with target analyte passes through membrane.
- Target displaces fluorophore labeled molecule to complex with antibody.
- Fluorescence response proportional to target analyte concentration.

Sample Preparation
FAST 2000
Research International

- Add 40 µL 0.5 M sodium phosphate/0.5% Tween 20 (surfactant) and 50 µL of ethanol to 1.9 mL of water sample.

- Inject 150 µL into system.

GC/IONSCAN
Barringer Instruments

- Two modes of operation: IMS or GC/IMS (gas chromatography/ion mobility spectrometry).
- In IMS, ions are generated via atmospheric pressure chemical ionization.
- Drift through buffer gas under influence of electric field. Rate of drift dependent on electrical and physical properties of ions.
- GC upstream used for prior separation of complex mixtures if necessary.

Sample Preparation
GC/IONSCAN
Barringer Instruments

- **Soil Sample Preparation**
  - Extract 2 g of soil with 10 mL of acetone for 2 – 3 min.
  - Dilute by 10x or 100x.
- **Water Sample Preparation**
  - Add 2 mL of sample to 1 g of sodium sulfate.
  - Add 1 mL of acetone to mixture, and extract.

Technology Performance Evaluated On:

- Precision
  - *How much scatter in responses to replicate samples imbedded in the random design?*
- Accuracy
  - *How close to the right answer? Evaluated using PE samples (spiked matrices).*
- Comparability
  - *How close to the fixed laboratory value on the same sample?*
- False Positive/False Negative rate
  - *Getting a "hit" when nothing is there, or missing a response when something is there*

Technology Performance Evaluated On: *continued*

- Completeness
  - *Can the technology analyze all the samples provided?*
- Ease of Use
  - *Subjective analysis*
- Sample Throughput
  - *Approximate number of samples per person per day*
- Cost
  - *Comparison with fixed lab analysis*

Reference Lab Method: SW 846 No. 8330

- Soil: Extract 2 g in acetonitrile for 16 hr. An aliquot is combined with calcium chloride to precipitate suspended solids.
- Water: Combine 400 mL sample with sodium chloride and acetonitrile. Separate and volume reduce organic layer to 2 mL. Mix with 2 ml water.
- Analyze via HPLC with UV detection on C-18 reverse-phase column. Confirm on secondary cyano column.

Sample Matrices: Soil

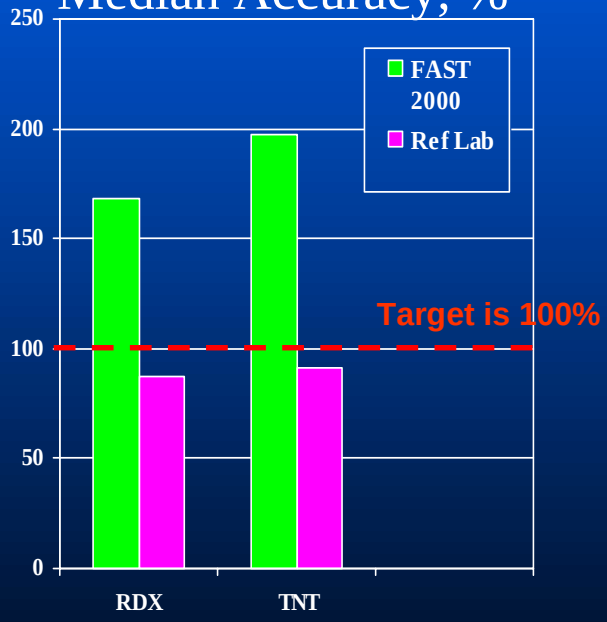
- 108 individual samples
  - 64 naturally contaminated from Ft. Ord, Iowa, Louisiana, Milan, and Volunteer.
  - 24 spiked top soils obtained from ERA, Arvada, CO
  - 20 blank soils from Monroe County, TN
- Primary contaminants: TNT, HMX, DNT, RDX
  - Secondary contaminants: Amino-DNT's and tri-nitrobenzenes.
  - Concentrations: 0 – 90,000 mg/kg

Sample Matrices: Water

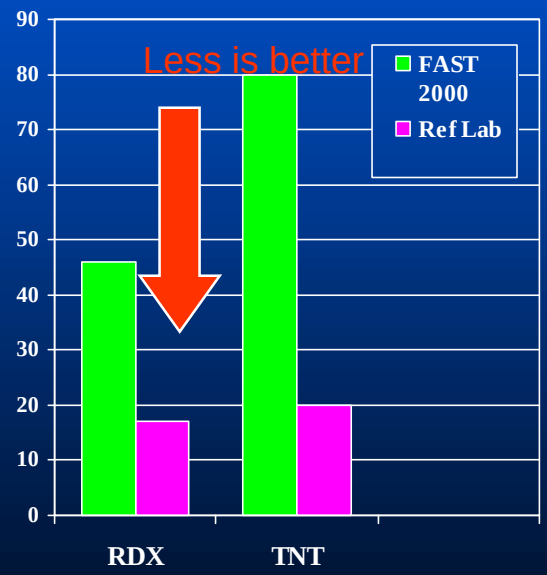
- 176 individual waters samples
  - 132 naturally contaminated from Louisiana, Milan, Umatilla, and Volunteer
  - 24 spiked distilled water samples
  - 20 blank distilled water samples
- Primary contaminants: TNT, RDX, HMX, DNT
  - Secondary contaminants: TNB, Amino-DNT, nitrotoluenes
  - Concentrations: 0 – 25,000 µg/L

Fast 2000 Performance

Median Accuracy, %

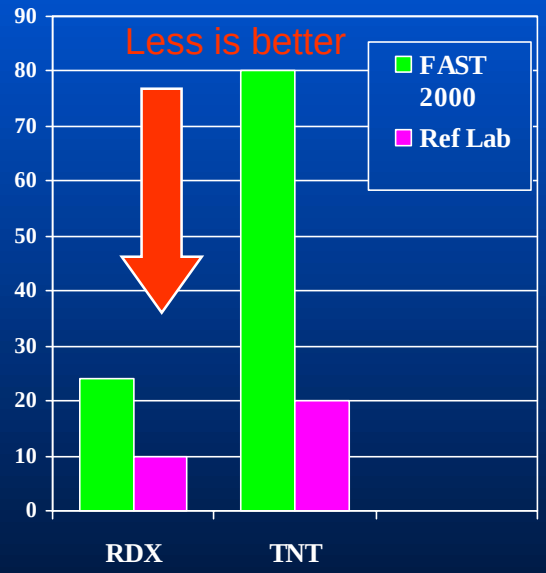


Median Precision, RSD %



Fast 2000 Performance

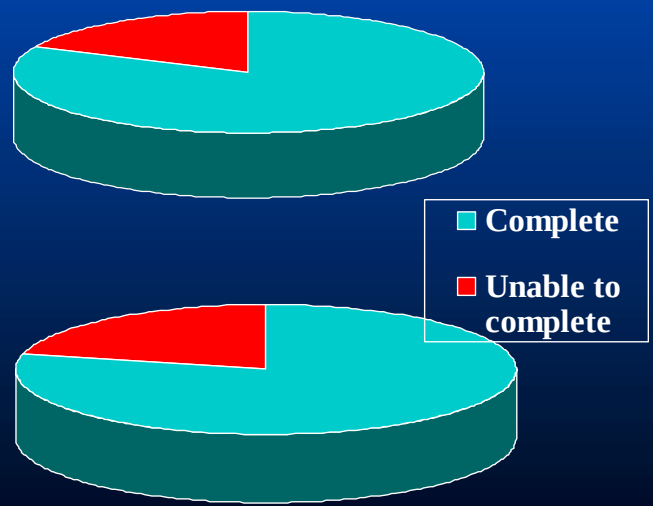
% False Positive Results on Blanks



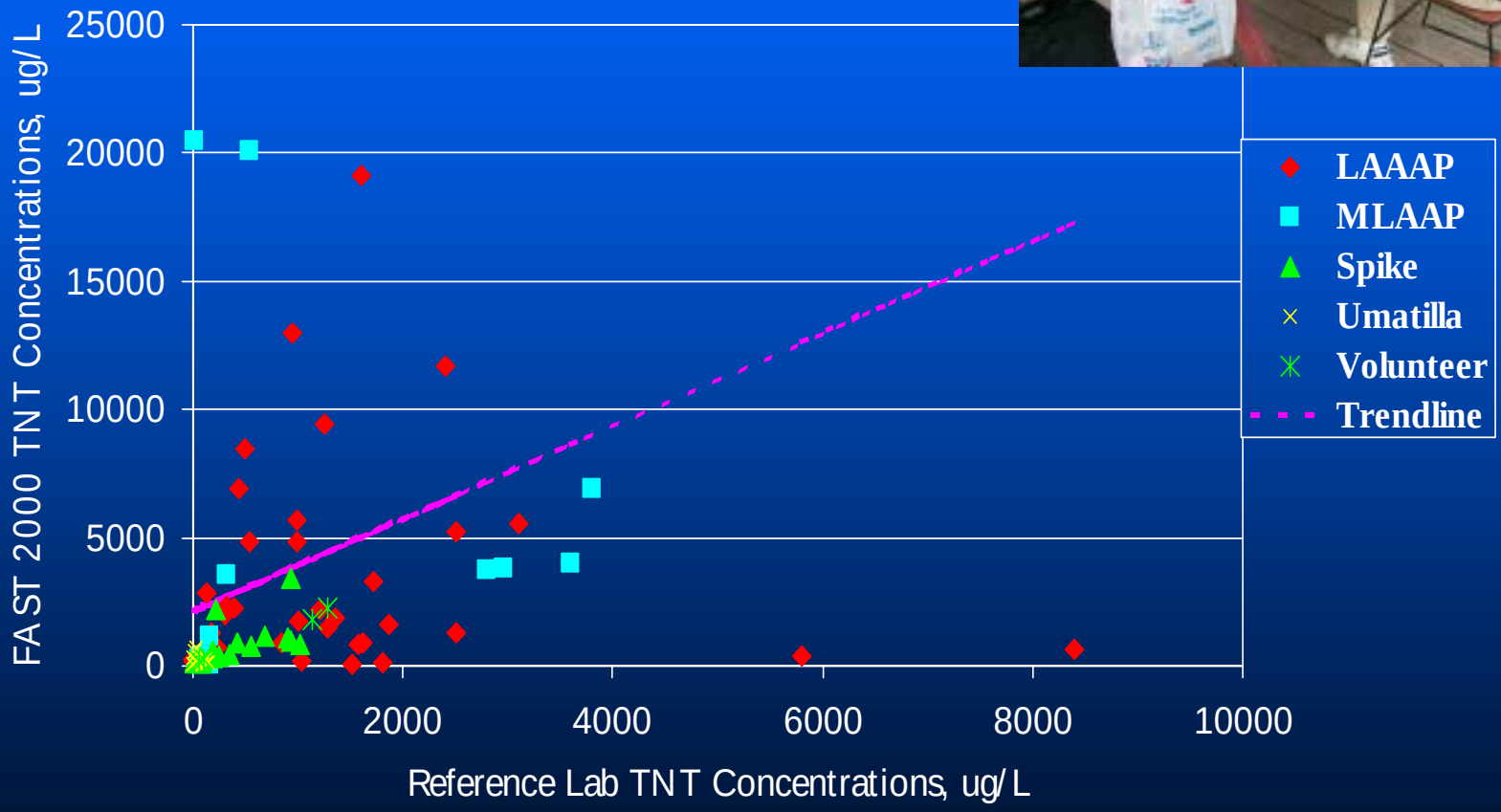
Completeness

RDX

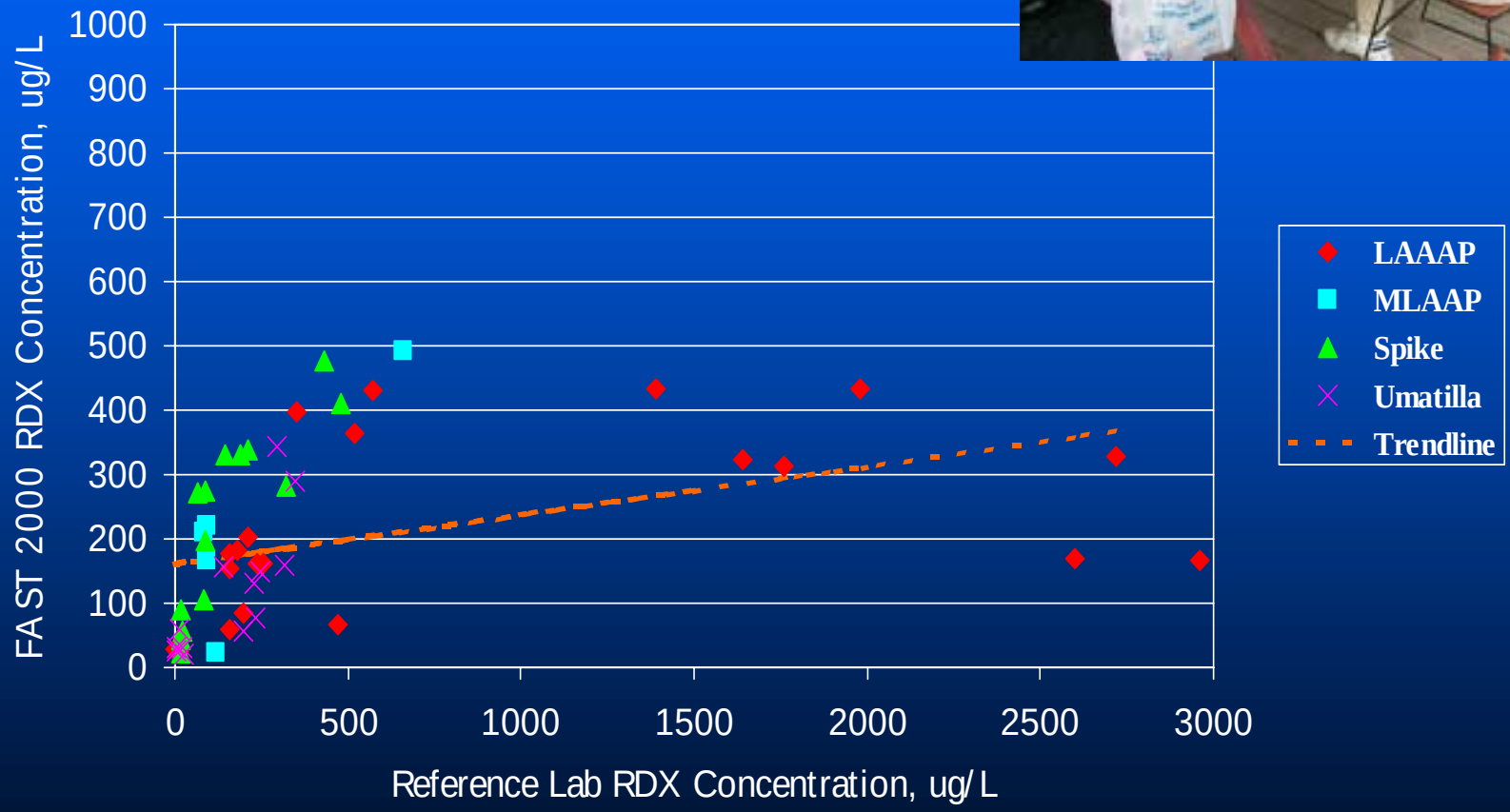
TNT



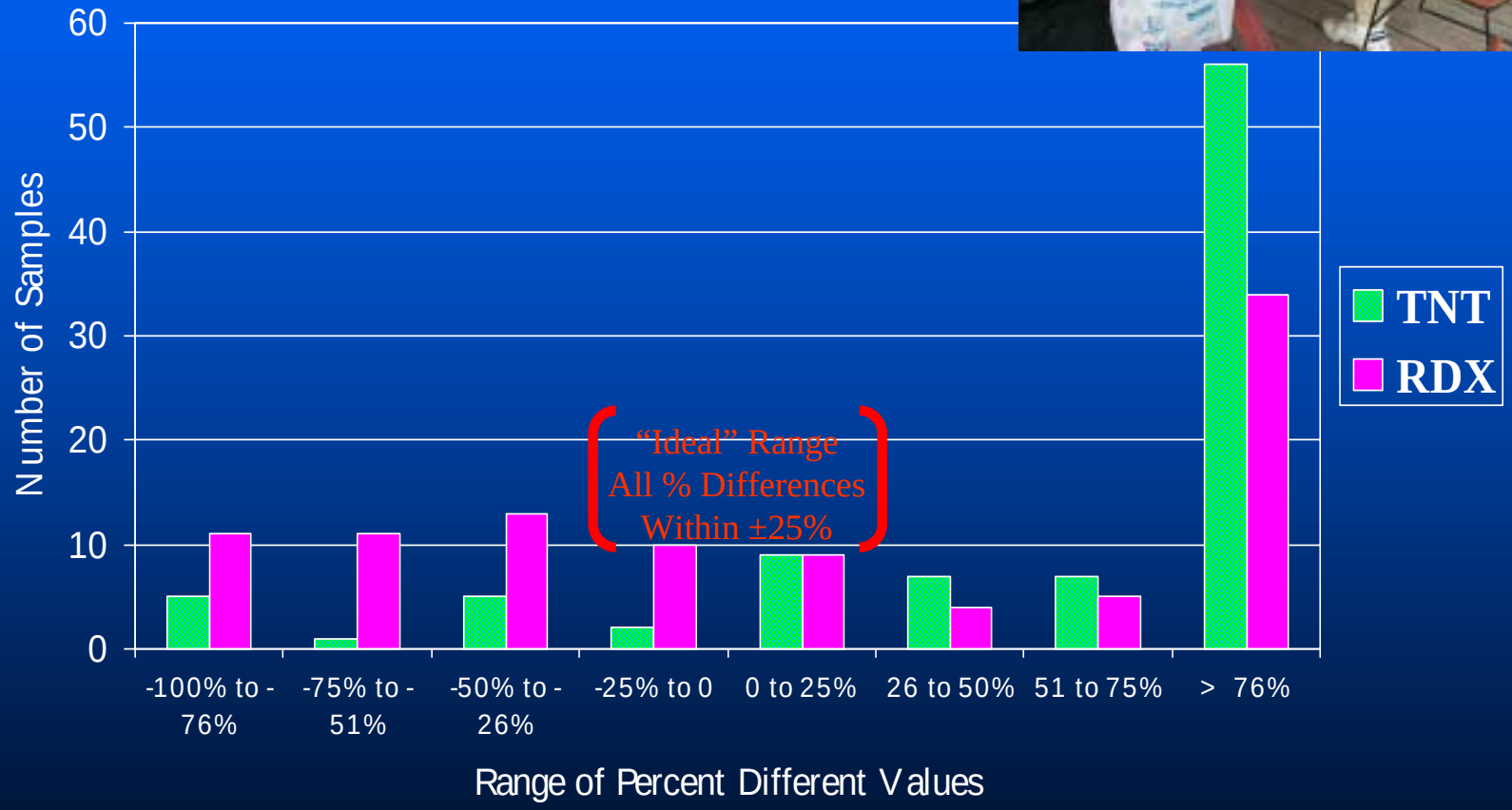
FAST 2000 Comparability for TNT



FAST 2000 Comparability for RDX



FAST 2000 Comparability: Percent Difference



FAST 2000: Additional Evaluation Parameters

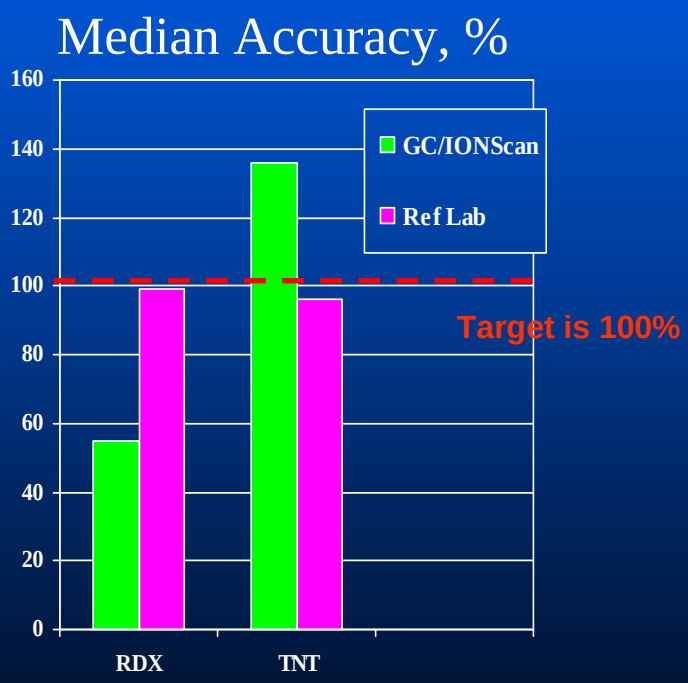
- Sample throughput
  - Three samples per hour for 3 operators. Separate instruments for RDX and TNT.
- Ease of use
  - One day training required, analytical chemical technician level.
- Cost Analysis
  - More detailed than can report here, but instrument is ca. $24K, and reagents run $43/sample.

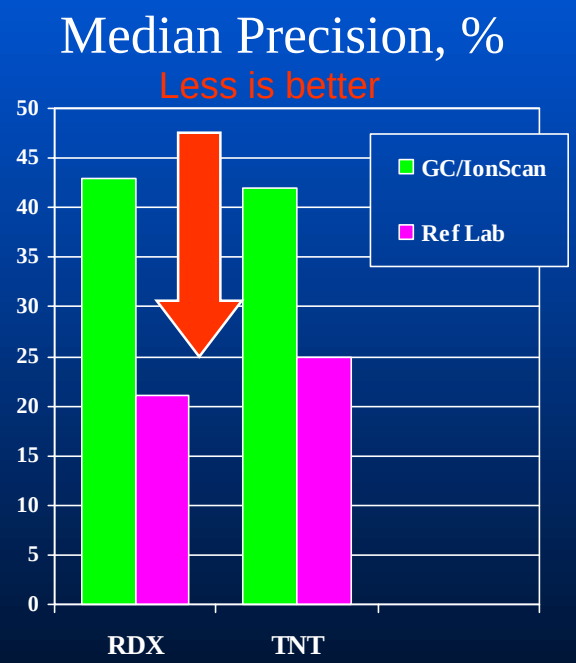
Summary: FAST 2000 Performance

- Small unit (3 lbs) + notebook computer. Less than 1 hour required for start-up.
- Apparent sample throughput hindered by self-imposed requirement to analyze each sample twice and bracket with standards.
- Very minimal sample prep for water.
- For RDX, biased high (but matrix dependent); Imprecise.
- For TNT, biased high, imprecise.

GC/IONSCAN Performance

Soil

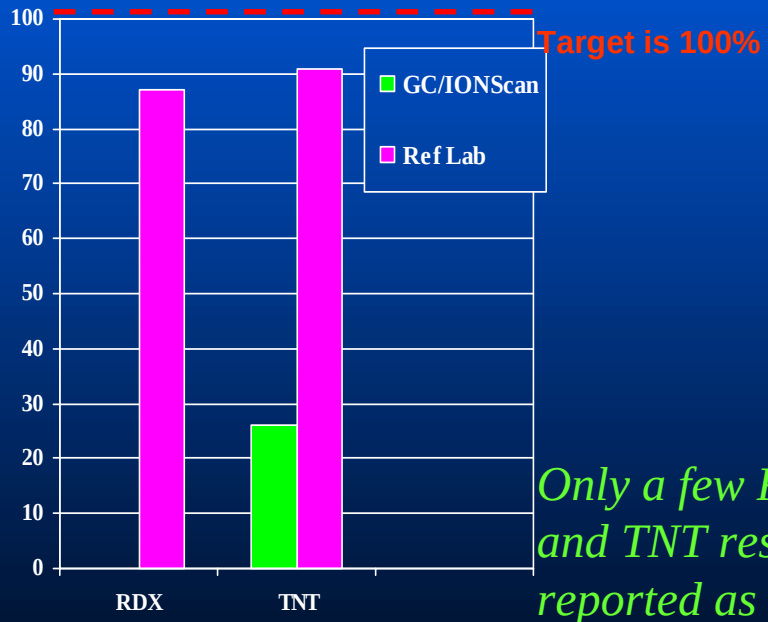




GC/IONSCAN Performance

Water

Median Accuracy, %

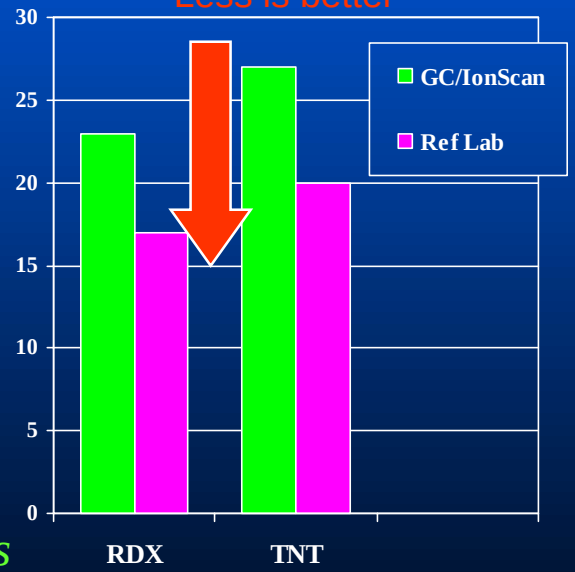


Target is 100%

Only a few RDX and TNT results reported as detects

Median Precision, %

Less is better



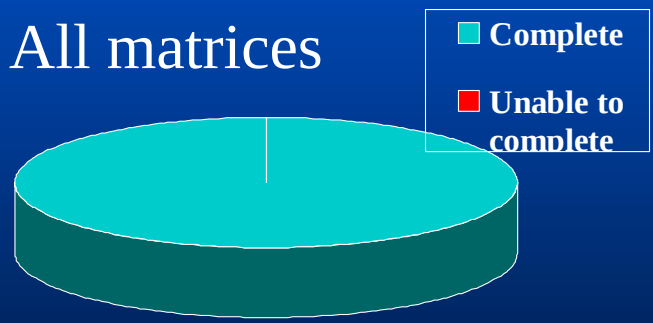
GC/IONSCAN Performance

% False Positive Results on Soil Blanks

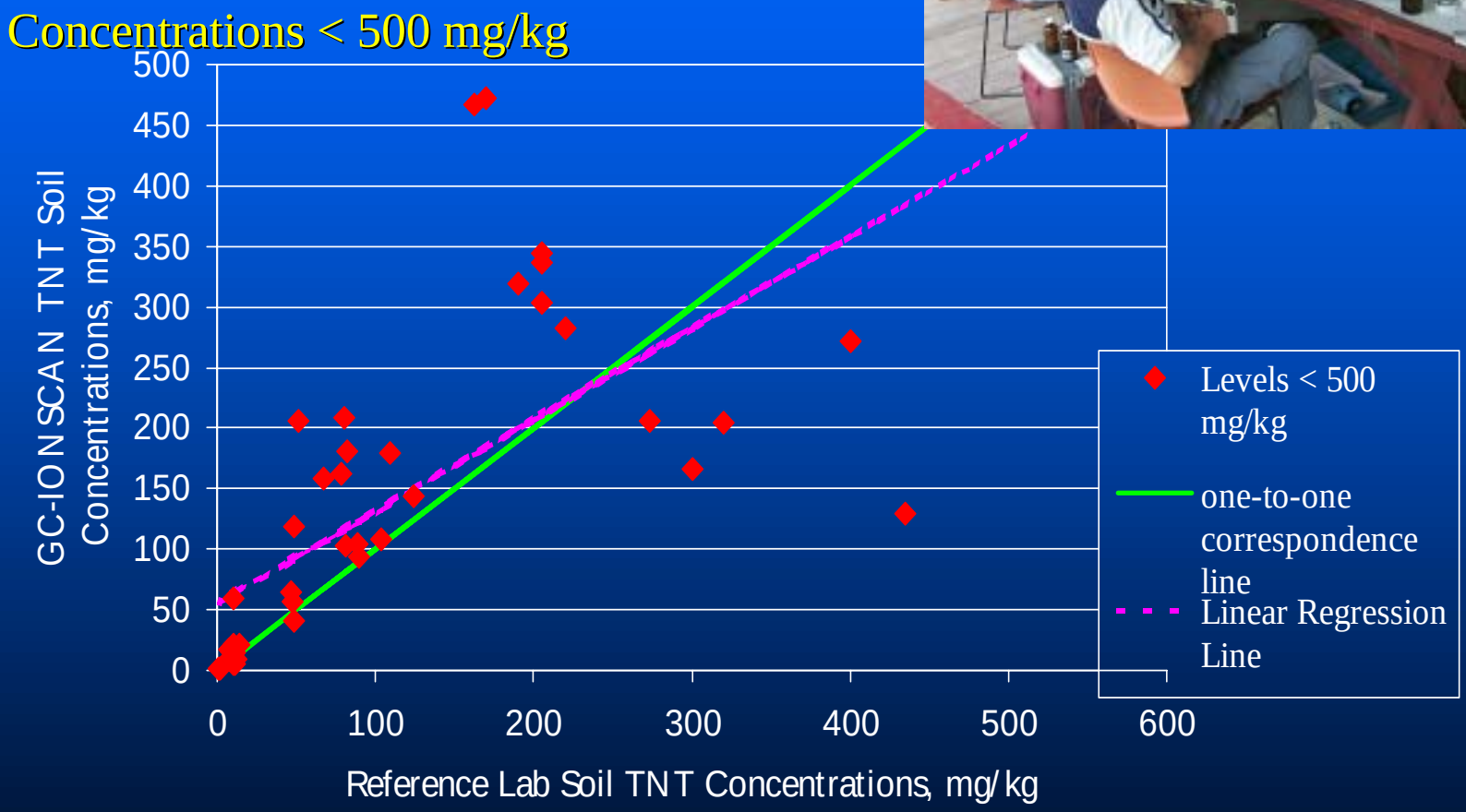
Values of zero not displayed

Completeness

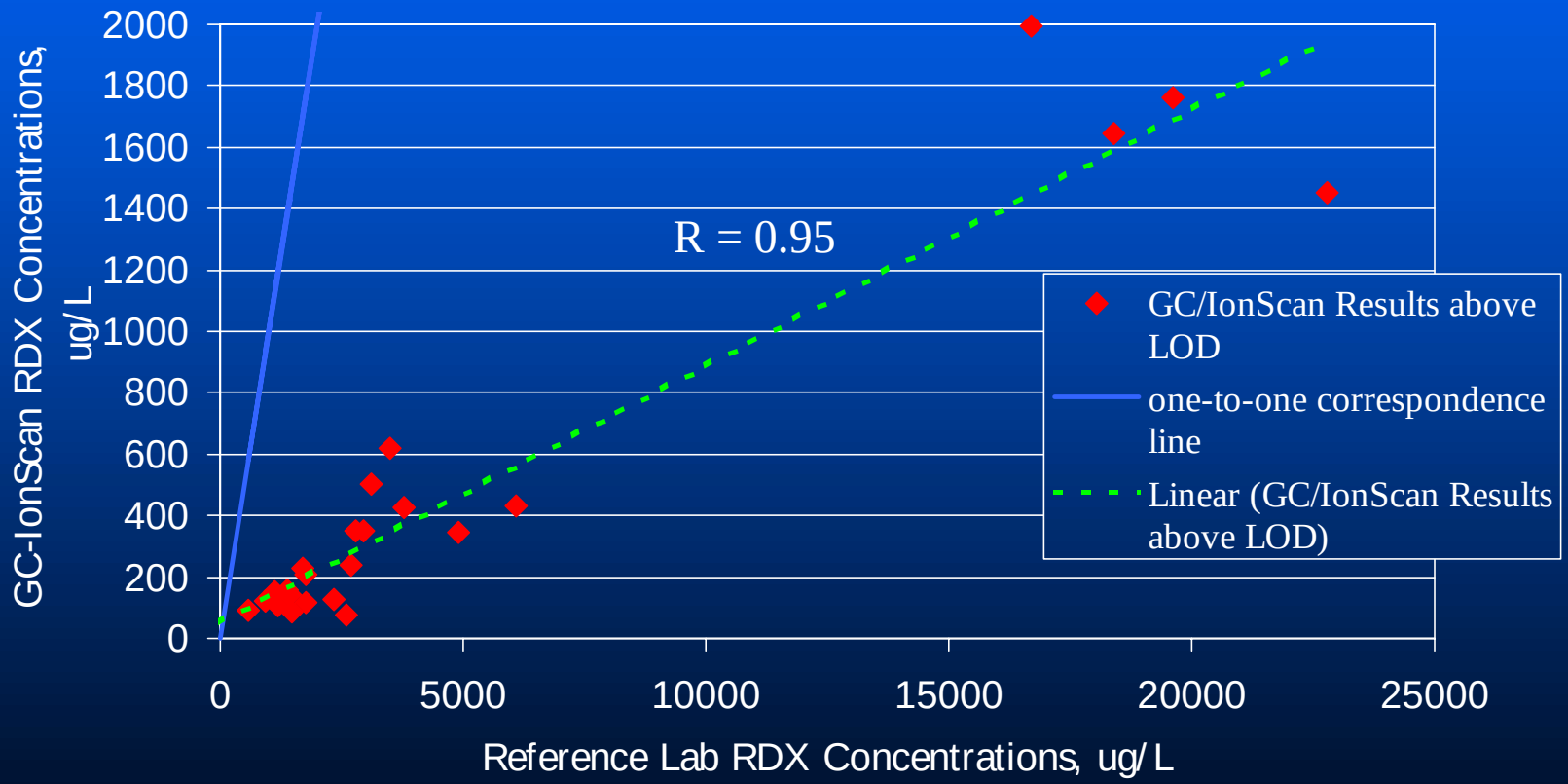
All matrices



Comparability Soil TNT Results

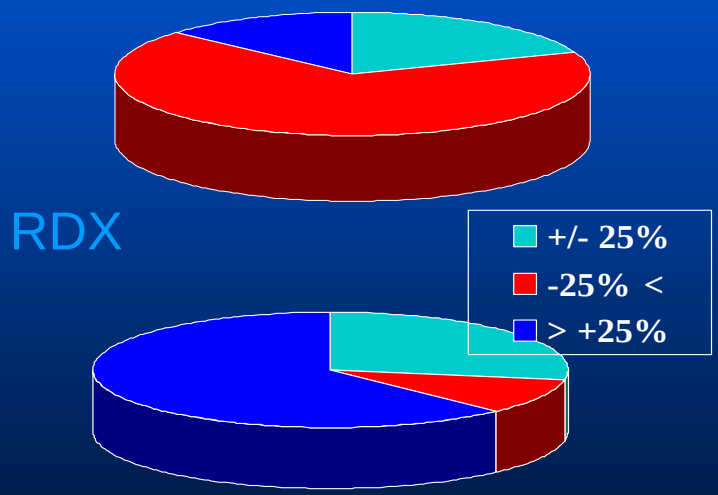


Comparability GC/IONSCAN RDX in Water

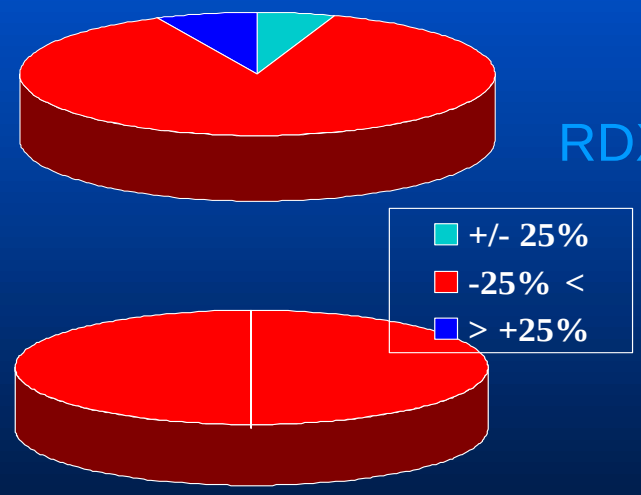


GC/IONSCAN Comparability: Percent Difference

Soil



Water



"Ideal" percent difference is +/- 25%

GC/IONSCAN: Additional Evaluation Parameters

- Sample throughput
  - Two person team: 3 samples/hr for soil, and 8 samples per hour for water.
- Ease of use
  - Two days training required, and some prior chromatographic experience. Analytical chemical technician level.
- Cost Analysis
  - More detailed than can report here, but instrument is ca. $60K and reagents are $1 per sample.

Summary: GC/IONSCAN Performance

- Easily transported, rugged, easy to fire up and take down.
- Rapid switching between screening and quantification modes.
- Screen required ~12 seconds, quant: a few minutes.
- For soil, biased low for RDX, biased high for TNT; Imprecise
- For water, biased low for both analytes; Precise
- Improvements in up-front sample processing likely to result in significant performance improvements.

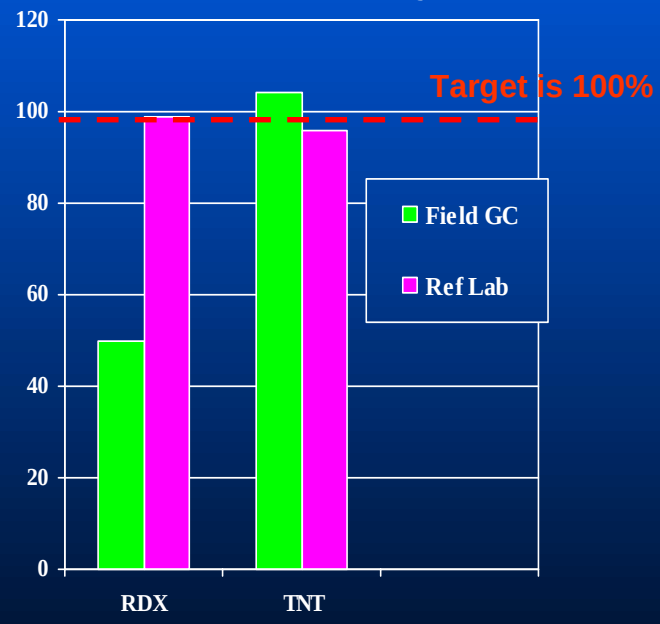
For a Bit of Perspective ……

CRREL In-Field GC Analysis of TNT (& RDX) in Soil

- Extract 20 grams of soil with 100 mL of acetone and shake for 2 minutes. Pass through 0.5 µm filter.
- Inject aliquot into a field “transportable” “gasless” GC (SRI 8610C) with a thermionic detector.
- Separation on 10 m x 0.53 mm i.d. 3 µm DB-1.

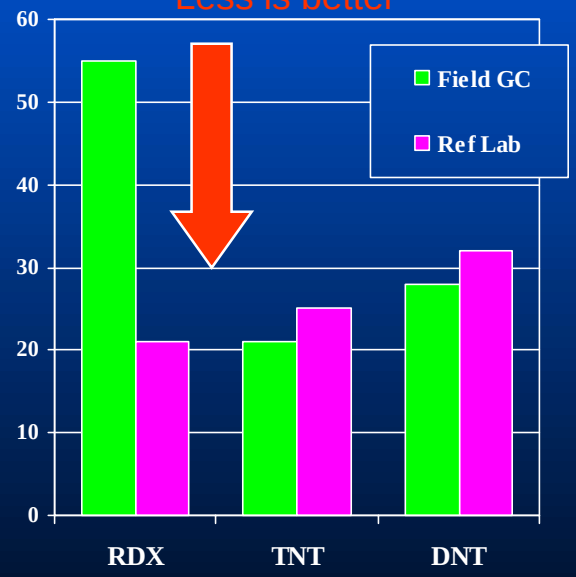
CRREL Field GC Performance

Median Accuracy, %



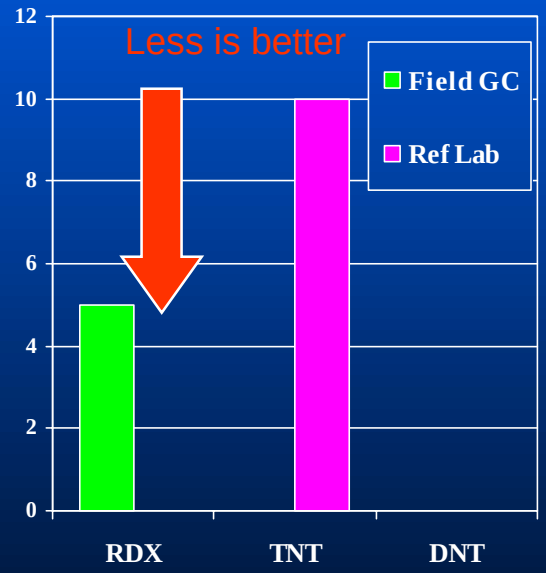
Median Precision, RSD %

Less is better

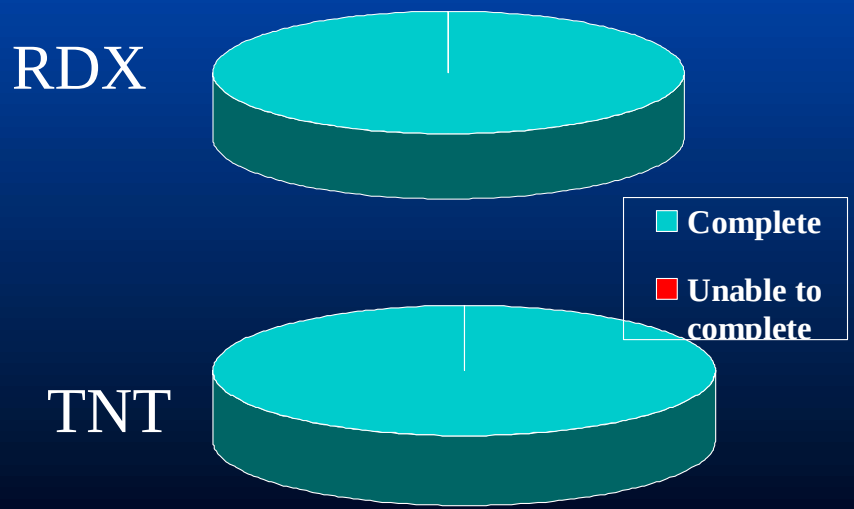


CRREL Field GC Performance

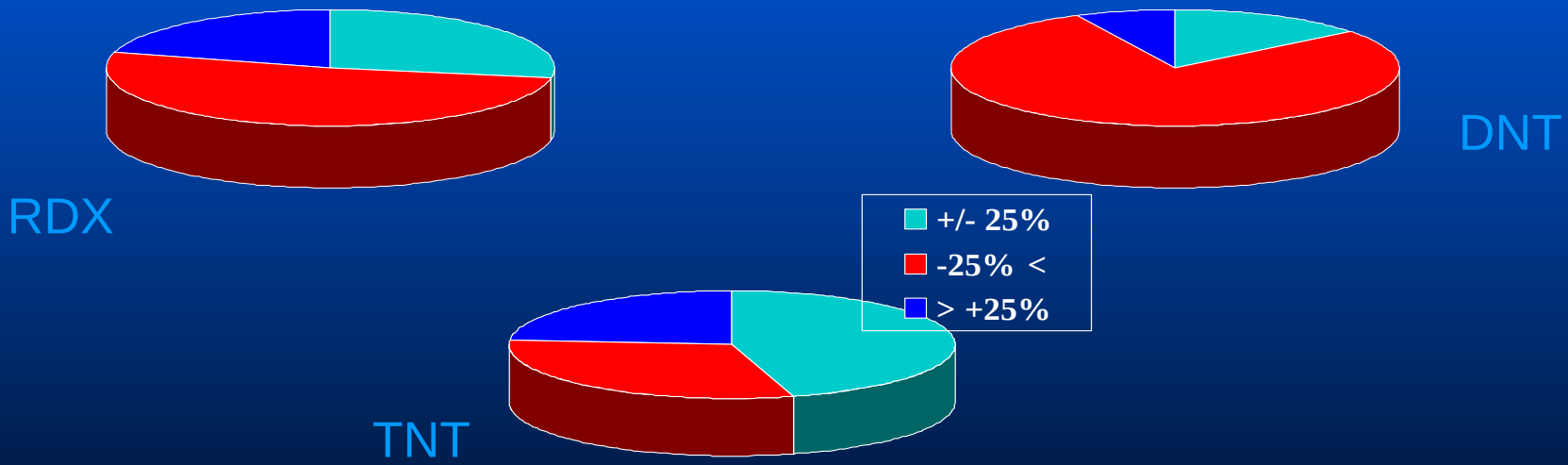
% False Positive Results on Blanks



Completeness

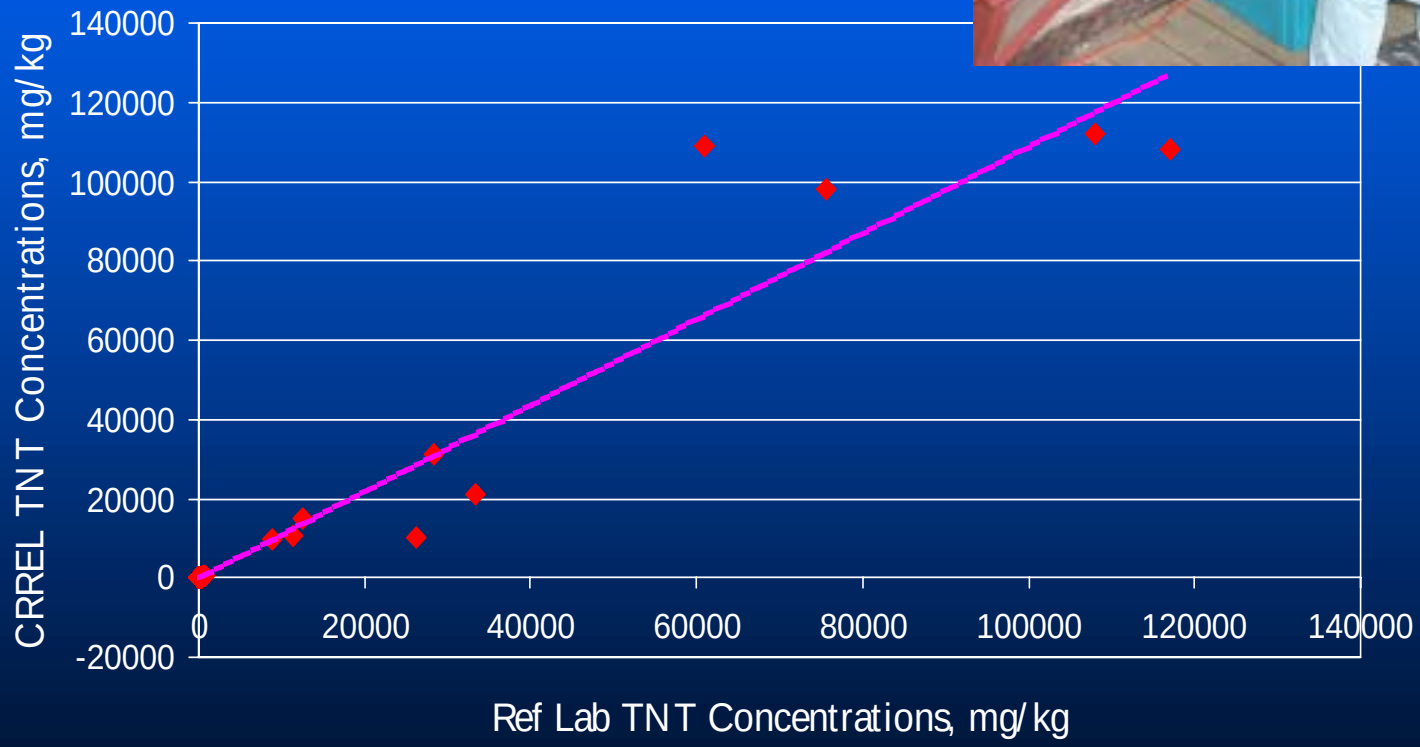


CRREL Field GC Comparability: Percent Difference for Soil

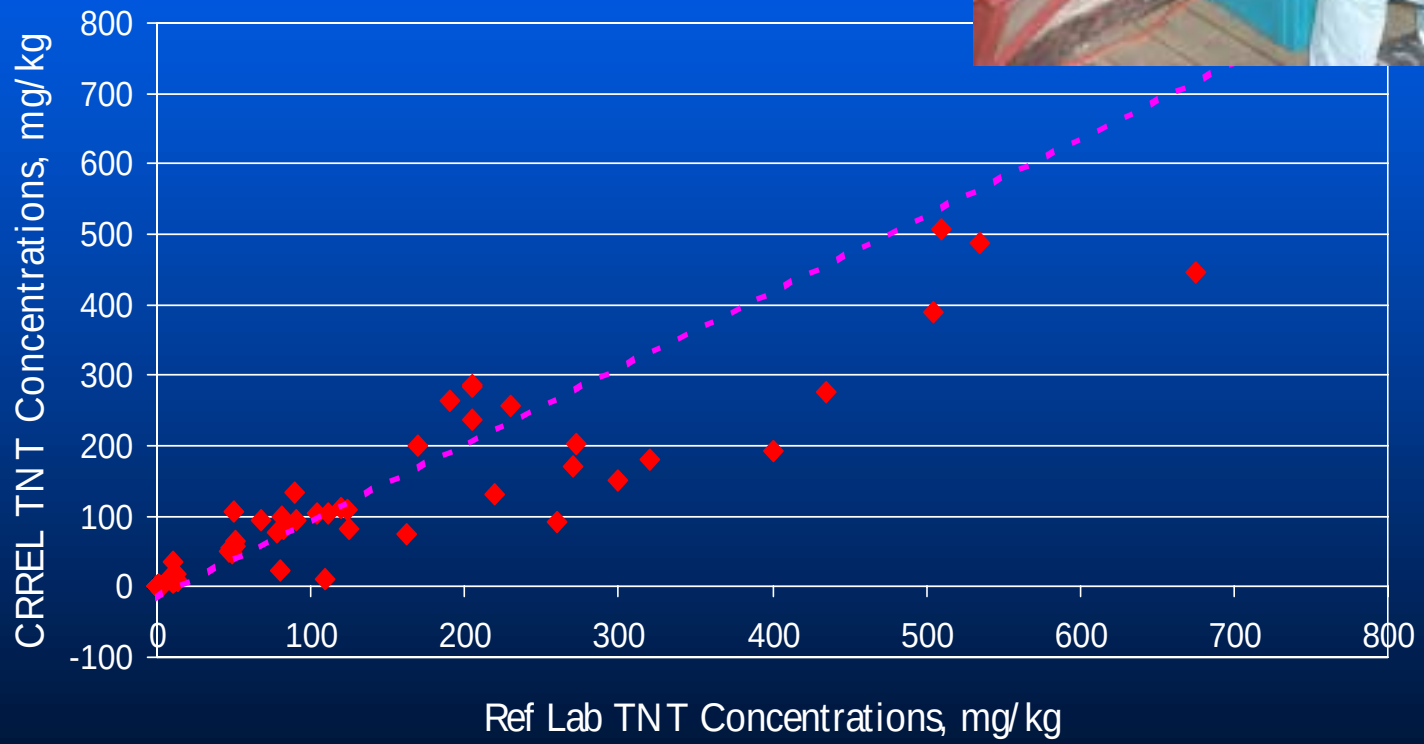


"Ideal" percent difference is +/- 25%

CRREL Field GC Comparability: All Soil Data



CRREL Field GC Comparability: **Soil Data <800 mg/kg**



CRREL Field GC Performance "Observations"

- Because of detector specificity, "hardware store" grade acetone can be used, eliminating requirement to ship solvents to field.
- 100 mL waste per sample likely to be reduced.
- SRI GC costs $6K
- For TNT in soil, accuracy, precision, false positive and completeness rate comparable to reference lab.
- RDX analysis hindered by lack of heated injector port. Is currently rectified.

Overall Conclusions

- Conducting a true performance verification can be a complex and time-consuming task.
- ETV Program does not do head to head comparisons. Listeners can best decide which “tools” they should have in their toolbox.
- Reports will soon be available at www.epa.gov/etv and www.ornl.gov/etv.