Radiochemistry Fundamentals

Est. Length: approx. 40 hours
The Periodic Chart of the Nuclides and Isotopes

STATE how information is arranged on the Periodic Chart

DESCRIBE the basic layout of the Chart of the Nuclides.

GIVEN a sample Chart of the Nuclides, IDENTIFY the following:

- Elements
- Isotopes

IDENTIFY where the “line of stability” resides on the Chart of the Nuclides and EXPLAIN why it is significant.

GIVEN a radioactive isotope and using the Chart of the Nuclides, DETERMINE the stable isotope that is at the end of the decay scheme.

DEFINE spontaneous fission and EXPLAIN how it differs from nuclear fission.
Objective Review

**Radiochemical Sample Preparation Techniques**

DESCRIBE the importance of radiochemical separations

DESCRIBE the basic principles of the following sample preparation techniques, including the sample type and the instruments used to analyze them:

- Complexation
- Precipitation
- Solvent extraction

EXPLAIN how ion exchange works to separate ionic species.

EXPLAIN why carriers are used in radiochemical sample preparation.

STATE why it is important to select carriers that are chemically similar to the radioisotopes to be analyzed.

STATE why radiochemical tracers are used in sample preparations.

EXPLAIN why there are no ideal choices in the selection of chemical carriers and tracers.
Objective Review

Radioactive Counting Systems

EXPLAIN the theory of operation of a gas proportional counter.
LIST the types of radiation that can be detected by gas proportional counters.
DESCRIBE the advantages and disadvantages of using gas proportional counters.
IDENTIFY the common errors in gas proportional counting data.
DEFINE self-absorption as it applies to alpha counting data.
EXPLAIN how sample preparation methods can affect counting data.
DESCRIBE the key factors that should be present when reviewing gas proportional counting data.
EXPLAIN the theory of operation of the liquid scintillation counting (LSC) system.
LIST the types of radiation that can be detected by the Liquid Scintillation System.
STATE the advantages and disadvantages of using the LSC system.

IDENTIFY the common errors that may effect the LSC system.

IDENTIFY the key parameters that aid in the interpretation of an LSC system.

EXPLAIN the theory of operation of the gamma spectroscopy system.

LIST the type(s) of radiation that can be detected by the gamma spectroscopy system.

STATE the advantages and disadvantages of the gamma spectroscopy system.

IDENTIFY the common errors that occur in gamma spectroscopy analysis.

DESCRIBE the key identification factors that should be present when reviewing gamma spectroscopy data.
Objective Review

EXPLAIN the theory of operation of the alpha spectroscopy system.

LIST the types of radiation that can be detected by the alpha spectroscopy system.

STATE the advantages and disadvantages of alpha spectroscopy.

IDENTIFY the common errors that may affect alpha spectroscopy data.

IDENTIFY which key conditions should be present to aid in the interpretation of an alpha spectrum.
Radiochemical Statistics and Quality Performance Indicators

Given formula for radiochemical calculation, DEFINE the following terms that are associated with each:

- Activity
- Efficiency
- Background
- Counts
- Recovery
- Attenuation
- Radioactive decay constant

IDENTIFY five general types of errors that can occur when analyzing radioactive samples, and DESCRIBE the effect of each source of errors on sample measurement.
Objective Review

Given a list of quality performance indicators, IDENTIFY how errors occur in each of the following:

- Radiochemical processing excursions
- Source preparation excursions
- Instrument-related excursions
- Other potential causes of excursions

DESCRIBE the difference between the minimum detectable activity (MDA) and the lower limit of detection (LLD), and EXPLAIN why each is important.
Introduction to Radiochemistry – A Historical Background

- Radiochemistry has its roots in the discovery of x-rays in 1895 by Wilhelm Conrad Roentgen.
- This information was further investigated by Henri Becquerel, who theorized that uranium salts could emit x-rays if they were exposed to light.
- The Curies went on to discover radium, thorium, and polonium, giving the name “radiation” to the energies that emanated from these compounds.
- The Curies’ daughter Irene and her husband Frederick Joiliot continued the research, producing medical isotopes.
Wilhelm Conrad Roentgen
Henri Becquerel
Marie and Pierre Curie
Irene and Frederic Joliot-Curie
Modern Day Contributors to Radiochemistry

After the discoveries of radium and x-rays, interest in the newly discovered science of nuclear physics increased.
In the 1930s, University of California at Berkeley physicist Ernest Lawrence developed an accelerator. This accelerator produced high-energy particles required for atomic disintegration. The original could fit in the palm of a human hand. Called the “calutron,” it was later modified to separate $^{235}$U that was used to build the uranium bomb.
Y-12 Calutron, Oak Ridge National Laboratory
Enrico Fermi

- By 1938, Fermi was the authority of neutrons.
- Noted that slow neutrons could cause a chain reaction in fissionable materials.
- Coordinated the first controlled chain reaction in Chicago.
- Along with Szilard and Einstein, authored a letter to FDR concerning the race to make the bomb before the Nazis.
- This was the beginning of the Manhattan Project.
- Travelled to Hanford in 1944 to place the first U slug in B reactor.
Glenn Seaborg, “Father of the Actinides”

- In 1941, led the research on the isolation of plutonium.
- Joined the Manhattan Project, and led the research to obtain enough plutonium to build a bomb.
- Two researchers under Seaborg developed the plutonium retrieval process known as PUREX.
- This plutonium was used in the Nagasaki bomb.
- Discovered Am and Cm, implemented changes to Periodic Table to include the actinides.
- Element 106, Seaborgium, is named in his honor.
Timeline of Events

- 1895: Wilhem Roentgen discovers X-rays
- 1898: Curies discover Po and Ra Th with Becquerel
- 1934: Joliot-Curies Artificial Radiation
- 1941: Seaborg discovers Pu
- 1942: Chicago Pile I critical
- 1944: B Reactor Critical
- 1945: Trinity Los Alamos
- August 15, 1945: Fat Man is dropped on Nagasaki
- Aug 6, 1945: Little Boy is dropped on Hiroshima
- September 1945: Japan surrenders End of WWII
- 1896: Henri Becquerel discovers radioactivity with the Curies
- 1939: Szillard -Einstein Letter
Correlations between the Properties of Elements and Their Atomic Weights - 1869

- Listed elements by relative atomic weights
- Proposed changes based on the concept of valence
- First valences assigned were hydrogen and oxygen
- Based on the stoichiometric amounts of hydrogen and oxygen in water
- Hydrogen 1 and Oxygen 2
# Periodic Chart, 1871

<table>
<thead>
<tr>
<th>Period</th>
<th>Group</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
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<td>?Yt=88</td>
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<td>Y</td>
<td>Zr</td>
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</table>

**Figure 8.—Werner’s Periodic Table**
Modern Periodic Chart
Chart of the Nuclides

Layout

- Each nuclide occupies a square in a grid where:
  - The atomic number Z is plotted vertically
  - The number of neutrons N is plotted horizontally

- *Each row represents a single element; each vertical column shows nuclides with the same number of neutrons.*

- The heavily bordered square at the left of the table is the *most common state of the element.*

- This is the same value found in the Periodic Chart.

- The rest of the row lists the *nuclide*:
  - Chemical symbol – Mass Number (e.g. C-14)
Chart of the Nuclides

- First developed by Fea in 1935.
- Segre published an updated version in 1946.
- General Electric published the first version of the current style in 1946.
- Primary change over the initial version:
  - Protons are vertical axis
  - Neutrons are horizontal axis
Tri-Linear Chart of the Nuclides

- Unlike the squares on the traditional chart, uses hexagons for the isotopes.
- First developed in 1957 by W.H. Sullivan.
- The example shows that isobars (nuclides with the same mass number) are arranged in a vertical line.
- The latest version of the Tri-Linear Chart of the Nuclides was published in 2005 by the Radiochemistry Society.
W.H. Sullivan’s Tri-Linear Chart of the Nuclides
Colors and Shading

Stable Nuclide

Ru 98
1.87

Tc 99
6.006h
2.13E5a

Long lived, naturally occurring but radioactive

C 14

Artificially radioactive

Cf 253
17.8 d

Two isomeric states, both radioactive
Element or Nuclide?

Common state of the element

Nuclide of the element
All of the stable nuclides fall along the line of stability.

As the neutron number increases, the further the nuclide falls from the line.

N to Z ratio for nuclides Z < 80 1:1.

As the N to Z approaches 80, the ratio becomes 1:1.5.

That is why there are no stable nuclides > Z = 80.

Nuclides below and to the right: negatron decay.

Nuclides above and to the left: positron decay or EC.

Nuclides in the upper-right hand region: alpha decay.
“Magic Numbers”
Modes of Decay: Alpha

- Reduction in:
  - Mass (A) by 4
  - Atomic number (Z) by 2
- Alpha particle is the size of He nucleus.
- Prominent modes of decay for:
  - Proton-rich nuclides \( A \geq 160 \)
  - Neutron-rich nucleus \( A \geq 211 \)
Modes of Decay: Beta

- A nucleus undergoing beta decay emits nuclear electrons.
- Positron decay, $\beta^+$, is associated with a particle known as a neutrino, $\nu$, which helps in the conservation of momentum and energy.
- Negatron decay, $\beta^-$, has the associated anti-particle, the anti-neutrino, $\bar{\nu}$, to accomplish the same function.
- Positron decay adds 1 to the Z number.
- Negatron decay subtracts 1 from the Z number.
Modes of Decay: Electron Capture

- Also known as \( k \)-capture.
- Excess protons in the nucleus interact with an inner shell electron (\( k \)-shell), combining to form a neutron and a neutrino.
- Characteristic x-rays are also produced.
- \( Z \) number is reduced by 1.
Modes of Decay: Gamma

- High-energy electromagnetic radiation that originates in the nucleus.
- Normally associated with:
  - Alpha
  - Beta
  - Electron capture
- Provides a method for nuclides decaying by the other modes to dissipate energy to return to ground state.
Decay Schemes and the Chart of the Nuclides
Spontaneous Fission (SF)

- Rare except in very heavy nuclei.
- Normally occurs in atomic number around 100 amu.
- Rate increases measurably when the atomic number is > 230.
- Two naturally occurring nuclides are subject to SF:
  - Niobium 93
  - Molybdenum 94
- Although subject, has never been observed.
- Thorium 232 has left evidence of SF.
Nuclear or Induced Nuclear Fission

- Occurs when a thermal (slow) neutron is absorbed by a nucleus.
- Normally a “man-made” reaction.
- Nucleus splits into smaller lighter fragments - AMU between 95 and 140.
- Produces free neutrons, gamma radiation, and a large amount of energy.
- Process is used in commercial and naval power reactors.
- The production of neutrons is moderated (slowed) so that the chain reaction may be controlled.
Fission Fragment Yield Curve: Nuclear Fission
Complexation Reactions in Radiochemistry

- Formation of compounds that share a set of electrons.
- Known as ligands, these can take several forms:
  - Anionic compounds of Br, I, Cl, N, S
  - Organic compounds: acetates, citrates
  - Chelates
- Reactions are based on the valence of the metal ion.
- Provides a method to isolate a particular nuclide.
Complexation Examples

Plutonium complexes

18-Crown-6 Np$^{+4}$ complex
Metal-chelant Complexes
EDTA and Ca-DPTA
## Some Common Ligands

<table>
<thead>
<tr>
<th>Ligand Type</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Unidentate</strong></td>
<td>Water ($\text{H}_2\text{O}$), halides ($\text{X}^{-1}$), hydroxide ($\text{OH}^{-1}$), ammonia ($\text{NH}_3$), cyanide ($\text{CN}^{-1}$), nitrite ($\text{NO}_2^{-1}$), thiocyanate ($\text{SCN}^{-1}$), carbon monoxide ($\text{CO}$)</td>
</tr>
<tr>
<td><strong>Bidentate</strong></td>
<td>Oxalate, ethylene diamine, citrate</td>
</tr>
<tr>
<td><strong>Tridentate</strong></td>
<td>Diethylene triamine, 1,3,5 traiminocylohexane</td>
</tr>
<tr>
<td><strong>Polydentate</strong></td>
<td>8-hydroxyquinolone, β-diketones, (thenoyltrifluoroacetone [TTA], ethylene diaminetetraaceticacid (EDTA), diethylenetriaminepentaaceticacid (DPTA)</td>
</tr>
<tr>
<td></td>
<td>Organophosphate: (octyl(phenyl)-N,N-diisobutylcarbamoyl-methylphophine oxide [CMPO]); tributylphosphosphate (TBP), trioctylphosphinic oxide (TOPO), quartenary amines (tricapryl-methylammonium chloride [Aliquat-336®], triisoctylamine (TnOA), tri-n-octylamine (TnOA), macrocyclic polyethers(crown ethers such as [18]-crown-6), cryptates</td>
</tr>
</tbody>
</table>
Precipitation Reactions

- Used to collect a specific radionuclide from other ions in solution by the formation of an insoluble compound
- Based on solubility
- Factors that affect precipitation reactions include:
  - Rate of precipitation
  - Temperature
  - pH
  - Solvent polarity
Solvent Extraction

- Process of selectively removing a solute from a liquid mixture with a solvent.
- Portioning process between two immiscible solvents:
  - Water and an organic solvent
- Solvents are shaken and allowed to separate.
- Layer that contains the desired ion is retained.
- Solvent can be back-extracted for further purification.

PUREX process
Ion Exchange

- The reversible exchange of charged ions, either cations or anions, between a liquid phase and a solid phase (resin).
- Solutions containing ions are passed through the resin.
- The metal ion exchanges with one of the counter-ions on the resin.
- The metal ion is held by the resin; counter-ion becomes part of the solvent.
- Most resins are polymers that contain sulfonate anion or carboxylate anions (cation resins) or the quaternary amine cation (anion resin).
- The ions are selectively retained by the resin, based on valence.
- Specially designed resins are available for the lanthanides/actinides.
Ion Exchange

Example of a typical anion resin with the quartenary amine functional group.

Example of a typical cation resin with sulfonate functional groups.
Radiochemical Carriers

- Used to separate and determine radionuclides present in extremely small quantities.
- Since most analyses are performed on larger scale, it is important to obtain enough of the material to analyze.
- Accomplished by adding a material that is different in isotopic makeup but similar or identical in chemical makeup.
- For example, stable barium is used as a carrier for $^{140}$Ba and stable strontium is used for $^{90}$Sr.
- An example of a non-isotopic carrier, stable barium is used as a carrier for radium.
### Common Radiochemical Tracers

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Tracer</th>
<th>Method of Detection</th>
<th>Issues</th>
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</thead>
<tbody>
<tr>
<td>$^{89}\text{Sr}/^{90}\text{Sr}$</td>
<td>$^{85}\text{Sr}$</td>
<td>Gross $\gamma$</td>
<td>Can be used for yield determination as long as $\gamma$ is accounted for in $\beta$ analysis</td>
</tr>
<tr>
<td>$^{99}\text{Tc}$</td>
<td>$^{99m}\text{Tc}$</td>
<td>Gross $\gamma$</td>
<td>Allow for $^{99m}\text{Tc}$ decay before analysis for $^{99}\text{Tc}$</td>
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<tr>
<td>$^{230,231}\text{Th}$</td>
<td>$^{229}\text{Th}$</td>
<td>$\alpha$-spec, ICP-MS</td>
<td>None</td>
</tr>
<tr>
<td>$^{234,235,238}\text{U}$</td>
<td>$^{232}\text{U}/^{233}\text{U}$</td>
<td>$\alpha$-spec</td>
<td>$^{232}\text{U}$ decays to $^{228}\text{Th}$ and must be accounted for with $\alpha$-spec</td>
</tr>
<tr>
<td>$^{238}\text{Pu}$</td>
<td>$^{242,236}\text{Pu}$</td>
<td>$\alpha$-spec</td>
<td>$^{236}\text{Pu}$ decays to $^{232}\text{U}$</td>
</tr>
<tr>
<td>$^{241}\text{Am, Cm}$</td>
<td>$^{243}\text{Am}$</td>
<td>$\alpha$-spec</td>
<td>Nuclides display similar behavior</td>
</tr>
</tbody>
</table>
Examples of Yield Tracers

- $^{235}\text{U}$ with 4.4 MeV
- $^{236}\text{U}$ with 4.2 MeV
- $^{238}\text{U}$ with 4.8 MeV

Tracer $^{232}\text{U}$ with 5.3 MeV

Plutonium isotopes:
- $^{242}\text{Pu}$
- $^{239,240}\text{Pu}$
- $^{238}\text{Pu}$

Graph showing counts per channel and intensity in counts per second (cps).
When attempting to choose a carrier or tracer for a radioactive analysis, there is no ideal choice.

Due to the nature of radioactive materials, the following issues have an effect:

- **The availability of a suitable isotope**: Many radioisotopes do not have a stable isotope.
  - Example: Using $^{243}$Am for $^{241}$Am or $^{239}$Am

- **Impurities that exist in the tracer**: It is difficult to obtain tracers that do not contain radionuclide or radiochemical impurities. *Radionuclide contamination* is nuclides other than the desired nuclide; *radiochemical impurities* is the nuclide in an undesirable chemical form.
Radiation Counting Systems
Gas Proportional Counting System

- Based on the number of ionizations produced when a decay particle interacts with a gas molecule.
- The higher the charge, the more interactions per distance travelled.
- Alpha particles have the highest charge, gamma the lowest.
- Gases with high electron densities also increase the number of ionizations per unit travel.
Ionization Detection

Practical Gaseous Ionisation Detection Regions

This diagram shows the relationship of the gaseous detection regions, using an experimental concept of applying a varying voltage to a cylindrical chamber which is subjected to ionising radiation. Alpha and beta particles are plotted to demonstrate the effect of different ionising energies, but the same principle extends to all forms of ionising radiation.

The ion chamber and proportional regions can operate at atmospheric pressure, and their output varies with radiation energy. However, in practice the Geiger region is operated at a reduced pressure (about 1/10th of an atmosphere) to allow operation at much lower voltages; otherwise impractically high voltages would be required. The Geiger region output does not differentiate between radiation energies.

Variation of ion pair charge with applied voltage

Charge collected – log scale

Voltage applied – linear scale

Experimental set-up of a cylindrical chamber

Cylindrical chamber with end window subjected to ionising radiation

Low-penetrating radiation enters via an end window, but high-penetrating radiation can also enter via the cylinder side wall.
Effects of Cross-Talk and Self-Absorption on Counting

- Pulse height discrimination is affected by:
  - Cross-talk
  - Self-absorption
- Can occur when:
  - Sample too dense
  - High-energy alpha/beta emitters
- Can be minimized by:
  - Adjusting pulse height discriminators
  - Adequate sample preparation
  - Knowledge of the nuclides present in the sample
  - Sample matrix
Self-Absorption Due to Source Thickness
Cross-Talk and Self-Absorption

- Cross-talk occurs when the detector is unable to discriminate the source of the pulse.
  - Occurs when samples contain high-energy beta and alpha particles.
  - These energies may bleed over to the alpha energy spectrum.
- Self-absorption occurs when alpha and low-energy beta particles are shielded when the sample is:
  - Too dense
  - Has an uneven surface
- While self-absorption can be controlled by the chemist, cross-talk is solely a detector function.
- To avoid cross-talk, the pulse height discriminators can be set based upon:
  - Knowledge of the samples being counted
  - Matrix that the radionuclide are presented in
Alpha-Beta Voltage Discrimination
Typical Liquid Scintillation Counting System

- Does not rely on ionization to provide information
- Used to count beta emitters
- Is not affected by:
  - Self-absorption
  - Backscattering
  - Loss of activity due to spattering
- Has benefits of:
  - Higher detector efficiency
  - Shorter sample preparation times
  - Shorter counting times
Liquid Scintillation Counting Systems

- Primarily used for:
  - Low-energy beta emitters
  - Volatile samples

- Can be used for alpha emitters, with reservations.

- Alpha particles give up all of their energy in a very short distance.

- Efficiency is high (99%), but poor resolution.

$^{241}$Am peak indicating poor resolution
How Scintillation Fluors Emit Light

- One method that particles lose energy is by causing excitation of the surrounding matter.
- Liquid scintillation counting relies on the transfer of energy to the solution component.
- These transfers are called eximers.
- The higher the kinetic energy, the more eximers.
- The eximers excite fluors in the solution which emit light at a larger wavelength.
- The fluors are in scintillation solution, mixed with an organic solvent.
Coincidence Counting in Liquid Scintillation Counting

- Once the sample has been prepared with the cocktail and placed in the vial:
  - Place the sample in the instrument
  - Care should be taken to avoid fingerprints on the vial!
  - Fingerprints will affect results
- The sample is placed between the PMTs.
- More than one fluor is produced per decay.
- PMTs pick up 100% of the pulses.
- If both PMTs detect flashes in a certain time frame, this synchronous detection is called coincidence counting.
Quench and Liquid Scintillation Counting

- Any process that interferes with the energy transfer of the radioactive decay particle to the fluor is called “quenching”.
- Using the correct sample to fluor volume provides the maximum response.
- From this, the analyst can establish a quench curve.
Three Major Forms of Quenching

- Three forms of quenching:
  - Physical, Chemical, and Color
- Physical: suspended solid/opaque materials
- Chemical: Materials that interfere with the process energy transferring to the fluor
- Color: Absorption of the fluor by colored materials in the sample
Key Parameters for Interpretation of LSC Spectrum
Gamma Spectroscopy System
Radiation Interactions - Photoelectric Effect

- Results when an incident photon transfers all its energy to an inner shell electron of the detector atom.
- All the energy is deposited into the detector.
Radiation Interactions - Compton Scattering

- Results when only part of the incident photon is transferred to an inner shell electron due to an interaction with a target electron.

- This causes part of the energy to be emitted as a recoil electron and the remaining energy as a photon.

- The electron is ejected with its energy minus the binding energy.
Radiation Interactions - Pair Production

- When an incident photon passes near the nucleus, it disappears and in its place a pair of particles (positron and electron), appear.
- The electron will eventually de-energize and join the electron pool.
- If all of the rest mass goes to energy, 0.511 MeV is produced.
- The positron is also equivalent to 0.511 MeV.
- Given the fact that no other fractional particles exist, the minimum energy of the incident photon must be 1.022 MeV.
- If the kinetic energy of the positron is lowered, it can annihilate or combine with an electron.
- This produces two photons of 0.511 MeV each.
Types of Gamma Detectors

- Scintillation detector
- Semi-conductor detector
HPGe and Scintillation Detectors
Cooling and Semi-Conductors

- At higher temperatures, the electrons can easily cross the band gap in the crystal and reach the conduction band where they are free to respond to the electric field.
- This produces an excess of electrical noise that limits the detector’s usefulness as a spectrometer.
- Cooling to liquid nitrogen temperature (77 K) reduces thermal excitations of valence electrons.
- This ensures that only a gamma ray interaction can give an electron the energy necessary to cross the band gap and reach the conduction band.
## Advantages/Disadvantages of Gamma Detectors

### Semi-conductor type

**Advantages:**
- High resolution
- Shorter response time and better linear energy response than NaI
- Better resolution

**Disadvantages:**
- Need for cryogenic cooling
- High environmental count times

### Scintillation type

**Advantages:**
- Operate at room temperature, no cooling required
- Portable, more economical to operate

**Disadvantages:**
- Poor peak resolution compared to semi-conductors
- Sensitive to electronic and environmental conditions
Primary Advantage of Using Gamma Spectroscopy

- Three factors that determine how a spectrum will appear:
  - Detector material: NaI or HPGe
  - Detector size
  - Photon energy
- Smaller crystals offer higher resolution but lower efficiency
- HPGe offers better resolution than NaI
- Photon energy will dictate the interactions with the detector:
  - Photoelectric effect
  - Compton scattering
  - Pair production
Gamma Spectroscopy

Errors

- Two distinct areas:
  - System performance
  - Interpretation of the spectrum itself
- Most system errors are due to electrical or mechanical effects
  - Random sum peaks are a function of sample geometry/detector efficiency
  - Presence of escape peaks are a function of detector material
  - Multiplet and interference peaks are a function of the FWHM
- Spectrum interpretation are a function of:
  - Temperature
  - Vibration
  - Low nitrogen levels
  - Voltage shifts
Key Considerations for Gamma Sample Preparation

- Both liquid and solids can be counted using gamma spectroscopy.
- Key considerations for samples:
  - Geometry
  - Size
  - Homogeneity
- Efficiency can be increased by:
  - Reducing size of liquid samples
  - Evaporation
  - Co-precipitation and filtration
  - Concentration on resin
Commercially Available Alpha Spectroscopy System
Typical Alpha Spectrum
Summing of $^{239}$Pu and $^{240}$Pu Peaks
Unique Issues in Counting Alpha Emitters

- The problems with counting alpha emitters stem from the very nature of alpha particles.
- Detector contamination can occur from the escape of the daughter nuclides from the sample.
  - As the alpha decays, its radioactive daughters escape the sample.
  - This "recoil" strikes the detector, causing contamination.
- If pulse height discriminators are not used, beta particles may interfere.
  - This is the "cross talk" between the beta and alpha channels.
- To compensate for these issues, the analyst should:
  - Generate a cross talk curve to account for beta.
  - Perform self-absorption corrections to ensure the efficiency is not affected by sample thickness or mass.
Alpha-Beta Cross Talk
Sample Preparation of Alpha Emitters

- Since alpha emitters are unique in the way that they travel, the size of the particle must be chemically separated for analysis.

- Care must be taken to ensure:
  - The samples that are precipitated are dry prior to counting.
  - The samples are not too dense or have an uneven surface.
    - Dense or uneven surface samples can cause self-absorption issues.
Effects of source thickness on resolution
Common Errors that may affect Alpha spectroscopy data

Alpha counting poses unique problems:

- Sample matrix
  - Soils
  - Air filters
  - Water
  - Biological samples
- Require sample treatment
  - Sample thickness
  - Sample dryness
  - Cross talk
Differentiation of the Origin of an Alpha

- Alpha radiation is very distinctive, making it easy to identify.
- Only one alpha per emission; may have different energies.
  - $^{239}$Pu has four different alpha energies
  - $^{240}$Pu has two different alpha energies
    - The six energies differ by only 64 KeV
- Spectroscopy systems for alpha counting must be able to:
  - Discriminate between alpha and beta
  - Discriminate between individual isotopes
- We use regions of interest (ROI) to look at a single energy.
- This is aided by the separation techniques that are used to isolate alpha emitters (with the exceptions noted above).
Radiochemical Concepts and Definitions

- Activity
- Efficiency
- Background
- Counts
- Recovery
- Attenuation
- Radioactive decay constant
- Detection Limits
Sample Activity

- $A = \frac{CPM}{2.22E6/V/Eff/%Rec}$

- For example:

A radioactive sample is counted and contains 4000 counts in 10 minutes. The background counts for the same time is 25. 0.5 mL of sample was used. The instrument efficiency is 0.85 and the sample had 95% (0.95) analysis recovery.

Therefore:

$CPM = \frac{(4000-100)}{10}$ or 390 cpm

$390 \text{ CPM} / 2.22E6 / 1 \text{ mL} / 0.85 / 0.95$

$A = 2.18E-04 \text{ uCi/mL}$
Half-Life

What is the half life of this sample?

1. Choose an activity from the Y axis that is easy to halve.
2. Using colour coding to avoid confusion, draw a line from that point on the Y-axis until it reaches your plotting line.
3. Take your coloured line vertically down to the X-axis.
4. Do the same for an activity of half the value.
5. Find the time interval between your coloured lines.
6. Repeat the whole process in a different colour for different values at least once.
7. Average the results.

LOJ (1998)

Time taken for the activity to halve from 30000 Bq to 15000 Bq

Time taken for the activity to halve from 20000 Bq to 10000 Bq

7 mins
Counting Efficiency

\[
\frac{\text{CPM} \times 100}{\text{DPM}} = \% \text{ Counting Efficiency}
\]

Where: CPM is counts per minute
DPM is disintegrations per minute
Sources of Background Radiation
Count Rate Determination

\[ R_2 = \frac{2300 \text{ counts}}{100 \text{ s}} - \frac{100 \text{ counts}}{10 \text{ s}} = 23 \text{ cps} - 10 \text{ cps} = 13 \text{ cps} \]

\[ \sigma_{R_2} = \sqrt{\frac{23}{100} + \frac{13}{10}} = 1.2 \text{ cps}. \]

\[ R_2 = 13 \text{ cps} \pm 2.4 \text{ cps} \]
Recovery of Matrix Spike

\[ \%R = \frac{\text{Observed value}}{\text{True value}} \times 100 \]
Attenuation

- Defined as the slowing down of a radioactive particle or gamma ray as it passes through material.
- This slowing down refers to the failure of the ray or particle to avoid interacting with the absorber.
- The intensity of the energy, the type of absorber material and its thickness affect attenuation.
Radioactive Decay Constant

“The number of atoms in a sample or the activity decreases exponentially with time.”

\[ A(t) = A(0)e^{-\ln(2)t/T_{1/2}} \]

Activity calculation using half-life
Detection Limits – MDA and LLD

- Refers to the statistically determined quantity of radiation that can be measured or detected at a set confidence level.

- Two detection limits that are commonly used in counting statistics are:
  - Lower level of detection (LLD)
  - Minimum detectable activity (MDA)

- MDA should be as low as practical, and can be reduced by:
  - Collecting larger sample volumes
  - Reducing the background
  - Longer count times
  - Increased counter efficiencies

- LLD refers to the smallest detectable activity by an instrument and is dependent on:
  - Instrument parameters
  - Total background counts
MDA Calculation

MDA = Bkg cpm + 3x (Bkg)\(^{1/2}\) ÷ t

Example: What is the MDA for a counter with a background of 750 counts in 10 minutes?

MDA = 75 cpm + 3x (750)\(^{1/2}\) ÷ 10 min = 83 gross cpm

Basic math shows that lowering background or increasing time can lower the MDA
Five general sources of error:

- **Self-absorption**: Commonly seen in alpha analysis.
- **Backscatter**: Alpha and high-energy beta analysis.
- **Resolving time**: Known as “dead time,” the time that has to elapse before another full size pulse can be counted.
- **Geometry**: Positioning of the sample in relation to the detector. Poor geometry will affect counting efficiency.
- **Random disintegration of radioactive atoms**: Radioactive decay itself is a random event; the use of statistics aids in reporting the effects of these effects.
Radiochemistry Analysis Errors

- Reagent purity questionable
- Human performance-related issues:
  - Lab blunders and process issues
  - Low carrier or tracer recovery
  - Excessive tracer or carrier recovery
  - Inadequate aliquot
  - Cross contamination of sample, glassware, equipment
  - Sample not dissolved or solution not homogeneous
Source Preparation Errors

- Improper geometry
- Improper sample mounting
- Improper/uneven distribution on planchette
  - Self-absorption
- Quench (discoloration)
Source Preparation Errors

- Geometry
- Recoil contamination
- Quench
Instrument Related Excursions

- Electronic malfunctions of:
  - ADC
  - High voltage
  - Pre-amplifier

- Improper geometry
- Peak shift or poor detector resolution
- Out of calibration
- Contamination
Other Potential Causes of Excursions

- Vibrations and temperature
- Interfering nuclides
- Calculation errors
- Software errors

Removal of interfering isotopes
As activity increases, recovery time increases, causing a loss of information.
Waste Sites in the US
Laws Regarding Radioactive Waste

- 40 CFR Part 191 – Federal Regulation
- Atomic Energy Act – 1954
- CERCLA – 1980
- Nuclear Waste Policy Act - 1982
Review

- The Fundamentals of Radiochemistry provides you with the basic information to perform your duties in the lab.
- We will review the learning objectives to ensure understanding.
- If there are any questions, now is the time to ask.
- It is our hope that this course was informative, and will help you in your daily work as a radiochemistry technician.