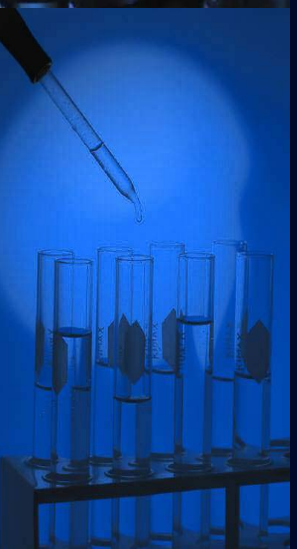
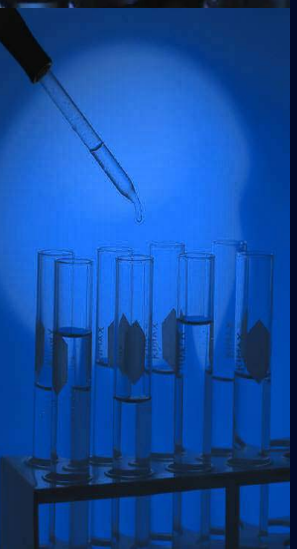


Laboratory Subsampling Strategies for Solid Samples: Controlling Analytical Measurement Uncertainty

William Ingersoll
Naval Sea Systems Command
ingersollws@navsea.navy.mil

Overview

- Factors in analytical measurement uncertainty
  - in field sampling
  - in laboratory subsampling
- Choosing the correct subsampling strategy
  - Minimizes analytical measurement uncertainty
  - Improves data quality available for making environmental decisions

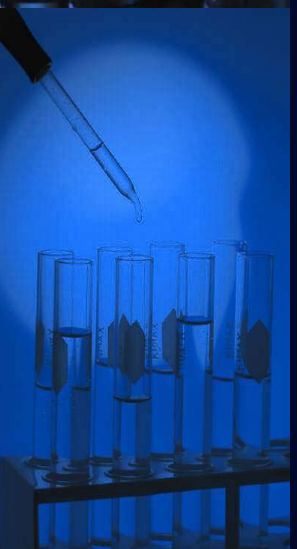


Analytical Measurement Uncertainty

Accurate
Instrumental
Analysis
+
Non-Representative
Subsampling

BAD DATA





Mathematical Model For Estimating Uncertainty

Total Data Uncertainty, $^{D}S^{2}$

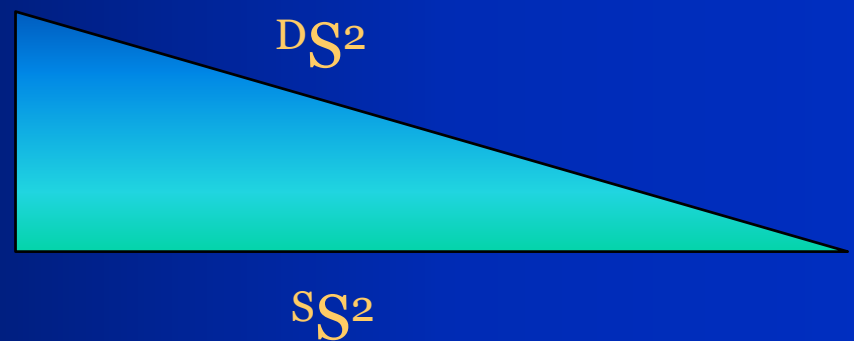
Subsampling Variability, $^{S}S^{2}$

Chemical Preparation and Instrumental Analysis Variability, $^{T}S^{2}$

$^{D}S^{2} = {}^{S}S^{2} + {}^{T}S^{2}$

$^{D}S^{2} = 30^{2} + 10^{2}$

$^{D}S = 32$



Systematic Planning Tools

- Uniform Federal Policy Quality Assurance Project Plan (UFP QAPP)
- Data Quality Objectives
  - Visual Sampling Plan (VSP)
  - Decision Quality
- Measurement Quality Objectives
  - Laboratory Quality Assurance
  - Analytical Measurement Quality
- Sampling and Testing Plan
  - Standard Operating Procedures
  - Field and Laboratory

Subsampling Strategy

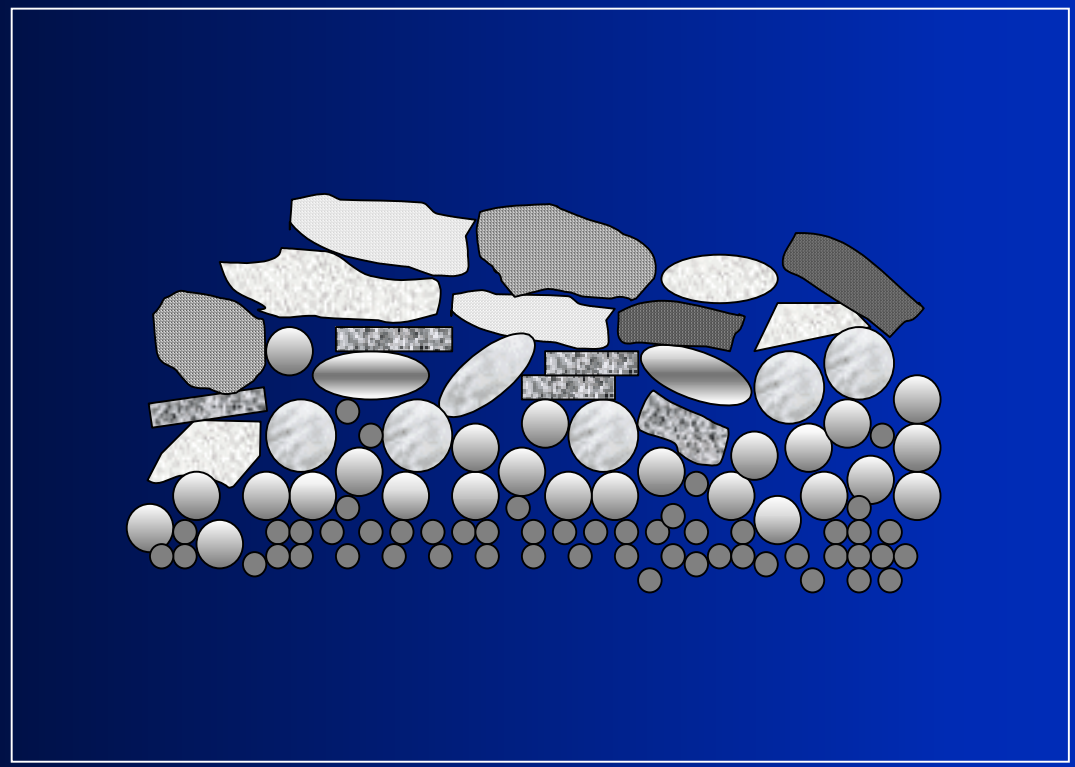
The subsampling strategy is chosen according to the output of the Systematic Planning Tools.

- Sample Material Preparation
  - Drying, Sieving, Milling, Blending
- Number of Increments per Subsample
  - Single Increment or Multiple Increment
- Subsample Collection Technologies
  - VOC
  - SVOC
  - Solid Particulate Material

"Sampling Errors Arise First and Last From the Existence of Heterogeneity" - *Pierre Gy*

- Compositional Heterogeneity
  - Size, shape, physical/ chemical properties of particles
- Distributional Heterogeneity
  - Spatial grouping or clumping of particles
  - Stratified segregation of particles

Compositional and Distributional Heterogeneity



Material Preparation

- Drying
- Sieving
- Milling
- Blending

- Minimizes Fundamental Error
- Minimizes Grouping and Segregation Error

Drying

- Air Drying
  - 40°C
  - Non-volatiles
- Mixing with Anhydrous Sodium Sulfate
  - Non-metals
- Freezing/Pulverizing
  - Volatiles

Sieving

- Removes Large Particles
- Soils >2 mm diameter are not part of the sample material
- Sample material is analyzed separately and weighted

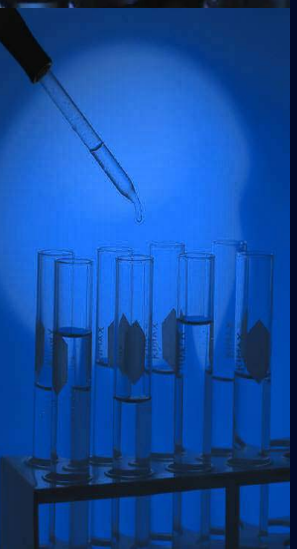
Milling

- Reduces Particle Size
  - Minimizes fundamental error
  - Minimizes grouping and segregation error
- Limited to Non-Volatile Constituents

V-Blender

- Mixing temporarily homogenizes material
- Gravity stratifies particles when blending stops





Material Delimitation and Extraction

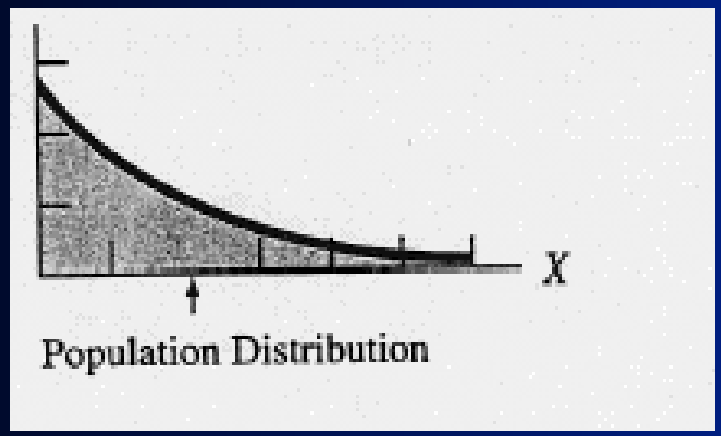
- Traditional Subsampling
  - 1 gram “off the top”
  - Non-representative
- Representative Subsampling
  - Every particle has equal probability of selection
  - Entire sample container subsampled (top to bottom)
  - Multiple increments collected
  - Minimizes grouping and segregation error

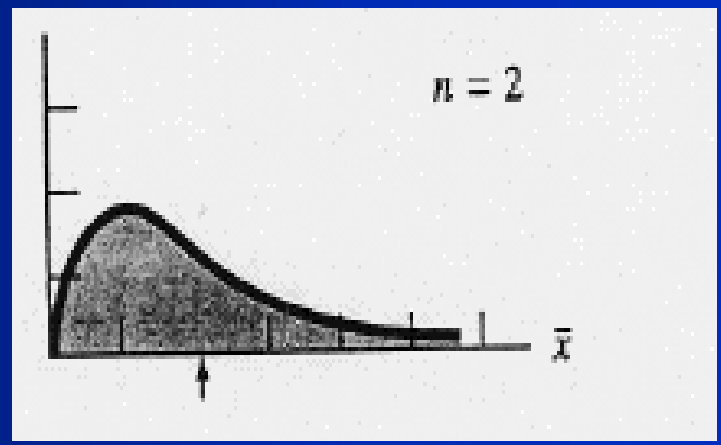
Central Limit Theorem

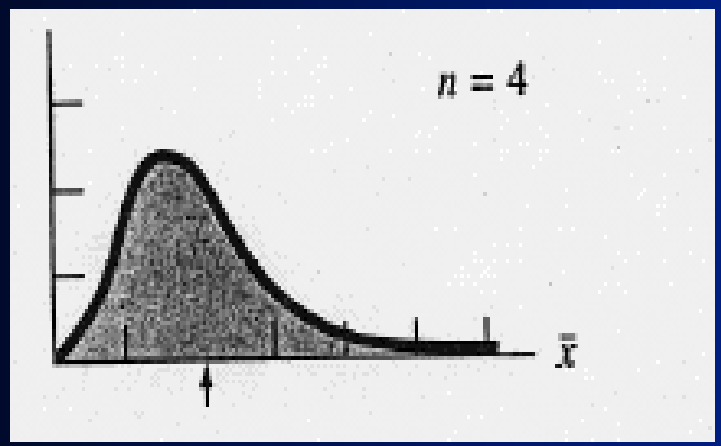
Even an extremely asymmetric population distribution *tends* to a normal analytical measurement distribution for the average

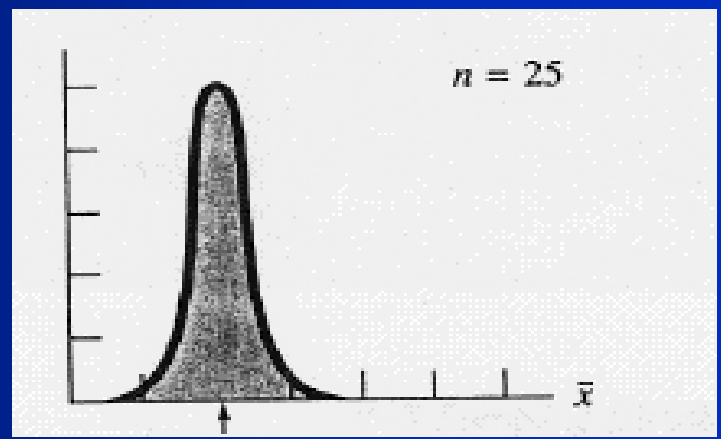
- number of increments per sample,
- number of samples,
- mass or volume of sample (number of particles),
- analyte concentration, and
- number of components in the sampling and analysis process.

Multiple Increment Sampling

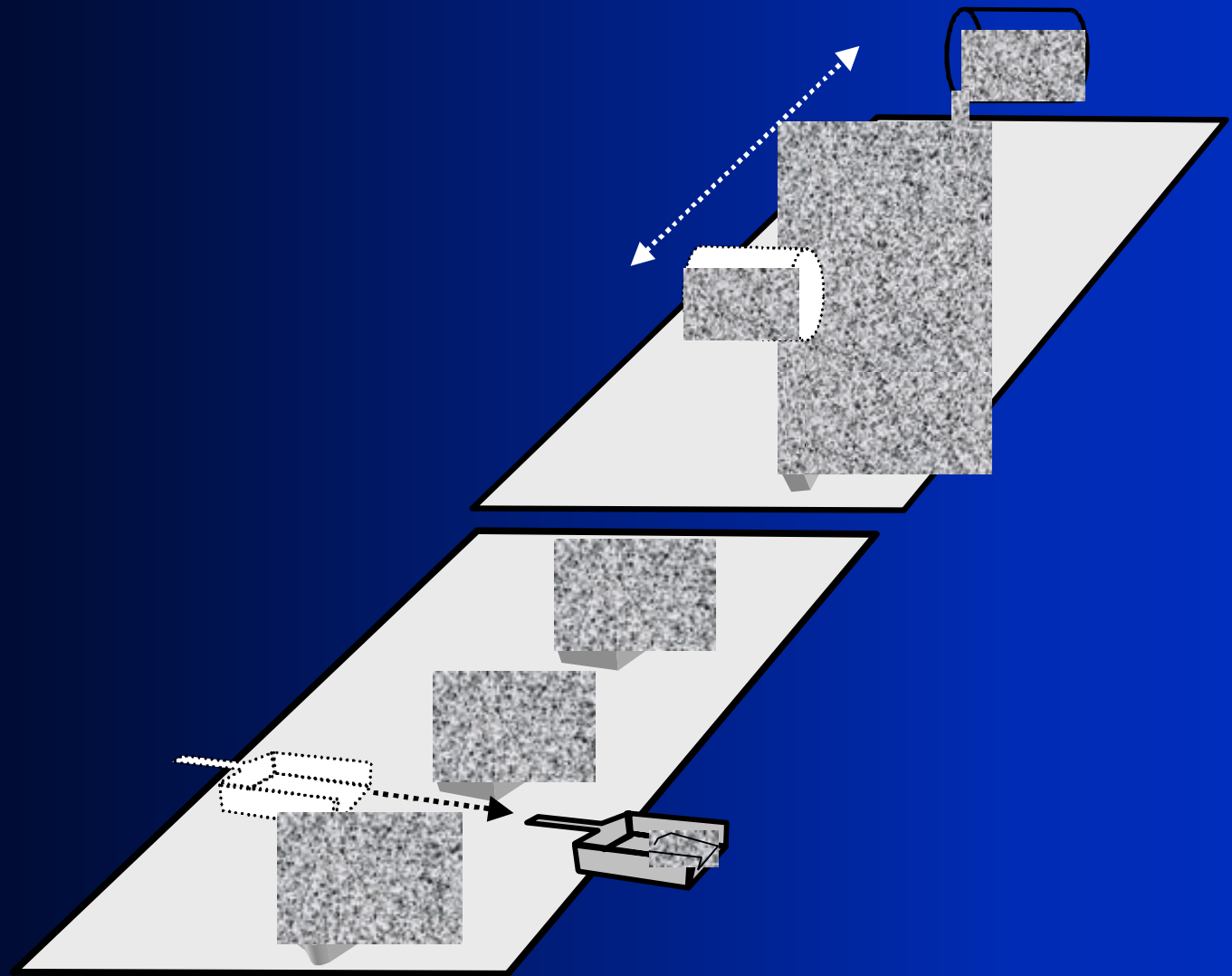


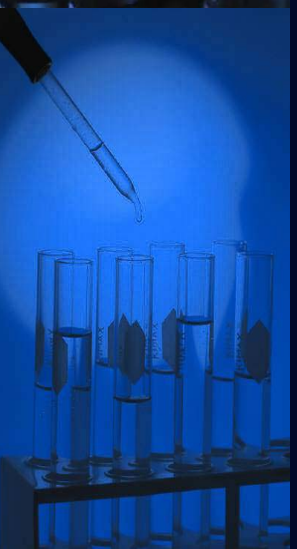




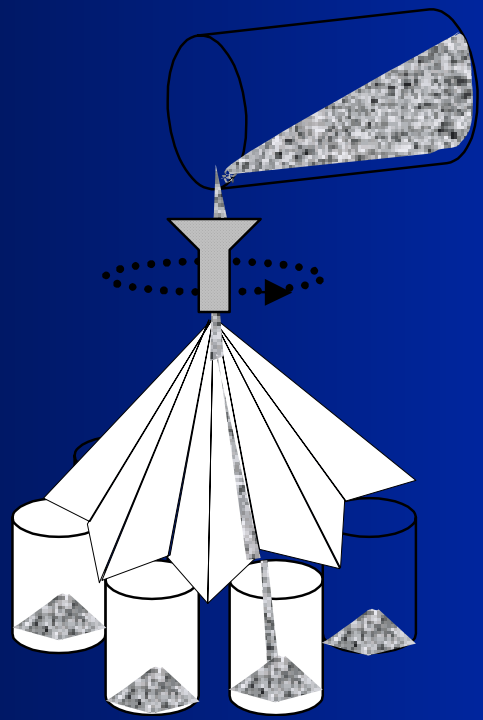


Multiple Increment Scoop Subsampling





Multiple Increment Splitter Subsampling



Sampling Effects

- Primary Sampling
  - Field sampling
- Secondary Sampling
  - Laboratory subsampling
- Volatile Organic Compounds
- Semivolatile Organic Compounds
- Dissolved/Adsorbed Inorganics
- Particulates
  - Metals
  - Explosive residue

Volatile Organic Compounds

- Soil samples collected for VOCs
  - Range: 3 orders of magnitude for same sampling point
  - Losses from volatilization
- Sealed sampling device: EnCore Sampler
  - MEK, DCE, TCE, BZ, TOL, PCE, EB, mpX, oX, DCB
  - $RSD_{95\%} < 20\%$
  - Subsample error negligible
- Analytical Error $RSD_{95\%} \sim 20\%$

PCBs

- Unmixed Sample
  - $RSD_{95\%}$ = 240%
- Automated Shaker Mixing Sample
  - $RSD_{95\%}$ = 40%
- Hand Mixing Sample
  - $RSD_{95\%}$ = 30%
  - Subsampling Error Negligible
- Analytical Error $RSD_{95\%}$ ~ 30%

Particulate Material

- Reduce Heterogeneity
  - Compositional heterogeneity
  - Distributional heterogeneity
- Grinding and Mixing
  - Particle size reduction
  - Breakup grouping and segregation
- Multiple Increment Sampling
- Splitter Sampling

TNT

- Without particle size reduction
  - $RSD_{95\%}$ = 315%
- With particle size reduction
  - $RSD_{95\%}$ = 6%
  - Subsampling error negligible
- Analytical Error $RSD_{95\%}$ ~ 6%

Perchlorates in Water vs. Soil

- Clean Water Analytical Measurement Variability
  - $RSD_{95\%}$ 11.6%
  - Independent of the matrix
  - Laboratory control sample
- Complex Soil Analytical Measurement Variability
  - $RSD_{95\%}$ 26.9%
  - Affected by matrix interferences
- QC-based Nested Approach
  - Matrix Interference Effect

$$MIE = (26.9\%^{2} - 11.6\%^{2})^{1/2}$$

$$MIE = 24.3\%$$

Subsampling Strategy

- No single subsampling approach will fit every sampling problem
- Incorporate soil science and sampling theory in design
- Evaluate how components of sampling and testing contribute to analytical measurement uncertainty
- Minimize the error of the dominant component to minimize study uncertainty

Contact Information

William Ingersoll
Naval Sea Systems Command
ingersollws@navsea.navy.mil