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Radiochemistry Webinars
Sample Matrices and Collection, Sample Preparation

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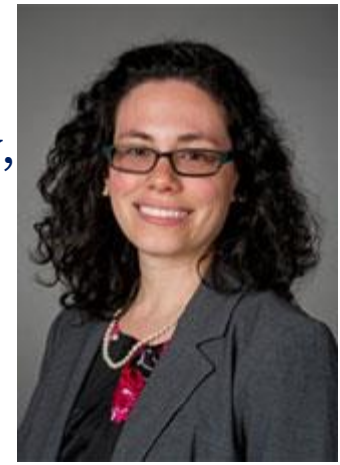
Meet the Presenter…

Dr. Amy E. Hixon



Dr. Amy E. Hixon is an Assistant Professor in the Department of Civil & Environmental Engineering & Earth Science at the University of Notre Dame, where she teaches courses in environmental and aquatic chemistry, actinide chemistry, and nuclear forensic analyses. She received her Ph.D. in Environmental Engineering & Earth Science from Clemson University under the direction of Dr. Brian Powell and her M.S. from the same institution and department under the direction of Dr. Timothy DeVol. Dr. Hixon's research integrates analytical chemistry, instrumental analysis, and modeling techniques to gain a fundamental understanding of the behavior of the actinide elements in natural and engineered systems. She currently supports three undergraduate students and five graduate students on three funded projects. Two projects are independently funded by the Department of Homeland Security to support studies on the environmental aging of nuclear materials and surrogate materials development in support of post-detonation nuclear forensics. The third is an Energy Frontier Research Center (EFRC), Materials Science of Actinides, funded by the Department of Energy and led by Dr. Peter Burns, which funds Dr. Hixon's group as part of a much larger project (~$12M for four years). Her work under the EFRC focuses on understanding interactions between uranyl peroxide cage clusters and solid phases in order to develop nanoscale control of actinides in an advanced fuel cycle.

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UNIVERSITY OF NOTRE DAME

Sample Matrices and Collection, Sample Preparation

Dr. Amy E. Hixon
University of Notre Dame

National Analytical Management Program (NAMP)
U.S. Department of Energy Carlsbad Field Office

TRAINING AND EDUCATION SUBCOMMITTEE

Nuclear forensics…

…seeks to determine the physical, chemical, elemental, and isotopic characteristics of nuclear material with unknown origin

…has two aspects

Pre-detonation nuclear forensics

Post-detonation nuclear forensics

Pre-detonation nuclear forensics

Lead pig and HEU oxide sample interdicted in Rousse, Bulgaria in 1999 (Kristo, 2011).

Focuses on the characterization of interdicted nuclear materials to determine their origin

- Critical signatures:
  - Morphological/microstructural features
  - Trace element abundances
  - U/Pu isotope ratios
- Spatially-resolved data may provide valuable information that is masked by bulk analysis techniques

Post-detonation nuclear forensics

Bottle green and red Trinitite glass (Eby et al., 2015)

Produces information about the design of the exploded device, level of sophistication, and origin of nuclear material

- High-quality analysis of debris and accurate device interpretation are needed
- Debris
  - Wide range of matrices
  - Heterogeneous in nature

Various Scenarios

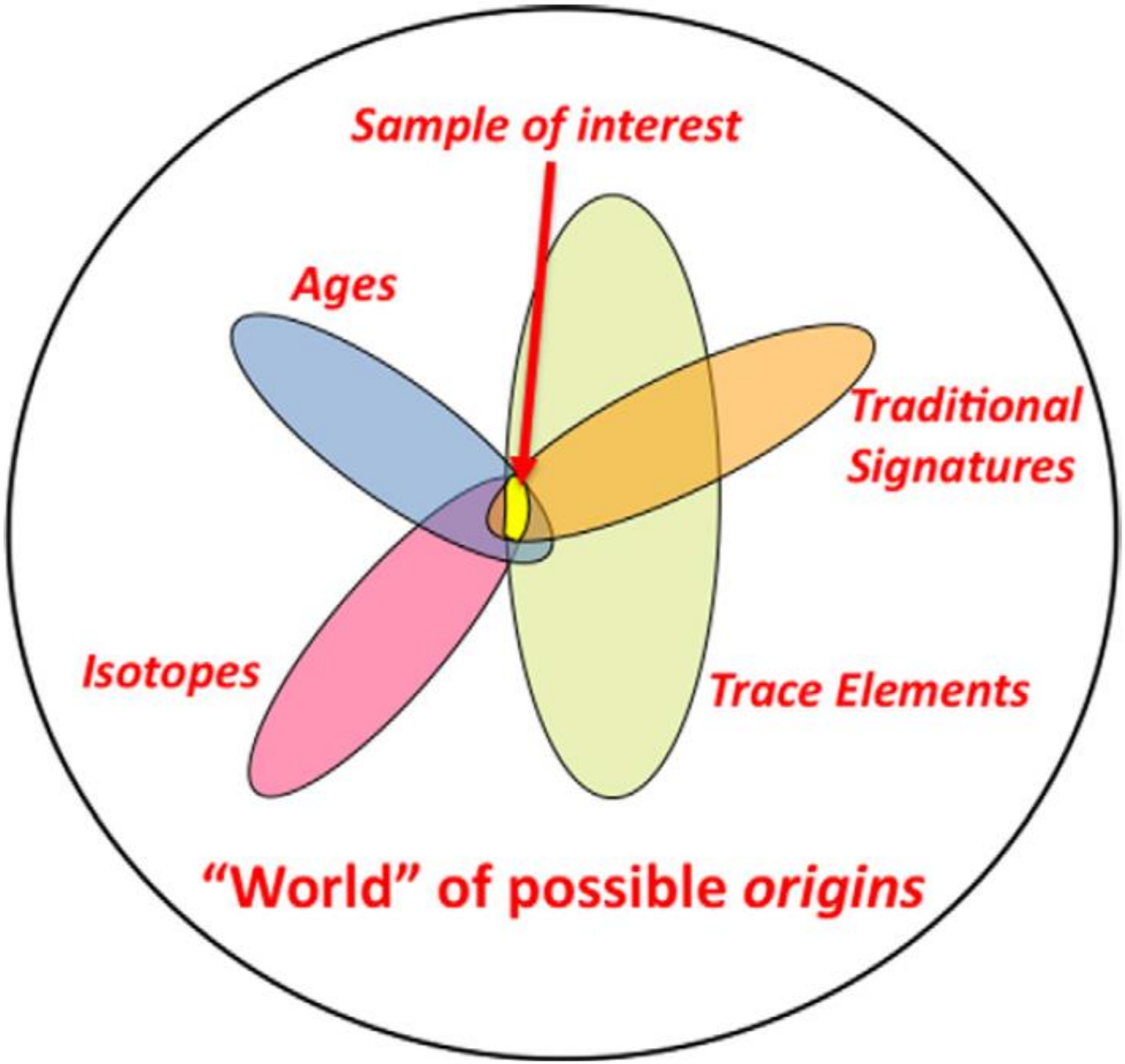
Pre-detonation

- Environmental monitoring to support safeguards
- Interception of nuclear material or intact device

Post-detonation

- Radiological dispersive device (RDD)
- Fissile or primitive device
  - Nuclear detonation with limited yield
  - 100s-1000s of casualties
- Nuclear explosion
  - Kiloton yield
  - 1000s-100,000s of casualties
  - Mass destruction

IAEA Category of Nuclear Material	Characteristics
SNM	
High enriched uranium (HEU)	>20% ^{235}U
Weapons-grade uranium (WGU)	Pure uranium metal, >93% ^{235}U
Weapons-grade plutonium (WGPu)	Pure plutonium metal, <7% ^{240}Pu
Super-grade plutonium (SGPu)	Pure plutonium metal, <3% ^{240}Pu
Reactor fuel	
Low enriched uranium (LEU)	<20% (typically 3-5%) ^{235}U
Reactor-grade plutonium (RGPu)	>19% ^{240}Pu, produced in nuclear reactor
Fuel-grade plutonium (FGPu)	7% < ^{240}Pu < 19%, produced in nuclear reactor
MOX-grade plutonium (MGPu)	>30% ^{240}Pu, recycled from mixed oxide fuel
Radioactive sources	
Medical diagnostic sources	Short-lived radioisotopes
Radiotherapy sources	^{60}Co and ^{137}Cs
Irradiators/sterilizers	^{60}Co and ^{137}Cs
Radiography/NDT	^{192}Ir
Gauging	^{60}Co, ^{137}Cs, ^{241}Am
Radioisotope thermoelectric generators (RTG)	^{238}Pu, ^{244}Cm, ^{90}Sr



Kristo and Tumey, 2013

Identifying Data Needs

- What types of samples need to be collected?
  - Collocated samples
  - Field replicates
  - Background samples
- What are the radionuclide(s) of interest?
- How will samples be preserved and shipped?
- What are the sample tracking and documentation requirements?

"Sampling is the process of collecting a portion of an environmental medium as representative of the locally remaining medium."

"Representativeness is a measure of the degree to which data accurately and precisely represent a characteristic of a population parameter at a sampling point."

– Multi-Agency Radiation Survey and Site Investigation Manual (MARSSIM)

Sample Collection Procedures

- Ensure that a sample is:
  - Representative of the sample media
  - Large enough to provide sufficient material to achieve the desired detection limit
  - Consistent with assumptions used to develop the conceptual site model and derived concentration guideline level (DCGL) for each radionuclide of interest
- Take into consideration worker exposure and special handling considerations

Soil/Sediment Matrices

- Why?
  - Integrate signature species over time
  - Wet and dry atmospheric deposition, accidental releases, transport activities
- Sample volume
  - Forensic specimens should be collected over a wide area and from minimal soil thickness
  - Large volumes: 100g – several kg
    - more representative than small volumes of soil
    - detection limits and multiple analyses

Soil Sampling Equipment

Equipment	Application	Advantages/Disadvantages
Scoop or trowel	Soft surface soil	Inexpensive, easy to use and decontaminate; trowels with painted surfaces should be avoided
Bulb planter	Soft soil, 0-15 cm (0-6 in)	Easy to use; uniform diameter and sample volume, preserves soil core; limited depth capability; can be difficult to decontaminate
Soil coring device	Soft soil, 0-60 cm (0-24 in)	Relatively easy to use; preserves soil core; limited depth capability; can be difficult to decontaminate

Sample containers: PE bottles, multiple PE bags

Vegetation Matrices

- Bioindicators
- Time-history intelligence
  - Pines and firs drop needles once every few years
  - Analyses of distinct layers of fallen needles
- Two possible collection modes:
  - The exposed portion can serve as an air collector
  - The root system samples ambient soil and groundwater

Source: Wikimedia Commons

Other Matrices

Primary containers for specimen storage and transport

Inorganic Analyses

- Teflon is optimal
- Solids/soils
  - multiple PE bags, polyvials
- Aqueous samples
  - polyvials
- Glass containers affect experimental blanks

Organic Analyses

- Ultraclean glass vials are optimal
  - Teflon-lined caps
  - Septum tops
- Plastic vials are a significant source of phthalates

Analytical Tools

- Bulk analysis tools
  - Inductively coupled plasma mass spectrometry (ICP-MS)
  - X-ray fluorescence (XRF)
- Imaging tools
  - Optical microscopy
  - Scanning electron microscopy (SEM)
  - Transmission electron microscopy (TEM)
- Microanalysis tools
  - Energy dispersive X-ray spectroscopy (EDX)

Technique/ Method	24 hours	1 week	2 months
Radiological	Estimated total activity Dose rate (α,γ,n) Surface contamination		
Physical Characterization	Visual inspection Radiography Photography Weight Dimension Optical microscopy Density	SEM (EDX) XRD	TEM (EDX)
Isotope Analysis	γ-spectroscopy α-spectroscopy	Mass spectroscopy (SIMS, TIMS, MC-ICP-MS)	Radiochemical separations
Elemental/ Chemical		ICP-MS XRF Assay (titration, IDMS)	GC/MS

General Guidance for Sample Preparation

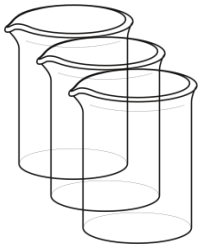
- Minimize potential sample losses:
  - Losses as dust or particulates
  - Losses through volatilization
  - Losses due to reactions between sample and container

Radioanalytical Chemistry

- Destructive technique
- Dissolution
  - Reagents must be purged with He to remove trace Xe and Kr
  - Any sample containing a significant quantity of Pu must be treated with HF
    - Fluoride can interfere with added tracers
    - $HClO_4$ or repeated nitric acid evaporations
    - Final matrix is usually HCl

Tracer exchange by redox

- Each solution is sampled three times:
  1. Solution is processed without added tracers
  2. Solution is traced with ^{246}Cm, ^{243}Am, and ^{236}Pu
  3. Solution is traced with ^{237}Np



Evaporate to near dryness

+ 9M HCl, HI

Evaporate to near dryness

+ 9M HCl

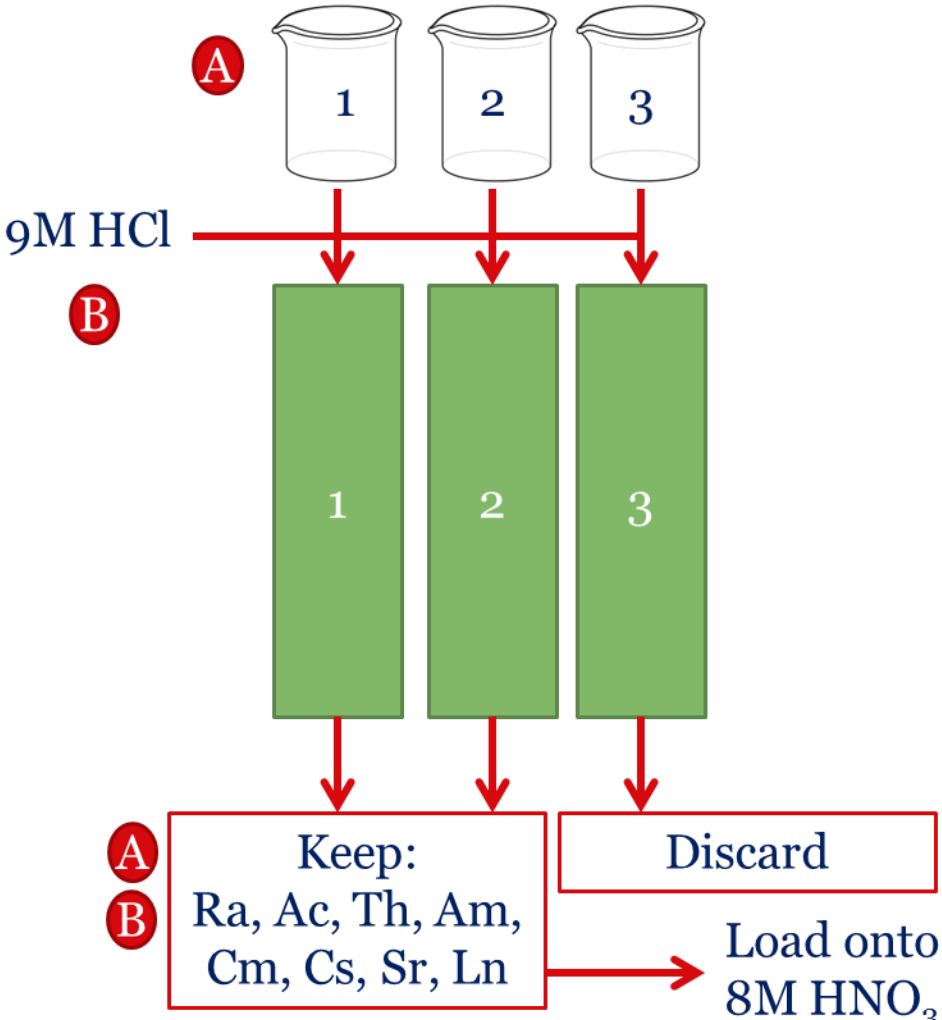
Evaporate to near dryness

+ 8M HNO_3 ...

Evaporate to near dryness

Chemical Separations

… 10M HCl



C Elute Pu with warm 10M HCl + HI
Keep all three fractions

D Elute Pa with 9M HCl + 0.02M HF
Keep fractions from columns 1 & 3

E Elute Np with 4M HCl + 0.1M HF
Keep fractions from columns 1 & 2

F Elute U with 0.1M HCl
Keep all three fractions

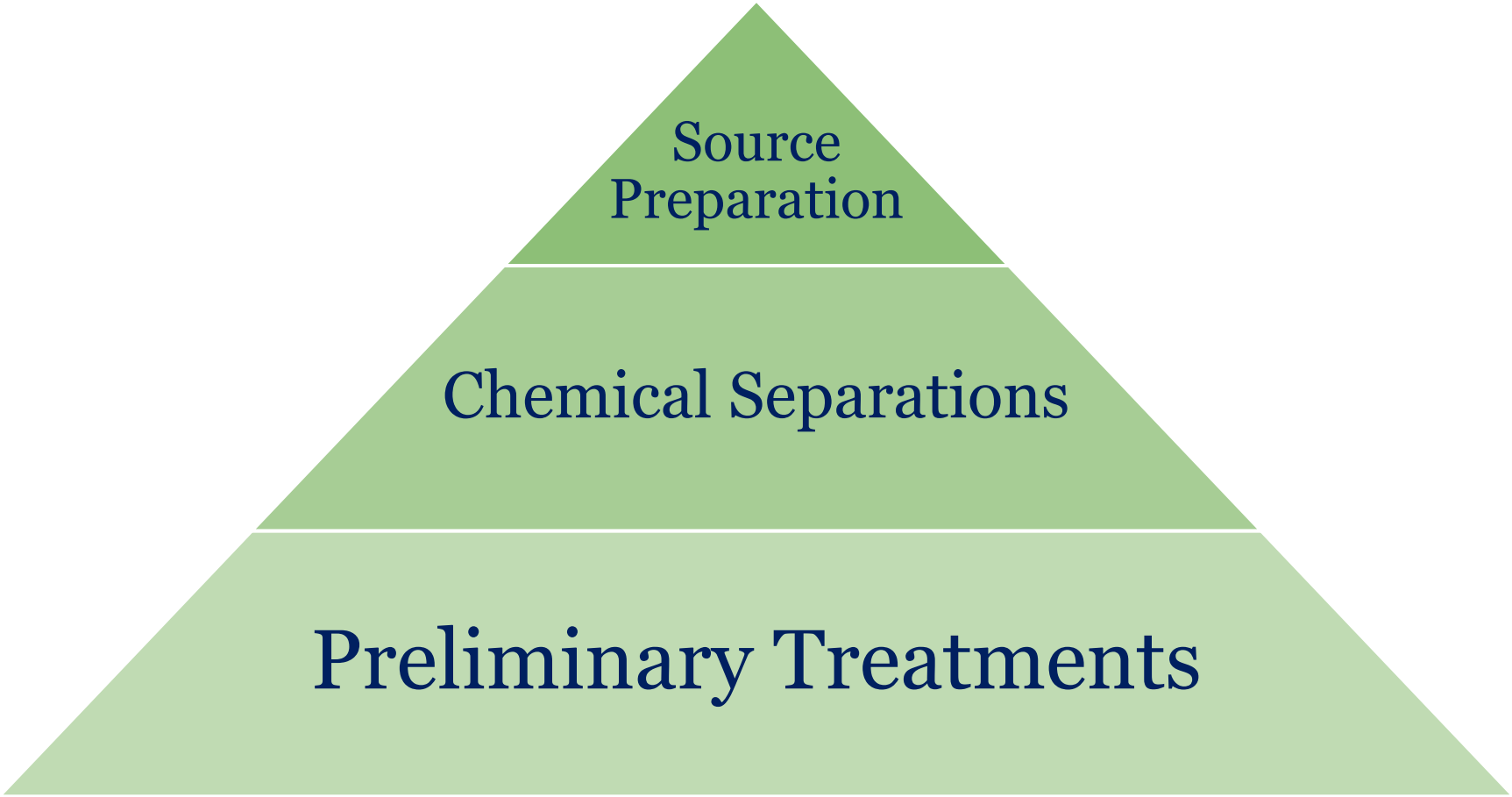
Alpha Spectroscopy

- Alpha spectroscopy is a widely used technique for the identification and quantification of alpha-emitting radionuclides.
  - Naturally occurring alpha emitters
  - Transuranium elements, special nuclear materials
- Characterized by high efficiency, low background, and low detection limits
- Can be applied for the assay of a variety of samples.

Sample Preparation: Alpha Spectroscopy

- Typically requires the separation of the element of interest from the bulk sample.
  - One source for each element of interest
- Ideal source is an infinitely thin, weightless source on a perfectly prepared substrate

Sample Preparation: Alpha Spectroscopy

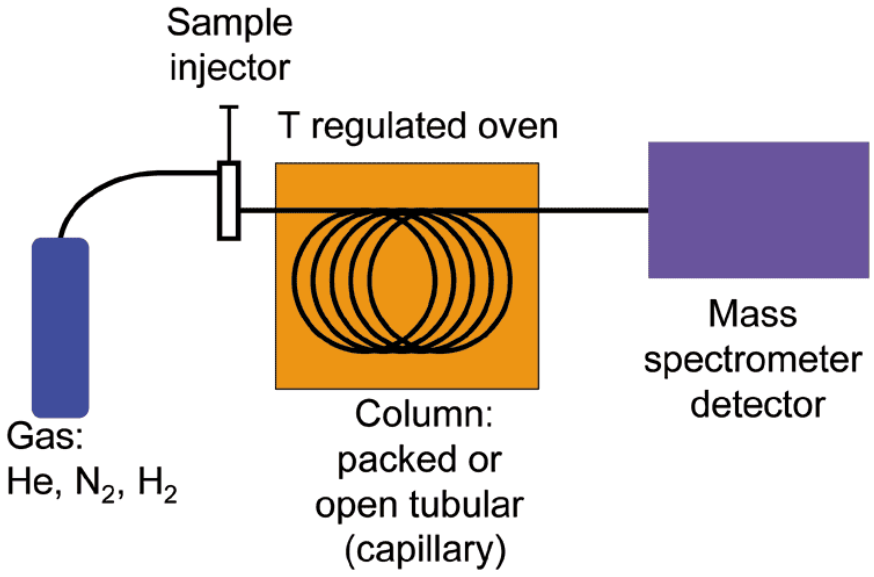


Source Preparation for Alpha Spectroscopy

- Evaporation
  - Tends to form inferior sources
    - Crystals/aggregates cause self-absorption
    - Spreading agents (e.g., tetraethylene glycol) are organics that must be burned off
- Electrodeposition
  - Widely used
  - Ion being deposited is reduced by the addition of electrons gained from an electrolytic solution
- Hydroxide and fluoride precipitation

Organic Sample Preparation

- Gas chromatography-mass spectrometry (GC-MS) is most versatile
- Chemical extraction
  - Ultrasonic extraction
  - Microwave-assisted extraction
  - Liquid-liquid solvent extraction
    - methylene chloride
    - 3:1 methylene chloride:isopropanol
    - Acetone
- Solid-phase microextraction (SPME)



Source: Wikipedia

"A measurement is only as good as the sample preparation that proceeded it."

– Multi-Agency Radiological Laboratory Analytical Protocols Manual (MARLAP)

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Questions?

Upcoming Webinars

- Nuclear Materials Analysis — Physical and Spectroscopic Methods
- Nuclear Materials Analysis — Chemical Methods
- Nuclear Materials Analysis — Non-Destructive Analysis

NAMP website: www.wipp.energy.gov/namp