Laboratory Support for Multi-Increment Sampling

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USACE Fort Worth and Sacramento Districts

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Objective of MIS Process

- Improve representativeness of field samples
- Improve representativeness of lab subsamples

Better estimate of the average concentration within an area of concern

Chasing Sources of Uncertainty

- Instrumental analysis
- Sample preparation
- Laboratory sub-sampling
- Field sample collection

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Smallest Source of Uncertainty

Laboratory instrumental analysis

Yet, this is the step that has historically been subject to more than 80% of quality control effort

Heterogeneity of Explosives Contamination in Soil

Results within 4' circle range from
0.14 to 43,000 ug/kg

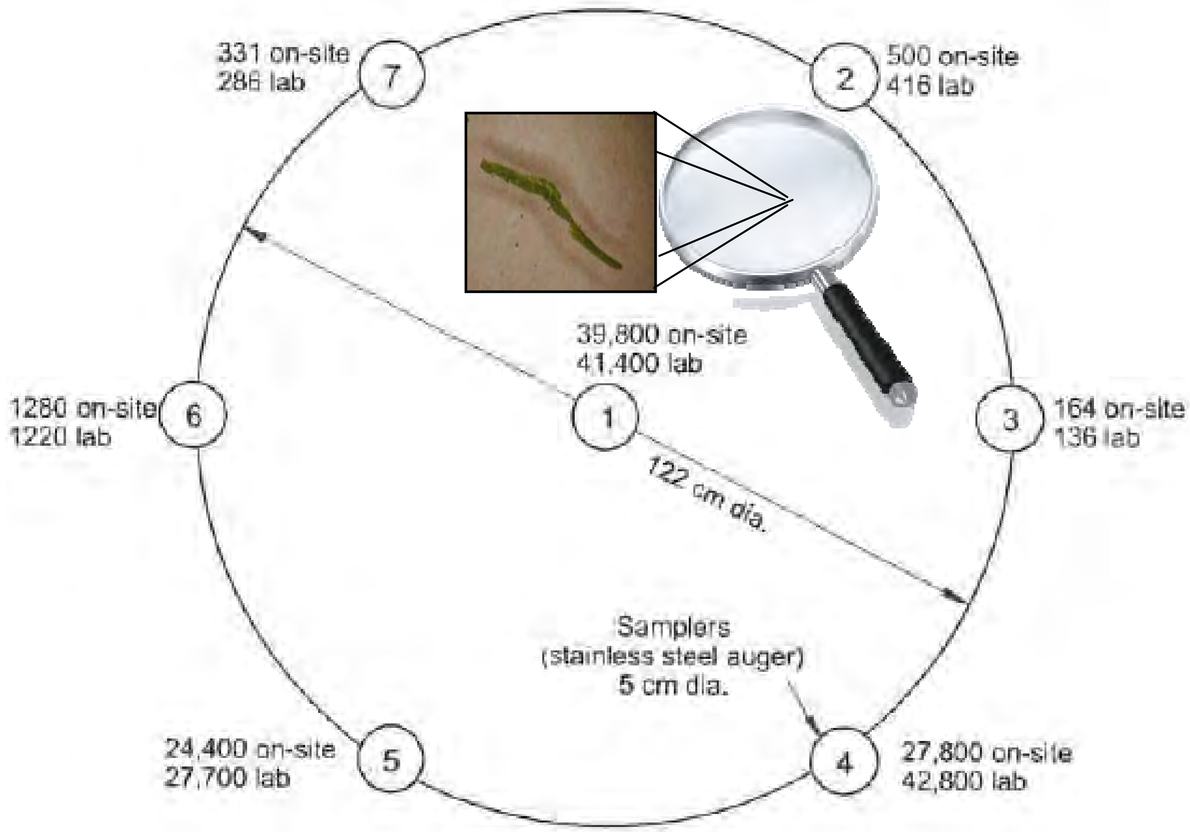
14 results

Mean = 14,900 ug/kg

RSD = 120%

Only 1.2% of the total area sampled

per Tom Jenkins, 1996



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MIS Sample Collection Technique Old News for Some

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**SAMPLE REPRESENTATIVENESS:
A NECESSARY ELEMENT IN EXPLOSIVES SITE CHARACTERIZATION**

T.F. Jenkins*, C.L. Grant, G.S. Brar, P.G. Thorne and P.W. Schumacher,
U.S. Army Cold Regions Research and Engineering Laboratory
Hanover, New Hampshire 03755;
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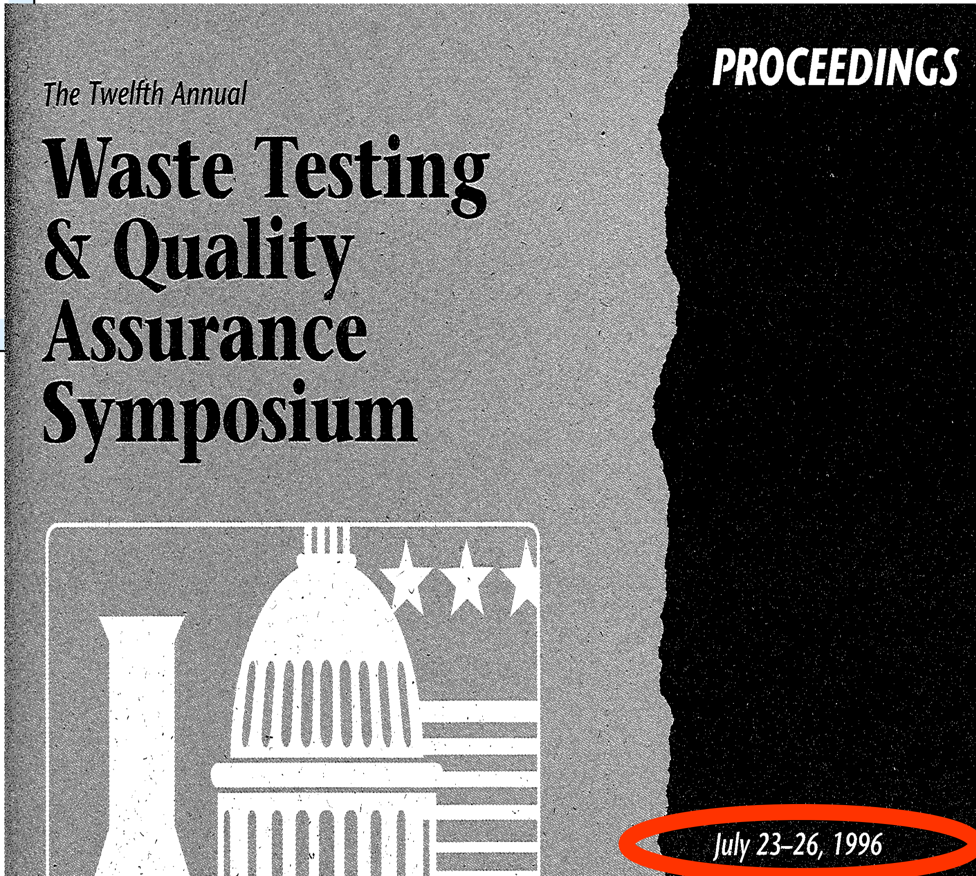
Science and Technology Corporation, Hanover, New Hampshire 03755-1290

ABSTRACT

Explosives-contaminated sites are generally characterized by collecting discrete grab samples of surface soil and shipping them to off-site laboratories for analysis. Decisions



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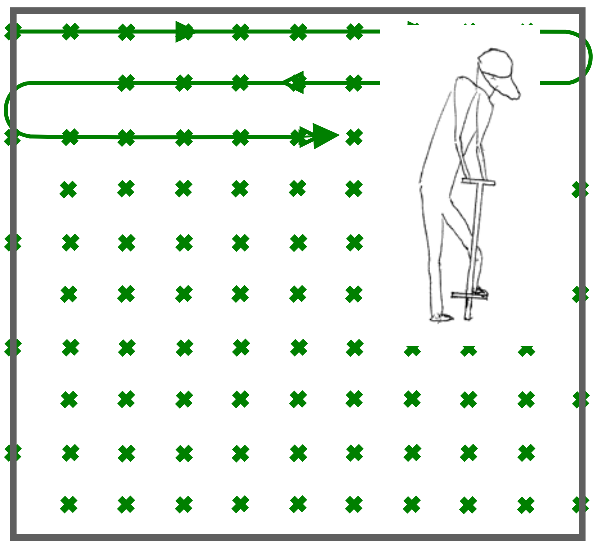
Largest Source of Uncertainty Is Field Sampling Error

MIS Solution:

Multi-incremental Sampling

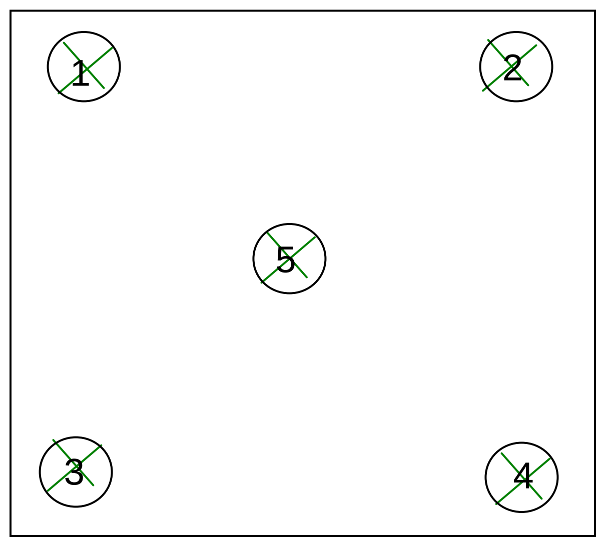


One sample comprised of many increments taken throughout area of concern

rather than

versus

Discrete sampling



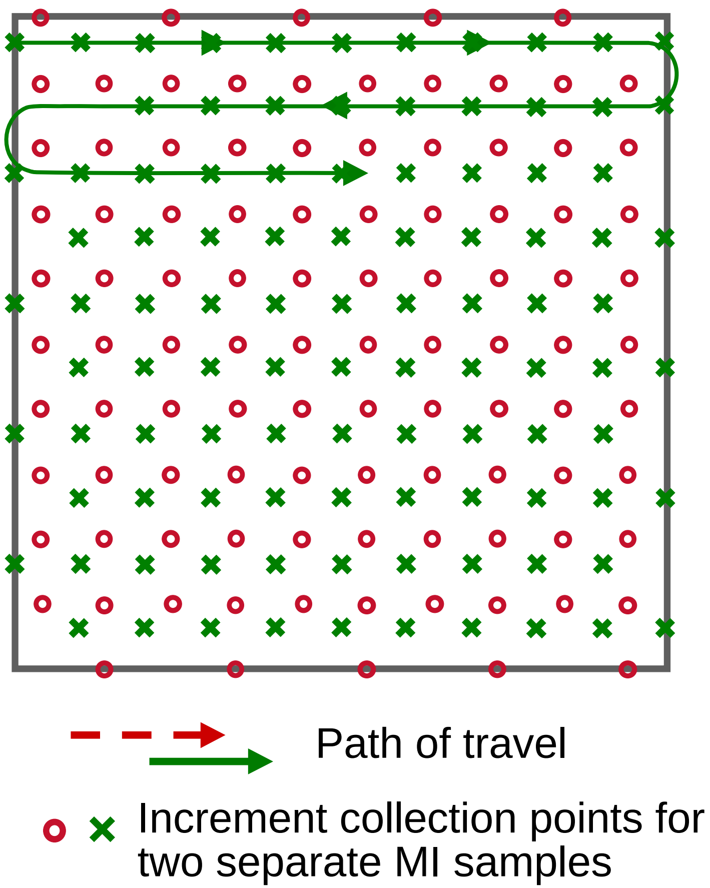
A few samples taken from non-random spots and analyzed separately

Entire Sample Delivered to Lab

- Field crew should not mix samples in a bowl and prepare splits

Picture from USACE-Alan Hewitt

versus



Produces Large Samples

Picture from USACE-Alan Hewitt

Lab Processes Entire Sample

- Lab cannot subsample off the top or discard sample

Process for explosive residues by EPA 8330B follows

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Air Dry

Sieve to Remove > 2 mm

Picture from USACE-Alan Hewitt

Puck Mill Grind

or

Ring and Puck

Puck & bowl

Shaker apparatus

Multi-Increment Subsample

or

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Larger Portion Used for Explosives Analysis

- 8330A used 2 grams
- 8330B uses 10 grams

Smaller particle size + Larger portion analyzed → Better precision

How Much Difference Does It Make?

- Firing range samples by 8330A often produce results for replicates with RSD > 100%
- 8330B, with appropriate
  1. Definition of decision unit
  2. MIS technique in field
  3. MIS technique in lab

↓

RSD < 10%

MIS Formalized in 8330B

METHOD 8330B

NITROAROMATICS, NITRAMINES, AND NITRATE ESTERS BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

SW-846 is not intended to be a
procedures are written based on the
formally trained in at least the basic
technology.

In addition, SW-846 methods,
of method-defined parameters, are i
information on how to perform an an
as a basic starting point for generati
either for its own general use or for a
included in this method are for guida
not be used as absolute QC accepta

1.0 SCOPE AND APPLICATION

1.1 This method is intende
residues by high performance liquid
detector. The following RCRA comp
determined by this method:

June 2008

DoD Environmental Data Quality Workgroup

Guide for Implementing EPA SW-846 Method 8330B

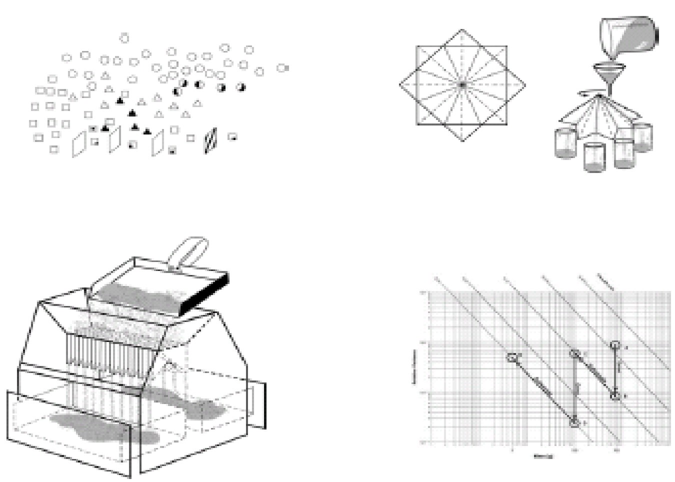
Introduction:

In November of 2006 the Environmental Protection Agency (EPA) published method 8330B.[1] The method provides instruction for the trace analysis of explosives and propellant residues by high performance liquid chromatography (HPLC). The method includes an appendix (A), which describes sampling methodologies for collecting and processing representative samples for analysis.

EPA General Subsampling Guidance

Guidance for Obtaining Representative Laboratory Analytical Subsamples from Particulate Laboratory Samples

Nov 2003



United States Environmental Protection Agency

Solid Waste and Emergency Response (5305W)

EPA530-R-99-015
July 1999
www.epa.gov/osw

Office of Solid Waste

EPA

RCRA Waste Sampling Draft Technical Guidance SW-846 Chapter Nine

Planning, Implementation, and Assessment

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One Good Idea Grows

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And Spreads Rapidly

TAL Metals

Cr, Ni, V Hg

Ring & Puck Mill

Mortar & Pestle Ball Mill

Blender Coffee grinder

Sieve #4, #10, #60, #200

Brass SS

Ceramic

Polymer

Organics

VOCs SVOCs

PCBs OCPs

air dry add water

as received

Ball Mill High “G” mixer

Coffee chopper bread mixer

Stainless Steel

Ceramic

Expanded Energetics

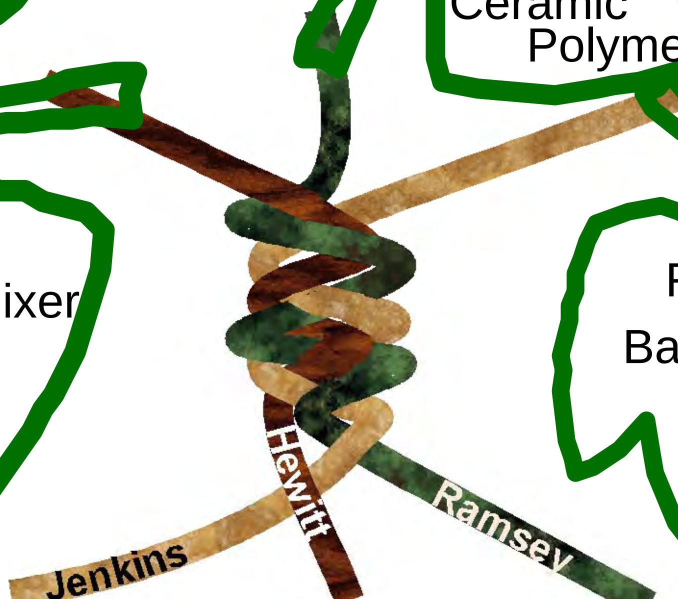
Ring & Puck Mill

Ball Mill

Mortar & Pestle

Stainless Steel

Ceramic



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Working with the Lab

- There is no “one way” to implement MIS
- Many options
- To apply MIS technique successfully
- Work with lab in advance to discuss
    - Project objectives
    - Lab capabilities for bulk sample processing
- Leading to a plan customized to the needs of the project

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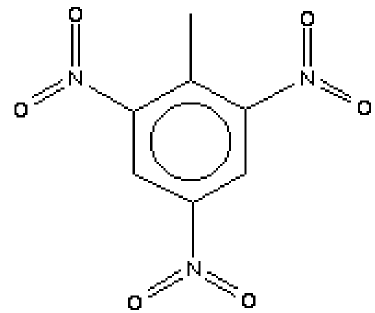
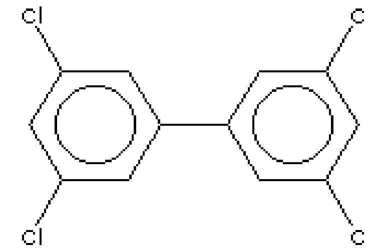
Look close at the options

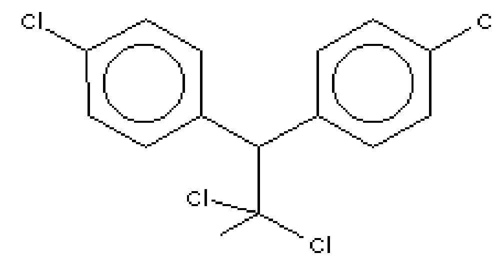
- Analytes
- Sample conditioning
  - ~ Dry - As is
- Sieve (exclude non-sample)
- Grind / disaggregate
- Sieve (max particle size)
- Mixing
  - ~ Dry – Wet - As is
- Sub sample
- Strengths & limitations

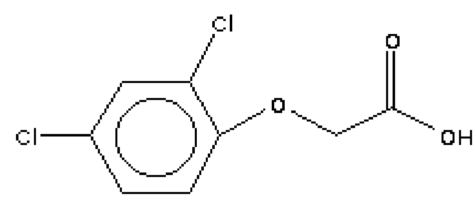
Choose your analytes

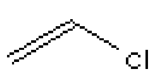


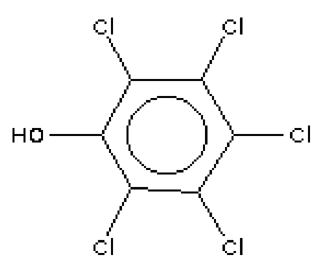


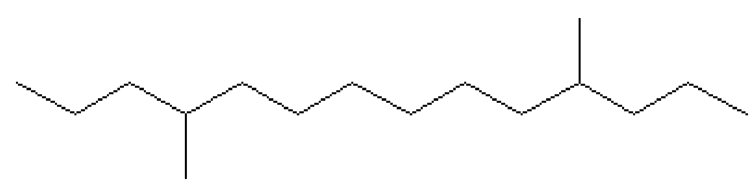
- Energetics
- Metals, Hg
- PCBs
- Organochlorine Pescticides
- Phenoxy acid herbicides
- Petroleum hydrocarbons
- Semivolatile organics
- Volatile organics











Sample – Not sample

- Sample jars often contain non-sample components
  - ~ Decantable water
  - ~ Sticks
  - ~ Leaves
  - ~ Rocks
- Specify particle size to remove

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Modifying moisture content

- Air dry
  - ~ Al foil or paper liner
  - ~ Ventilation hood
  - ~ Strength – easy to crush sample
  - ~ Limitation – volatile analyte loss

- Add water
  - ~ Make paste
  - ~ Strength – retains low boiling analytes
  - ~ Limitation – hinders extraction
- As is
  - ~ Strength – least analyte loss
  - ~ Limitation – hard to mix & grind

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Sieve to separate sample from non-sample

- Disaggregate soil clumps
  - ~ Pestle, hammer
  - ~ Coffee chopper
  - ~ Blender
- Most common sieves
  - ~ #4 (6 mm), #10 (2 mm)
    - Also #1, #30, #36, #100
- Strength – reproducible size exclusion
- Limitation – requires dry sample

To grind or not to grind

- Yes
  - ~ Crystalline particles, fibrous threads
  - ~ Energetics, metals
  - ~ Strengths - facilitates mixing, improves precision, reduces sub-sampling error
- No
  - ~ Volatile, thermally labile, increased “availability”
  - ~ Low boiling PCBs, OCPs, TPHs, SVOCs, metals
  - ~ Strengths - better analyte retention, “accurate” metals risk assessment

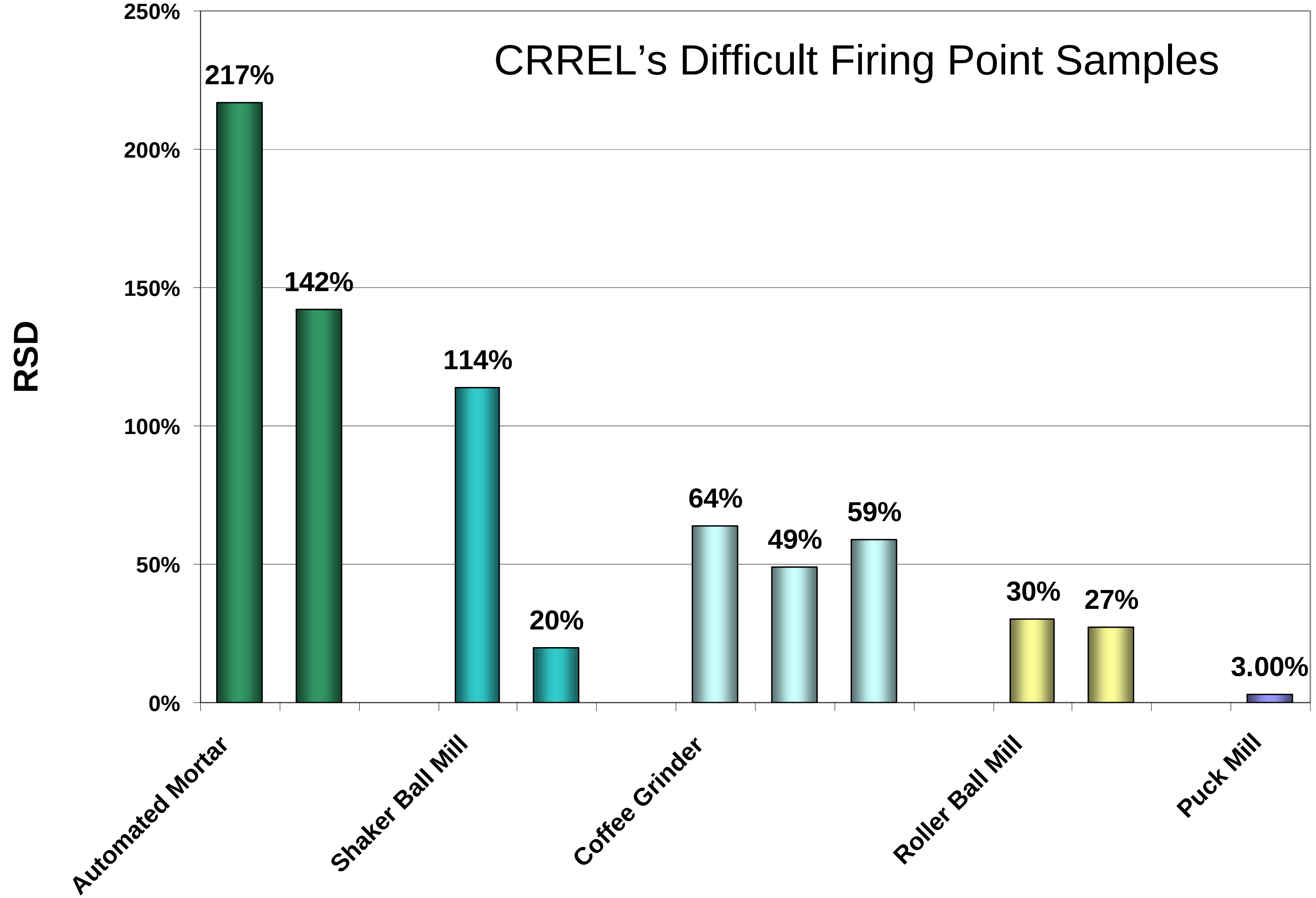
Picture from USACE-Alan Hewitt

How best to grind

- Puck mill or ring and puck mill
  - ~ “stable” energetics
- Ball mill
- Mortar and pestle
- Consider
  - ~ Analytes
  - ~ concentration of interest
  - ~ grinder materials
  - ~ Particle size needed

Picture from USACE-Alan Hewitt

How Much Difference Does It Make



How fine is the grind?

- What is the target particle size?
- How to determine completeness
  - ~ Visual inspection
  - ~ Pinch of “flour”
  - ~ Sieve #200 (~75 um)

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Mixing to reduce heterogeneity

- Tumble in container
- Benchtop bulldozers
- “Bread dough” mixer
- Grinders
- High “G” mixer

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Sub-sampling Options

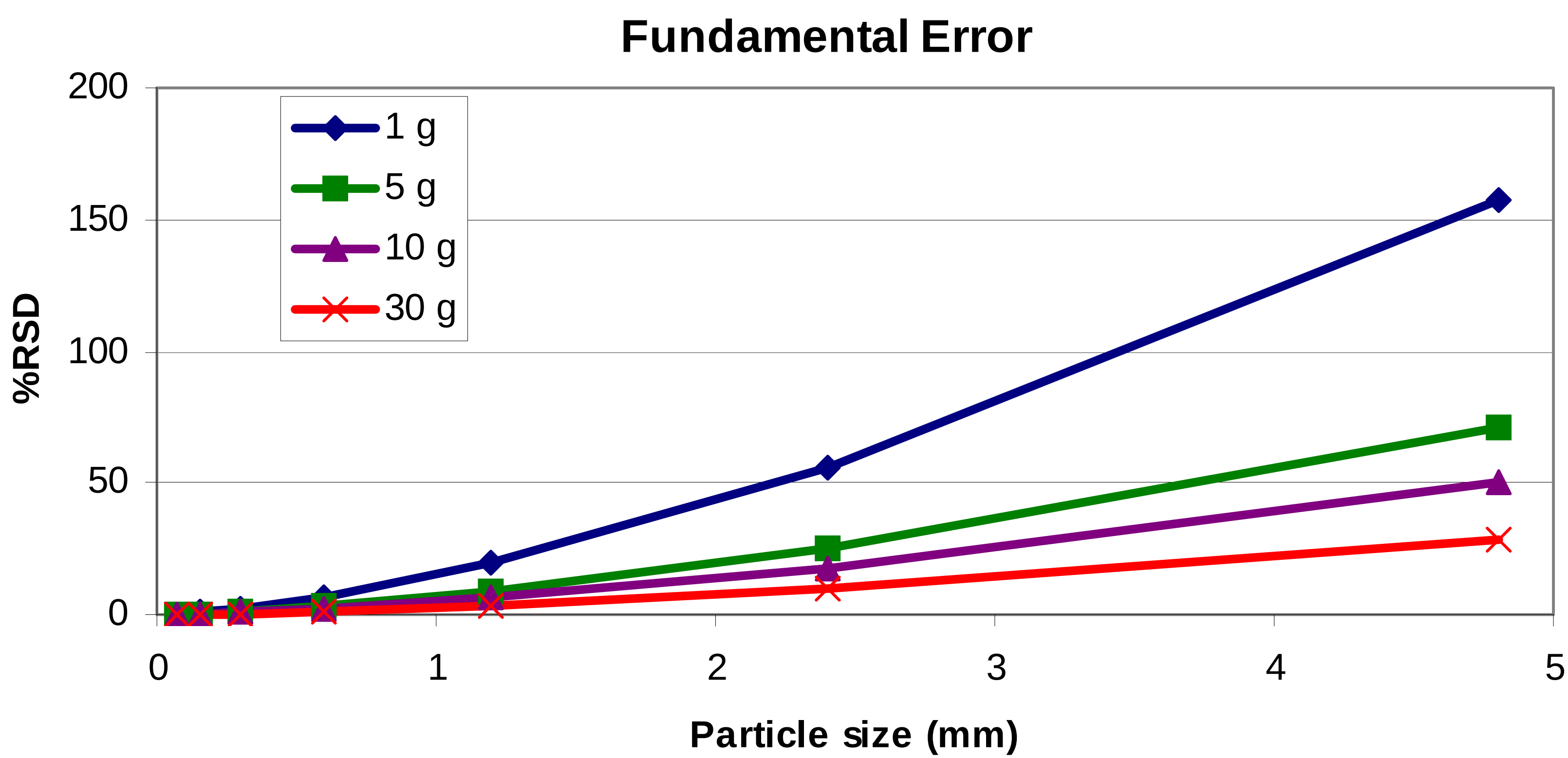
- Sequential scoops (fractional shoveling)
- Rotary Sectorial splitter
- Line & scoop
- Mix & dig-a-spot
- MIS pancake (8330B)

Picture from USACE-Alan Hewitt

Using large subsamples

Larger particles

- Produce larger errors or require larger subsamples



ASTM D6323 Sec. A1.1

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How to choose?

- Talk with your laboratory
- Specify the performance wanted/needed to make the decision
  - ~ List all Analytes
  - ~ Sample mass range
  - ~ Particle size to include/exclude
  - ~ Analyte accuracy - %R
  - ~ Analyte precision - %RSD
  - ~ Pebbles, crystalline material
    - Grind or not
      - If yes to what max particle size

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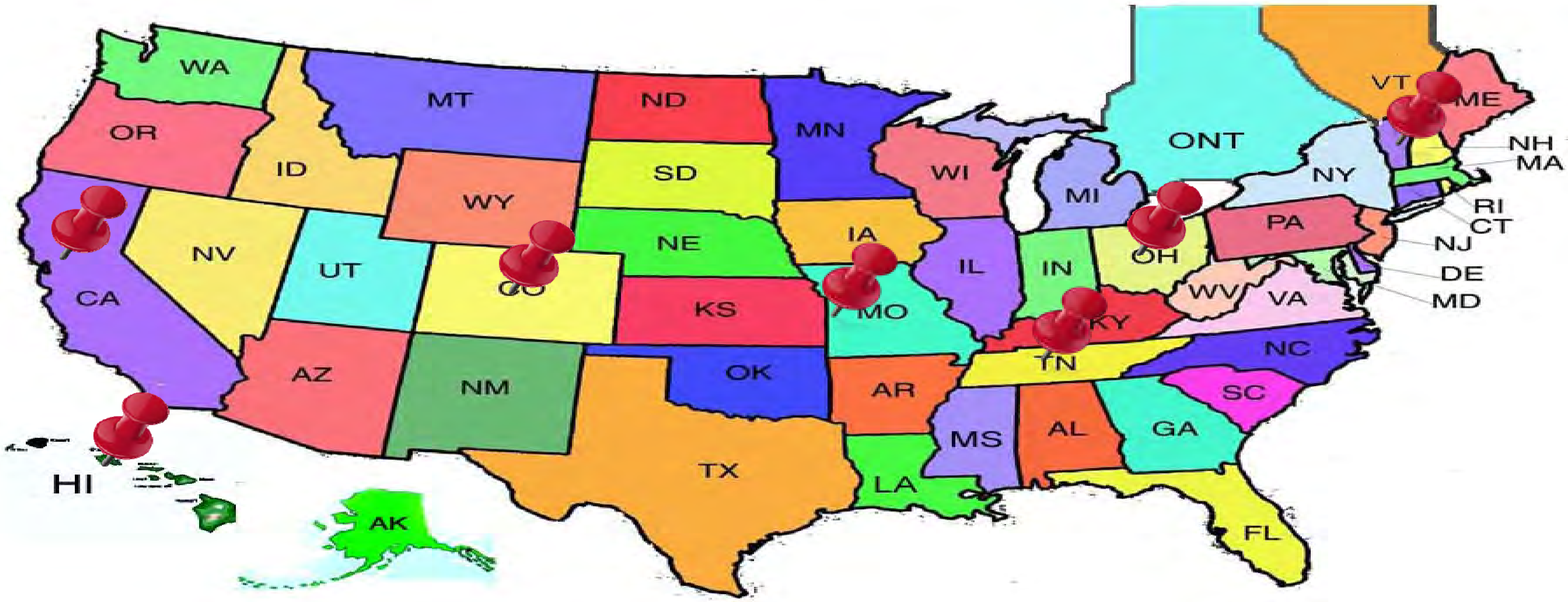
Consider Experience of the Laboratory in Dealing with Options

TestAmerica Laboratories Supporting MIS



Locations: Burlington, Denver, Honolulu, Knoxville, North Canton, Sacramento, St. Louis

Experience: MIS support since 2003

More to Follow

- Grinder tests, e.g., Bico ceramic grinder for metals
- Lab MIS tests, manual versus mechanical splitter
- ACIL 8330B Position Paper
- ITRC MIS Workgroup
- Training, discussion, training, discussion….

Acknowledgements

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