Radiochemistry Webinars

Laboratory Sub-Sampling

In Cooperation with our University Partners

Meet the Presenter… *Dr. Robert Litman*

Robert Litman, PhD, has been a researcher and practitioner of nuclear and radiochemical analysis for the past 46 years. He is well respected in the nuclear power industry as a specialist in radiochemistry, radiochemical instrumentation and plant systems corrosion. He has co-authored two chapters of MARLAP, and is currently one of a team of EMS consultants developing radiological laboratory guidance on radionuclide sample analyses in various matrices, radioactive sample screening, method validation, core radioanalytical laboratory operations, contamination, and rapid radioanalytical methods. Dr. Litman has worked with the NRC in support of resolving GSI-191 issues (chemical effects following a loss of coolant accident) at current nuclear power plants and reviewed designs for addressing that safety issue for new nuclear power plants. Currently he is working on several projects with ChemStaff involving the analysis of environmental materials for NORM and TENORM, and groundwater contamination at nuclear power facilities.

His areas of technical expertise are gamma spectroscopy, radiochemical separations and validation of radiochemistry data. Dr. Litman has been teaching courses in Radiochemistry and related special areas for the past 28 years.

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EMS

Topics for Laboratory Sub-Sampling

- Definitions related to sampling
- Matrices of concern
- Sub-sampling vs whole sample analysis
- Sub-sampling requirements
- Sample homogenization techniques
- Advantages and disadvantages of certain subsampling methods
- Uncertainty

Definitions (1)

***aliquant*:** A representative portion of a homogeneous sample removed for the purpose of analysis or other chemical treatment. The quantity removed is not an evenly divisible part of the whole sample.

aliquot: A representative portion of a homogeneous sample removed for the purpose of analysis or other chemical treatment. The quantity removed is an evenly divisible part of the whole.

Definitions (2)

Heterogeneity

(1)Spatial heterogeneity - non-uniformity of the distribution of an *analyte* of concern within a matrix. Spatial heterogeneity affects sampling, sample processing, and sample preparation.

(2)Distributional heterogeneity of a lot depends not only on the variations among particles but also on their spatial distribution. Thus, the distributional heterogeneity may change, for example, when the material is shaken or mixed.

(3) Constitutional (or compositional) heterogeneity of a lot is determined by variations among the particles without regard to their locations in the lot. It is an intrinsic property of the lot itself, which cannot be changed without altering individual particles.

Definitions (3)

homogenization**:** Producing a uniform distribution of analytes and particles throughout a *sample*

replicates**:** Two or more *aliquants* of a homogeneous *sample* whose independent measurements are used to determine the *precision* of laboratory preparation and analytical procedures.

What Matrices Require Laboratory Sub-Sampling?

- Liquids
- Soils and Solid (abiogenic) materials
- Vegetation
- Air particulate filters
- Biomaterials
- Standards
- Samples of an irregular nature

Naturally Occurring and Anthropogenic Radionuclides

Distribution of radionuclides in the matrix:

- How was the radionuclide deposited?
  - Surface or internal incorporation?
- Chemistry of radionuclide from source?
- Chemistry of the environment?
- Time radionuclide in contact with the matrix?

Sub-sampling vs Whole Sample Analysis

Taking the whole sample for analysis:

- Minimizes risk of loss of analyte
- Can achieve a lower detection limit
- Sub-sampling problems are obviated

But is there a drawback for each of these?

Aqueous Samples

Is Sub-sampling Really a Problem?

Mass vs Activity Concentration

The limit for ^{228}Ra + ^{226}Ra in DW is 5 pCi/L

5pCi/L of ^{228}Ra = 4.84×10^{7} atoms/L = 1.83×10^{-14} g/L

5 pCi/L of ^{226}Ra = 1.34×10^{10} atoms/L= 5.10×10^{-12} g/L

Depending upon the method, between 0.25 and 1.0 L of sample are used

Homogeneity

- Visual observation of the sample
  - –Particulates
  - –Colloidal particles
  - –Oily residue
- Preservation that was used
  - –In the field
  - –For transport
  - –During storage at the laboratory prior to analysis
- How does the aliquanting technique ensure representativeness of the sub-sample?

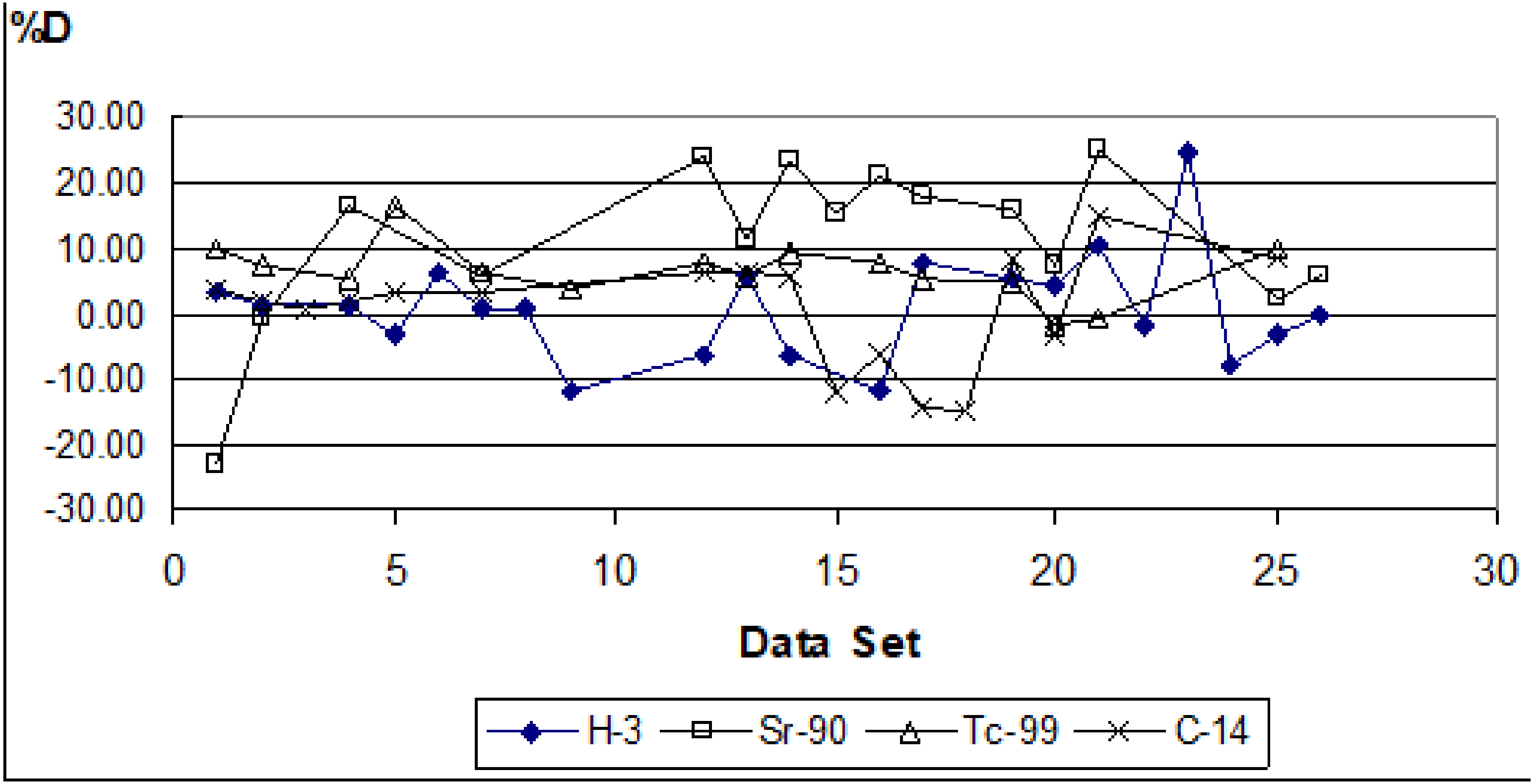
LCS: An Ideal Liquid Sample?

It's made from:

- A primary standard or reference material
- Made in Grade B or Type II water
- Acidified and routinely tested
- Maintained in a secure chemical and physical environment

What should we expect for % deviation from a solution that is so carefully controlled?

Laboratory Control Samples
Aqueous with Chemical Separation



$$\%D = 100 \times \frac{A_M - A_S}{A_S}$$

Sub-sampling vs Whole Sample Analysis - Liquids

If the whole sample is used:

- Cannot perform a MS
  - Don’t know if matrix effect exists
- Cannot perform a batch duplicate using that sample
  - Don’t know if sample inhomogeneity exists
- Is container wall completely free of analyte?
  - Method for sample transfer
- Do not have back up sample
  - in case of blunder
  - If needed for legal purposes

Solids

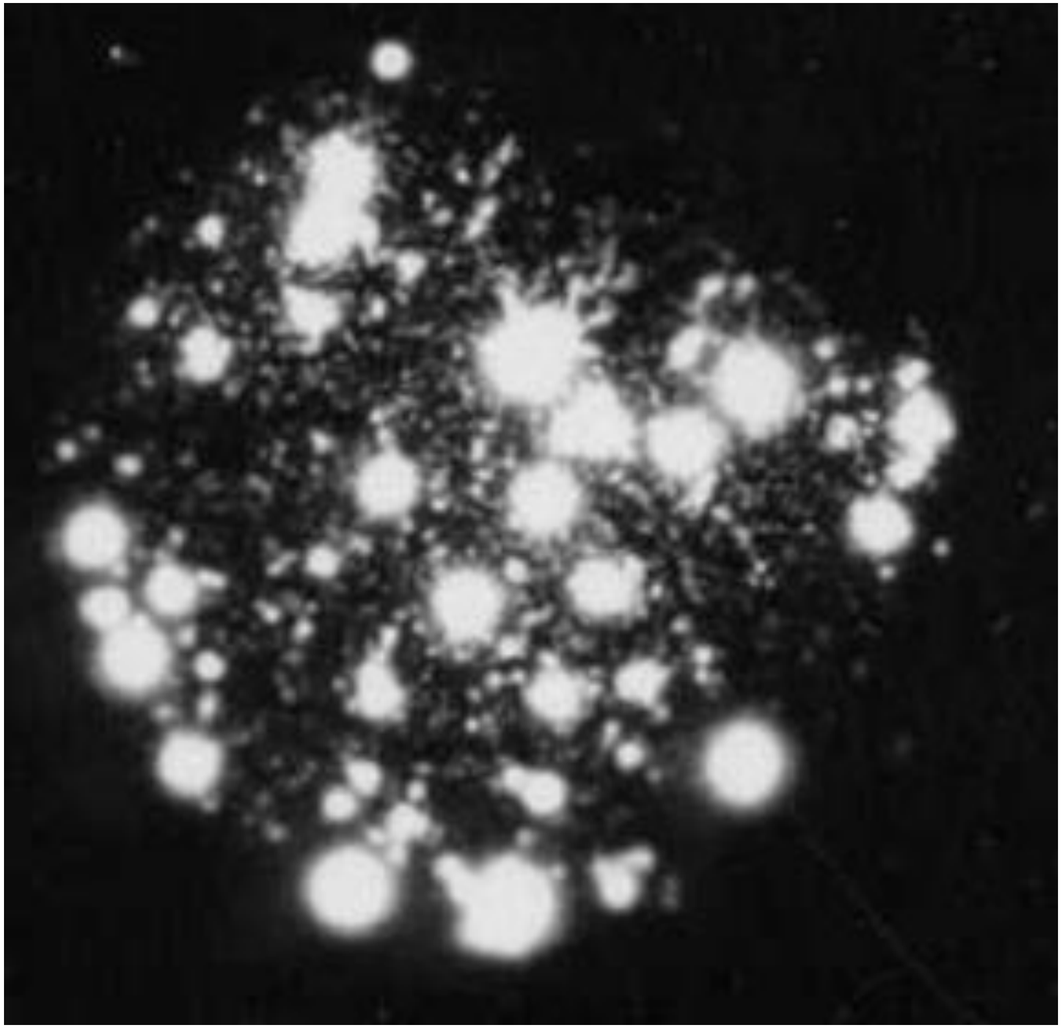
Homogeneity and Aliquanting

Radionuclide vs Mass Concentrations

Does activity concentration affect the ability to obtain a representative laboratory sub-sample?

	^{60}Co	^{90}Sr	^{226}Ra	^{99}Tc	^{232}Th
$t_{1/2}$, years	5.26	28.8	1.60E+03	2.13E+05	1.40E+10
atoms of radionuclide	4.42E+08	2.42E+09	1.35E+11	1.79E+13	1.18E+18
Activity concentration, pCi/g	50	50	50	50	50
mass concentration, g/g	4.41E-14	3.62E-13	5.05E-11	2.95E-09	4.54E-04

Can Homogeneity be Detected Visually?



Sample grain size was 125 - 250 µm. The white spots are particles of plutonium while the entire dark area is due to soil particles

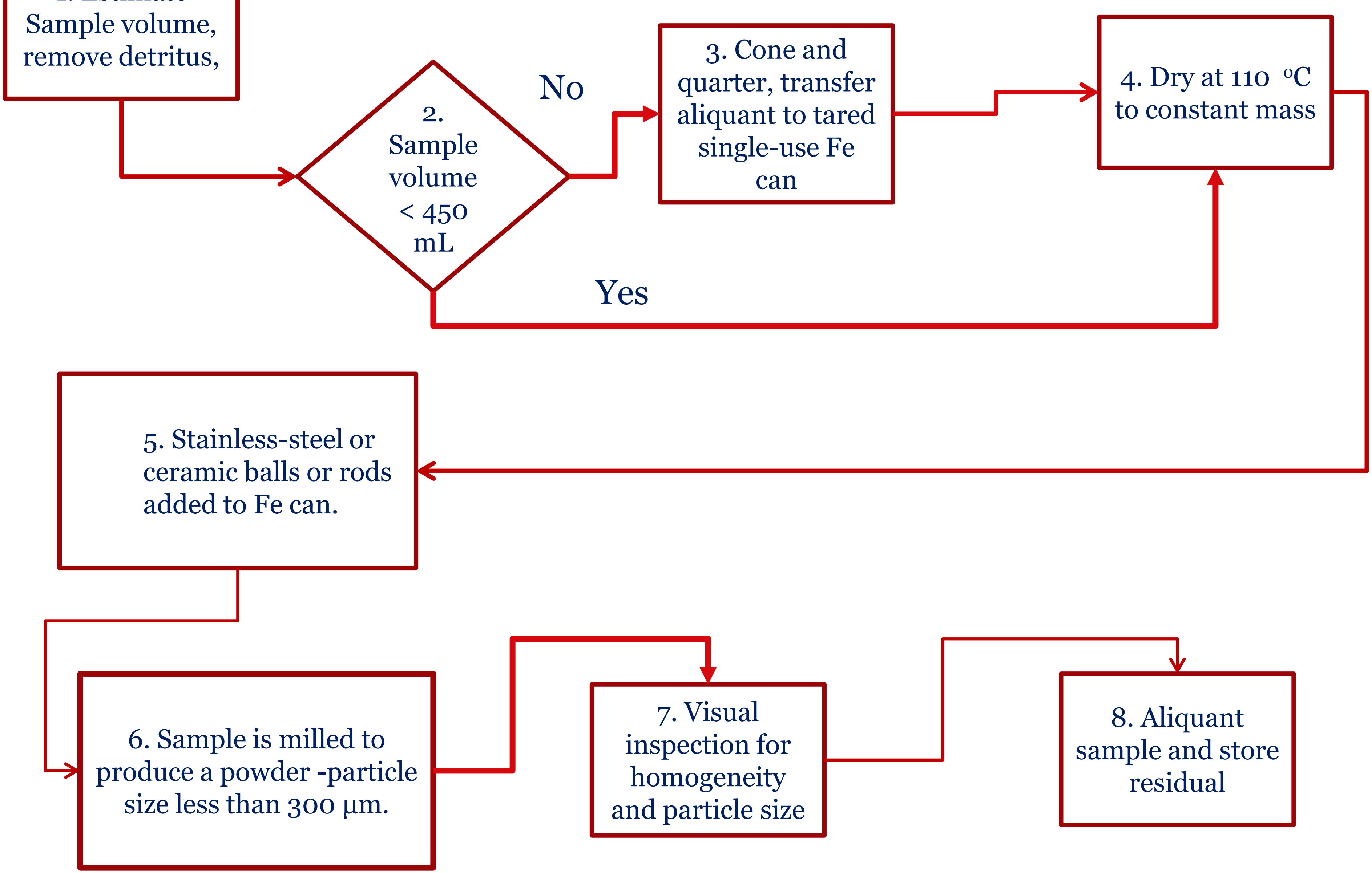
without radionuclides.

Can Homogeneity be Detected Visually (2)?

Sample Homogeneity - Solids

- Environmental solid samples are by their nature inhomogeneous
- Blending: can produce a degree of short-lived homogeneity,
  - Without pulverizing to a uniform mesh size particles of varying
    - sizes,
    - shapes, and
    - densities
  - will immediately start to segregate under the influence of gravity, vibration and general movement.
- Gravity and vibration tend to cause larger, flatter particles to migrate upward and smaller, rounder particles to migrate downward.
- Scooping off the top tends to get the larger, flatter particles.

Soil Homogenization



Otero Soil: as Found

Does it belong?

Test of Homogenization with ^{99m}Tc

‘Paint Shaker Method’

- 5 g aliquant of dried soil spiked, dropwise with ^{99m}Tc standard solution
- Dried at 105 ^{o}C
- Transferred to 150 g of originally dried soil sample in a 1 pint paint can
- Five ½” diameter SS balls placed in paint can, covered and shaken for 15 minutes using a paint shaker.
- 10 ~ 1 g aliquants removed, counted by gamma spectrometry.

Sample	1	2	3	4	5	6	7	8	9	10
Aliquant (g)	1.004	1.009	1.003	1	0.999	0.998	1.001	1.004	1.009	0.998
net counts	19712	19630	17943	18411	19940	18376	17378	19559	16506	17797
Mean net counts	18525									
Standard deviation of net counts	1155									
% Relative standard deviation	6.23									
Percent Deviation from mean	6.41	5.96	-3.14	-0.62	7.64	-0.81	-6.19	5.58	-10.90	-3.93

Was the Method a Success?

% RSD = 6.23 %

- Is that good enough?

Sub-sampling vs Whole Sample Analysis
Solids

- Solid sub-samples
  - Less mass needed to achieve detection limits
  - Requires homogenization and particle size reduction leading to representative sample
  - Provides additional mass for QA samples and back up analyses
- Whole sample
  - Needs lots of chemicals to digest
    - More waste
    - More time
    - One shot at getting it right
    - Matrix effect on subsampling may be unknown

Vegetation

What is Really Part of this Sample?

Types of Vegetation

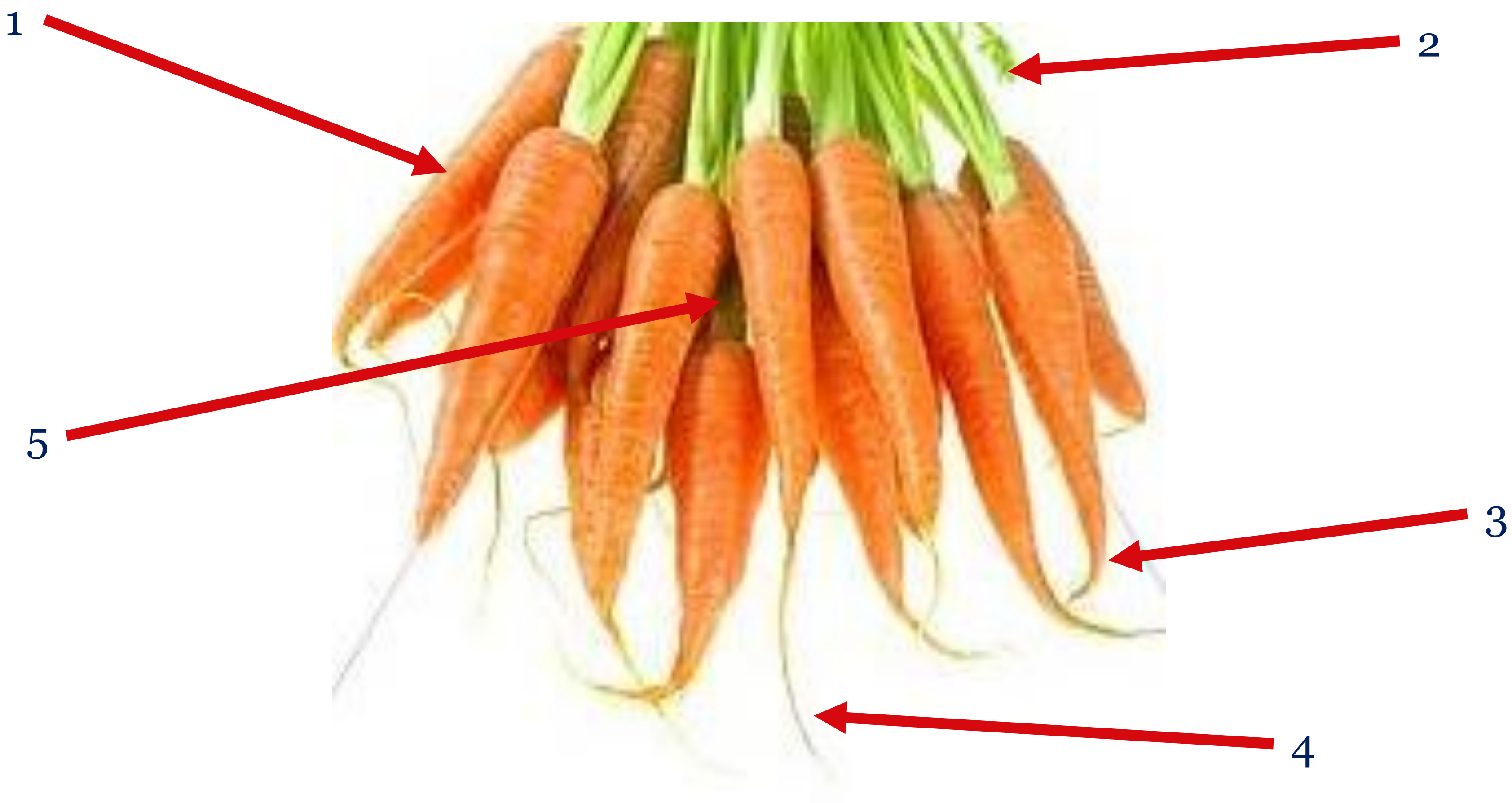
Fruits:

- Only the edible portion of the fruit analyzed?
  - Are seeds to be part of the sample analysis?
  - Pulp (e.g., citrus fruits)
- For whole fruits (e.g., apple, tomato, etc.):
  - To wash or not to wash?
  - Edible skin analyzed separately?

Veggies:

- If plants are the sample (e.g., wheat, beans, etc.)
  - Are the roots part of the sample analysis?
  - Are plant stems part of the sample?

Sample Decision: Carrots



Sub-sampling vs Whole Sample Analysis

Specific parts of the vegetation/fruits to be analyzed is determined:

- Puree
- Cryoshatter
- Freeze dry

Advantages/Disadvantages (1)

- Blending / pureeing / food processing
  - Advantages
    - Size reduction and homogenization in a single step
    - Rapid and thorough
  - Disadvantages:
    - Can result in biphasic samples that require gelling
    - Equipment requires clean-up
    - Potential risk of contamination
    - More expensive equipment

Advantages and Disadvantages (2)

- Manually chop / cut samples into pieces, the mix / homogenize by tumbling/stirring/shaking
  - Advantages
    - Less expensive equipment
    - Easy clean-up
    - Less likely to result in biphasic samples
  - Disadvantages:
    - Less rapid
    - Size reduction and homogenization in separate operations
    - Risk of personnel contamination
    - Manual operations less efficient than equipment

Advantages and Disadvantages (3)

- Cryo-shattering / cryo-milling followed by homogenization by tumbling/stirring/shaking
  - –Advantages
    - Rapid and effective size reduction for complex matrices (e.g., sinuous matrices such as stalks, stems, grasses)
    - Cryo-shattering – less equipment - simple
  - –Disadvantages:
    - Personal safety: Working with cryogenic material (LN2, alcoholic dry ice)
    - Cryo-shattering may require second step to finish size reduction and homogenization
    - Cryo-milling – more complicated, expensive, hard to clean

Advantages and Disadvantages (4)

Freeze Drying (Lyophilization)

– Advantages
  - Tremendous volume reduction
  - Allows homogenization of a large mass
  - Subsequent digestion is easier

– Disadvantages:
  - Personal safety: Working with cryogenic material (LN2, alcoholic dry ice), vacuum.
  - Need a large enough vessel to hold initial material
  - Cannot be used for volatiles

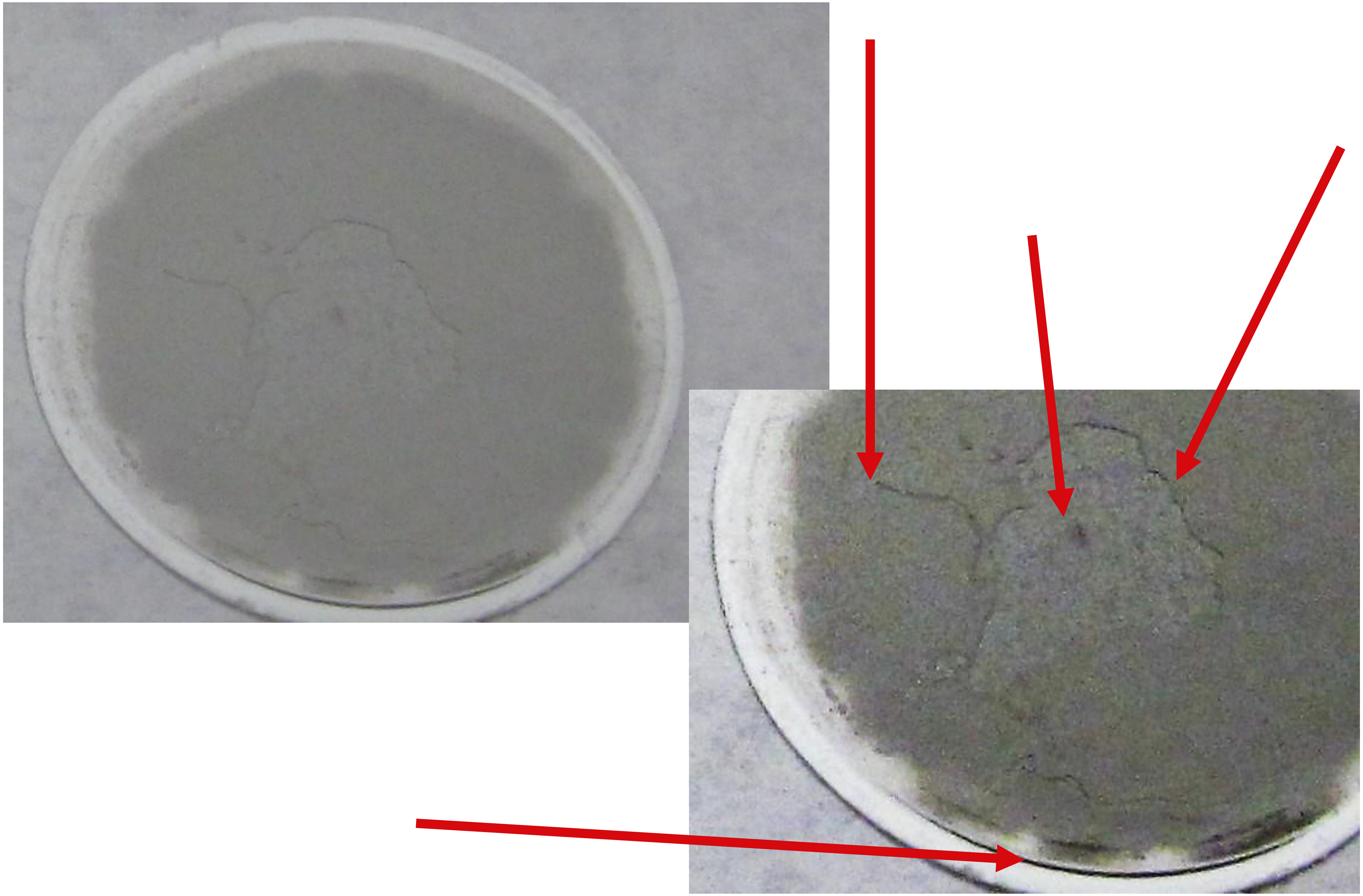
Air Particulate Filters

A Unique Subsampling Issue

Air Particulate Matter

- Is it uniformly distributed on the air filter?
- Can the radionuclides be uniformly distributed within the particulate matter:
  - Areally?
  - By penetration depth?
  - By particulate size?

Dust Laden Air Particulate Filter



Sub-sampling vs Whole Sample Analysis

- Whole filter must be dissolved
- Subsampling - performed on the final solution
- Undissolved solids - retained for subsequent analysis
- Subsampling of the final solution
  - Has same disadvantages as any other liquid solution
  - Additional disadvantage is that colloidal particles may result if visible material is filtered

Biomaterials

The Meat of the Problem?

Edible Portions?

- Consider a pig…
- Consider a chicken…
- What is the biggest whole animal you can accept?

Once the Edible Portion is Selected…

All of the edible likely *will not be used*

- Most of the biomaterials contain
  - Protein
  - Fat
  - Grease
  - Carbohydrates
- Will the subsampling/homogenization process
  - Separate out certain materials

Advantages and Disadvantages (1)

Freeze drying

- Advantages
  - Rapid and effective size reduction for complex matrices (e.g., sinuous matrices such as beef and pork)
- Disadvantages:
  - Personal safety: Working with cryogenic material (LN2, alcoholic dry ice)

Cryo-shattering

- Advantages
  - less equipment - simple
- Disadvantages:
  - Personal safety: Working with cryogenic material (LN2, alcoholic dry ice)
  - Doesn't reduce sample mass/volume

Different Sample Matrices

What Else is There?

Paints

- Mixture of solids, coloring and smoothing agents (and other stuff)
  - –Suspended particulates
  - –Different types of solids
  - –Water or oil based
- Sampling the dried paint
  - –Surface contamination?
  - –Contribution from underlying wall material?
- Rollers, brushes, rags and drop cloths…

Immiscible or Complex Liquids

- Oil-water
- Lubricant-water
- Solvent-water
- Solvent-lubricant
- Fracking fluids

Miscellaneous Solids

- Concrete
- Asphalt
- Fracking solids
- Quarry rocks
- Wood
- Metals

How to Subsample?

- What does the client need?
- Unique composition?
- Mass needed for representative sample?
- The concentration of the radionuclide?

Sub-Sampling

Uncertainty

What Type of Uncertainty?

- Contributes uncertainty to the analytical result due to inherent inhomogeneity.
  - Measurement accuracy is unimportant if the aliquot being analyzed isn't representative of the original sample.
- Sampling by increments: better than a single grab.
  - The more increments the better.
- Larger subsamples: more representative than smaller subsamples.
- Pierre Gy: "Homogenizing solid material is mostly wishful thinking"
  - Reasonably reduces heterogeneity: accept that it still exists.
  - Minimizes heterogeneity with good subsampling techniques.

Estimate of Uncertainty?

- Type A
  - Perform homogeneity test on a minor concentration analyte to get a % RSD
    - Will likely be different for different matrices
- Type B
  - Best judgment
    - Based on experience from other analyses

Uncertainty

- Never ignore that it exists
- Minimize the subsampling contribution
- Advise client that it is part of the CSU

Thanx for you Attention!

Questions?