# Radiochemistry Webinars

## Tritium: Sample Collection, Preservation and Analysis

*In Cooperation with our University Partners*

# Meet the Presenter…                    <sup>Tritium</sup>

*Dr. Robert Litman*

Robert Litman, PhD, has been a researcher and practitioner of nuclear and radiochemical analysis for the past 44 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. He authored the Radionuclides section of the EPRI PWR Primary Water Chemistry Guidelines, and has been a significant contributor to the EPRI Primary-to-Secondary Leak Detection Guidelines. 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. His areas of technical expertise are gamma spectroscopy and radiochemical separations. Dr. Litman has been teaching courses in Radiochemistry and related special areas for the past 31 years. He consults infrequently as he is now retired.

Phone: 603-944-2557

Email:  drbob20@centurylink.net

**EMS**

# Tritium: Sample Collection, Preservation and Analysis

Robert Litman, PhD

**National Analytical Management Program (NAMP)**

TRAINING AND EDUCATION SUBCOMMITTEE

# Formation of Tritium

- A Radioisotope of Hydrogen
- Naturally Occurring
  - Spallation reactions on N, O by high energy solar particles in the upper atmosphere
- Anthropogenic Sources
  - Nuclear fission (about 0.03 atoms per event)
  - Activation of deuterium ($^2H$) in nuclear reactors or particle accelerators
  - Nuclear reaction of neutrons with B and Li in Pressurized water reactors
  - Nuclear detonations in the atmosphere and underground

# Is Tritium a Commercial Radioisotope?

- Yes!
- Mostly used for "betalights' on some equipment
  - Exit signs use tritiated gas
  - Markers on firearms night sights
  - Watch dials
  - Instrument dials
  - D-T neutron generators (a tritium battery)
- An oceanic/environmental tracer based on
  - Currents
  - Vertical water displacement

# Tritium: Natural Distribution in the Environment

- Equilibrium concentration of rainwater
  - Between 10 and 50 pCi/L
- Surface water
  - Will contain in this range
- Groundwater
  - Will have less; depends on turnover with surficial water
- Deep wells
  - With little surface water incursion will have much lower activity concentrations; "Dead" water usually < 1 pCi/L

# Anthropogenic Tritium

- Initial formation as hydrogen radical during fission, neutron activation or accelerator production
- T-T within fuel cladding of reactor
  - Diffuses slowly through fuel clad into RCS
  - Reacts rapidly (free radicals) in RCS to become H-O-T (>90 %)
  - In PWRs diffuses slowly to steam system (~100 % H-O-T)
- Release Mechanisms
  - In BWRs released to offgas system and plant vent
  - In both PWRs and BWRs released to plant vent thru SFP evaporation
  - Steam leaks and releases from both PWRs and BWRs
- Present in the environment as H-O-T

# Diffusion from Spent Nuclear Fuel



Tritium in a Spent Fuel Pool

Radioactive decay, only

Dilution only

$y = -4E-05x + 1.541$
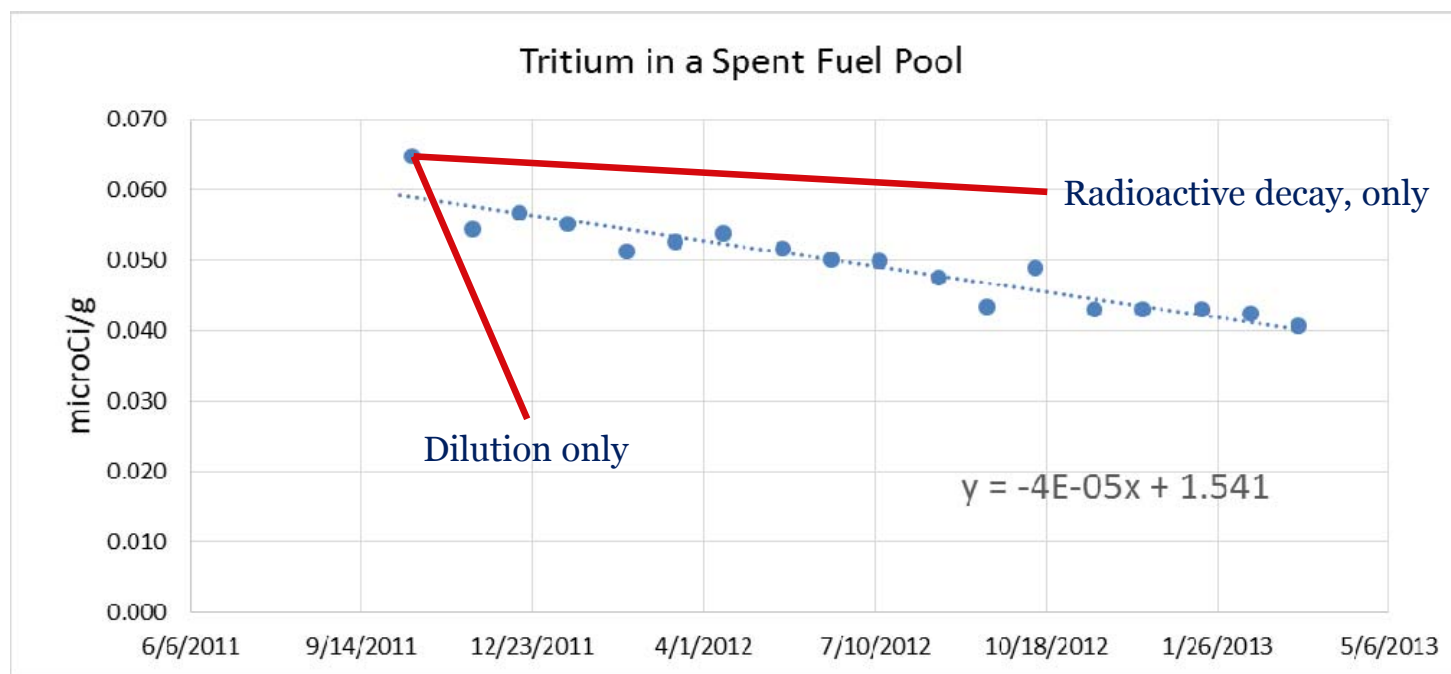
# Tritium in the Environment

- As H-O-T in the environment (100 %)
- Anyplace water goes, H-O-T will go too

- However!
  - As it interacts with the environment it gets diluted rapidly
- When discovered above background
  - Source must have concentration > environment
- Incorporation into biomolecules
  - Organically bound tritium (OBT)
  - In the environment-very, very small due to rapid exchange with $^1$H in water molecules

# Tritium Drinking Water Trend in the US
## 1976-2014
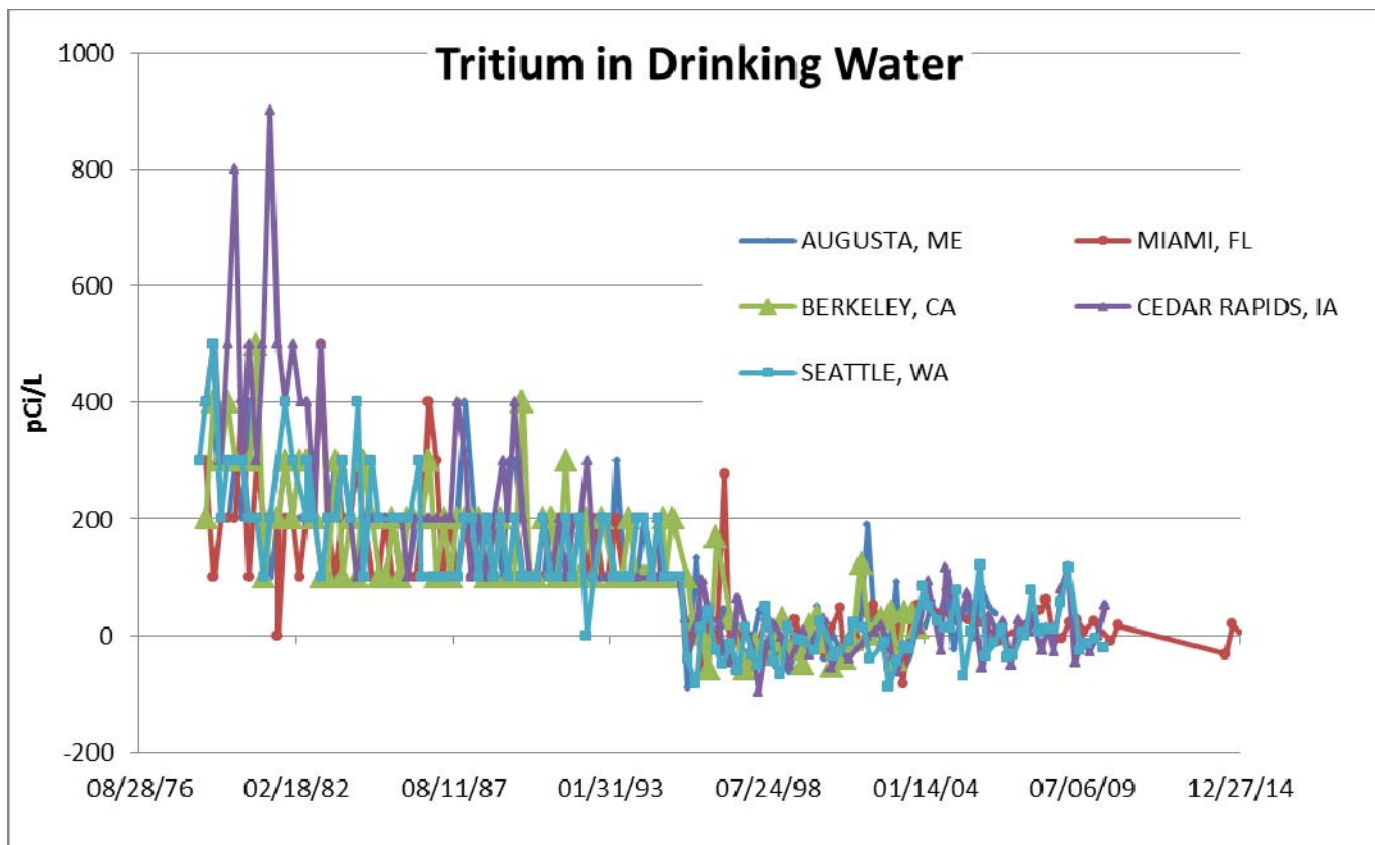
# The Tritium Unit

- The tritium unit (TU)
  - Used to measure migration of water throughout the environment (most frequently water and soil)
  - estimated ratio of $^3H$ atoms to stable $^1H$ prior to weapons testing.
  - Value is set at 1:1 x $10^{18}$ atoms.

# The Tritium Unit

– One TU is equivalent to 3.231 pCi/L of water.

$A = \lambda N$

$= [.693/(12.3 \times 3.15 \times 10^7)][55.6 \text{ Molar} \times 2 \text{ H atoms/mole} \times 6.02 \times 10^{23} \text{ Molecules/mole}]$

$\{1 \times 10^{18} \, ^1H/^3H\}$

$= 3.23 \text{ pCi/L}$

# Tritium in the Environment

Power plant releases

- Up until about 20 years ago -   only thru plant vent or liquid releases

The profile has changed

- Several plant systems have shown unexpected pathways
  – PWR steam systems
  – Spent fuel pool
  – Drift from plant vent to local environment

# Comparison of Tritium, Hydrogen, and Helium

•The figure on the right illustrates the relationship between the isotopes of hydrogen and helium.

•"Common helium" ($^4$He) contains 2 protons and 2 neutrons. The decay product of tritium is an isotope of helium ($^3$He) that contains 2 protons but only 1 neutron.
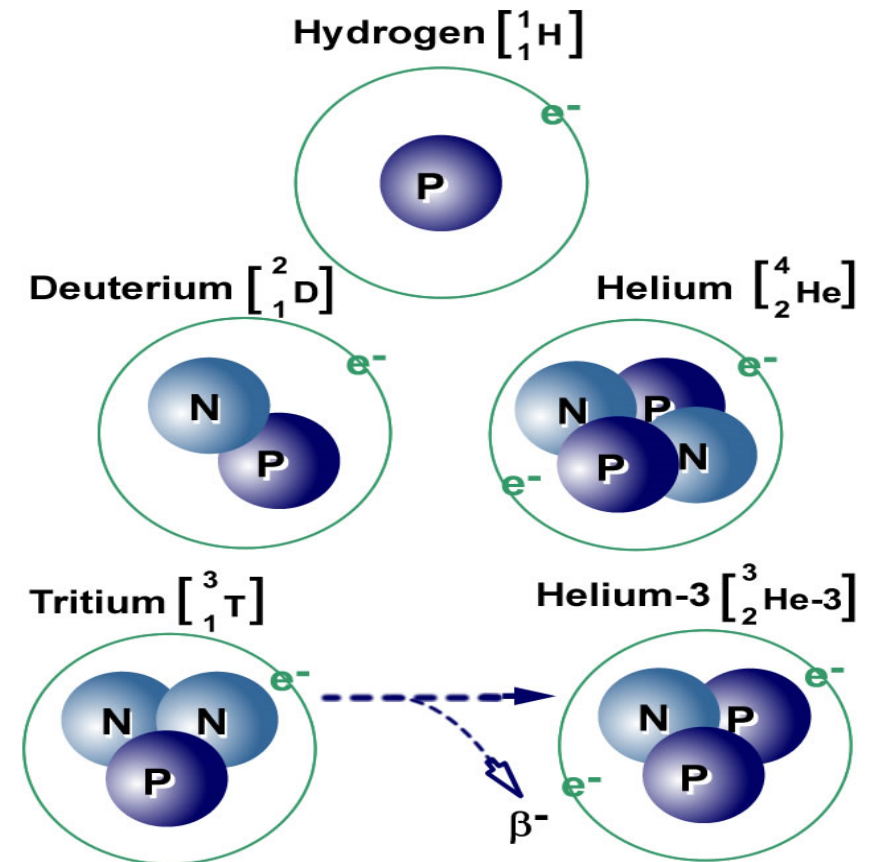
# Atomic vs. Ionic Radii of H and T

•The nuclear radius is on the order of $10^{-15}$ meters while the atomic radius is on the order of $10^{-10}$ meters.

•In the environment, hydrogen and tritium almost always occur as naked nuclei.

•This gives $^3$H (tritium) and $^1$H (stable hydrogen) the unusual ability to migrate freely from one water molecule to another because they are ionically bound.
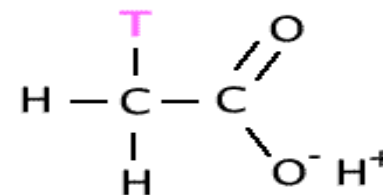


Atomic Radius

Ionic Radius
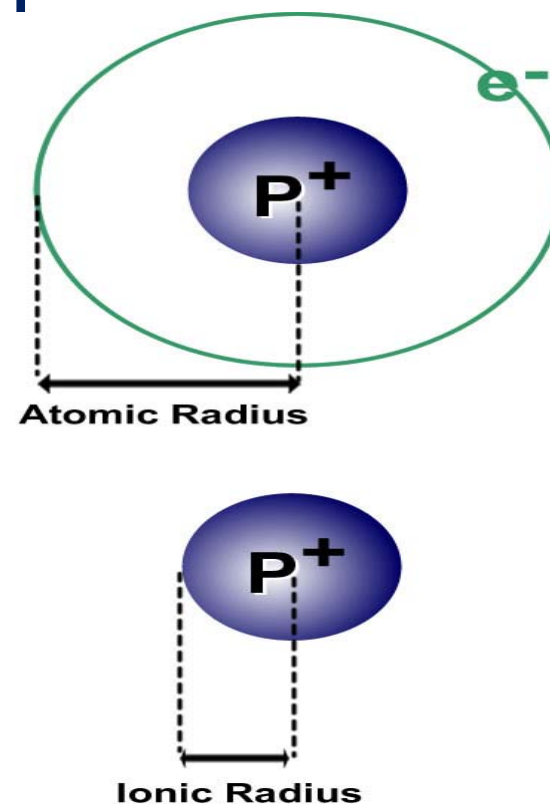
# Tritium Exchange in Ionic vs. Covalent Molecules

- Tritium can exchange with and substitute for hydrogen in most chemical reactions.

- Ionic compounds, T is labile.
- $H^+ + (H\text{-}O\text{-}T) \leftrightarrow H\text{-}O\text{-}H + T^+$

- $T^+ + H\text{-}O\text{-}H \leftrightarrow H\text{-}O\text{-}T + H^+$

- Covalently bound, T is non-labile.

**Tritium in an ionic bond is labile and exchanges easily with hydrogen.**
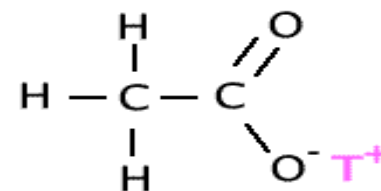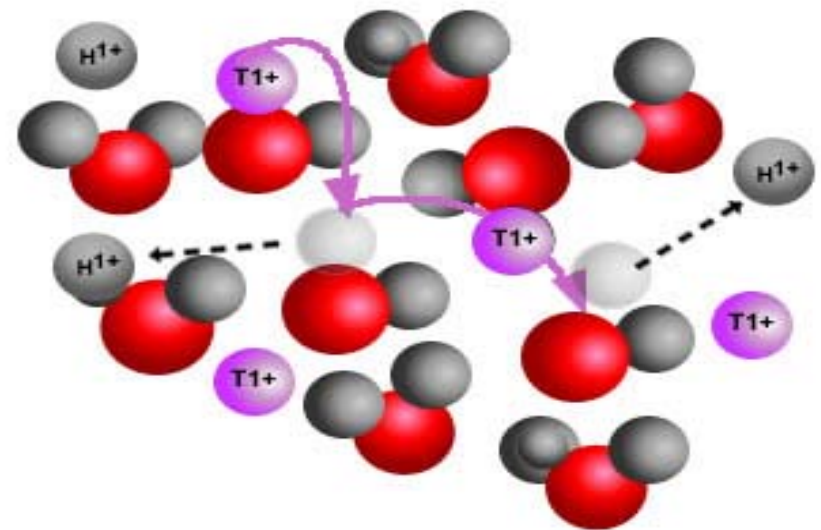
**Tritium in a covalent bond is non-labile.**

# Traveling T!

One tritium ion can quickly jump from water molecule to water molecule by displacing hydrogen ions.

Because tritium bonds, like hydrogen bonds, are so labile, the radionuclide can easily move from molecule to molecule, from air to water to soil and back again, wherever water is present.

# Tritium Goes Everywhere!

•T moves easily and can actually move against the groundwater flow gradient to enter and contaminate the drinking water. For this reason, it is very important to be alert for sources of tritium that can affect groundwater even if it is down-gradient from the water source being examined.
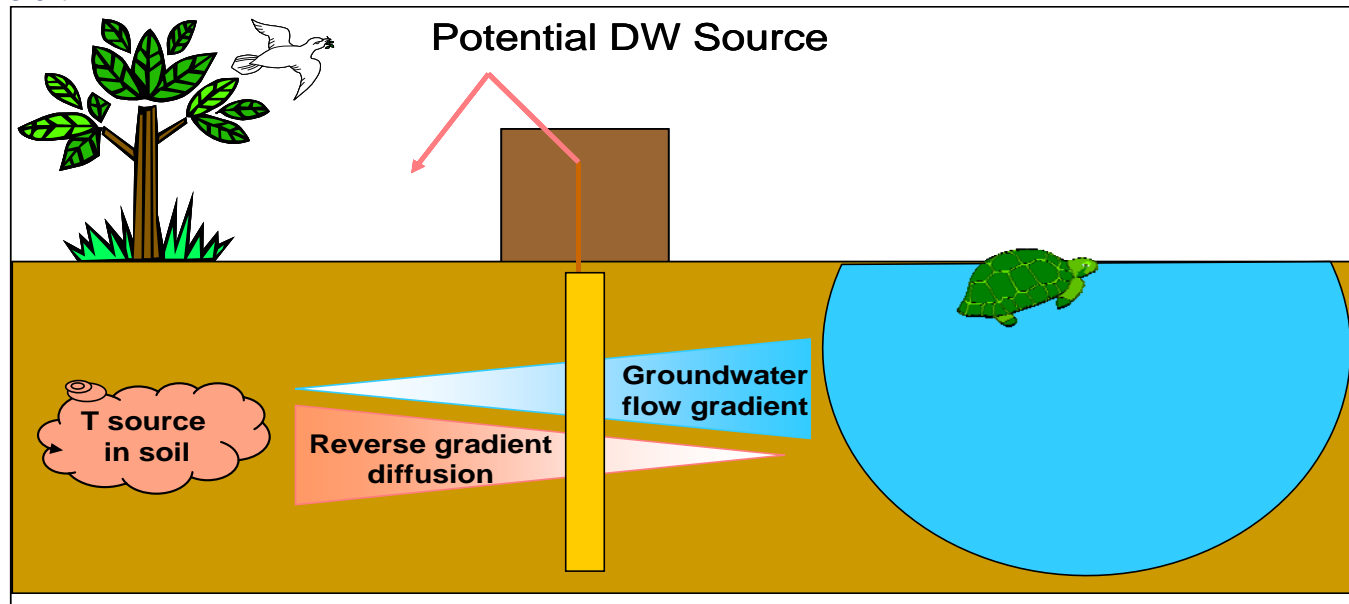
# Radioactive Decay of Tritium

- $t_{1/2}$ = 12.3 years, Beta decay to $^3$He (stable)
- $E_{\beta max}$= 0.018  MeV
- $E_{\beta avg}$= ~0.004 MeV

- Low beta energy - analytical problem with traditional methods
  - Windowless proportional counting
  - Liquid scintillation counting
- Other Methods
  - Atom counting methods
  - Progeny atom counting methods

# Dose Consequence as H-O-T

- Maximum Contaminant Level (MCL):
  - EPA, DW – 20,000 pCi/L - 4 mrem/year
- Derived Intervention Levels (DIL):
  - Foods (some examples from WHO)
    - Cereals 95,000 pCi/kg (~500 mrem/year)
    - Vegetables 135,000 pCi/kg
    - Milk 122,000 pCi/kg
- Air concentration :
  - 150 pCi/m$^3$ at 10$^{-4}$ Risk

# Methods of Analysis (I)
## Atom Counting Methods

# Accelerator Mass Spectrometry
## (solid samples)

- AMS requires a very small sample (less than 1 mg of solid material)
-  Samples are combusted, and tritium reduced to hydrogen gas by reaction with $Ti^0$ to form solid $TiH_2$, the AMS target.
- Level of detection ~$10^{-15}$ g (about 10 pCi/g)
- Useful in tracing tritium flow in regions with tritium source materials such as
  - near nuclear power generating stations, or
  - tritium handling/manufacturing facilities

# Mass Spectrometry
# (low-level analysis)

Low concentrations in solids and liquids

Sample is contained so that the decay gas $^3$He is captured

- After ingrowth of *several weeks*, the gas is introduced into a gas separator purifying the $^3$He and then passed into a mass spectrometer
  - Number of $^3$He atoms - used to calculate number of $^3$H atoms
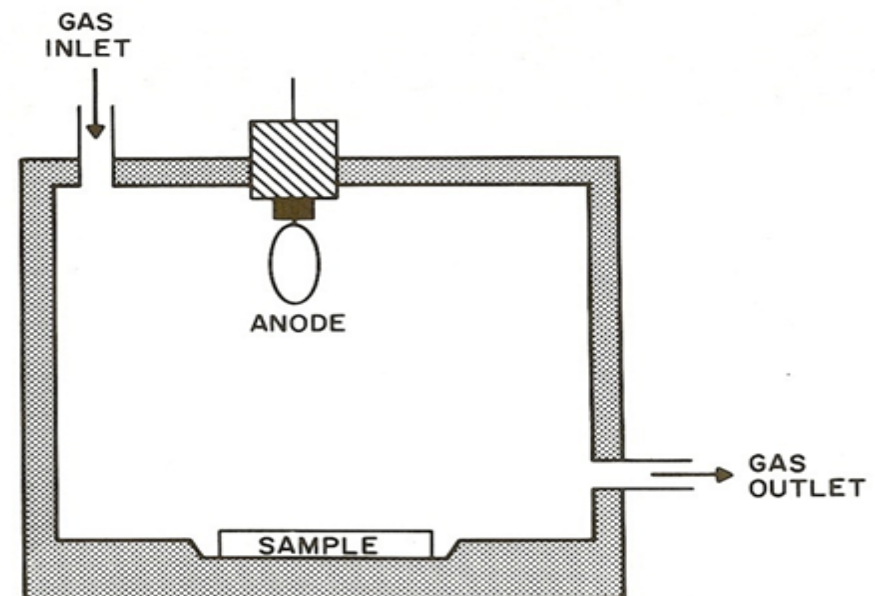  - Decay equation used to calculate activity in the sample

# Methods of Analysis (II)
# Windowless Gas Proportional Counting

# Gas Proportional Counting

- $^3$H by GPC -- 'windowless' Counter
  - $E_{\beta max}$ =0.018 MeV
  - Direct interaction with counting gas
- Sample
  - must be solid
  - Must be infinitely thin

# Methods of Analysis (III)
## Liquid Scintillation

# Liquid Scintillation Counting (LSC) Tritium

- LSC is the oldest, and still most utilized method for tritium analysis
  - Pure beta emitter (no gamma rays emitted)
  - Average beta particle energy, $E_{\beta avg}$ is ~6 keV
  - Most common (environmental) chemical form is liquid (H-O-T)

Tritium

# LSC – Basic Diagram
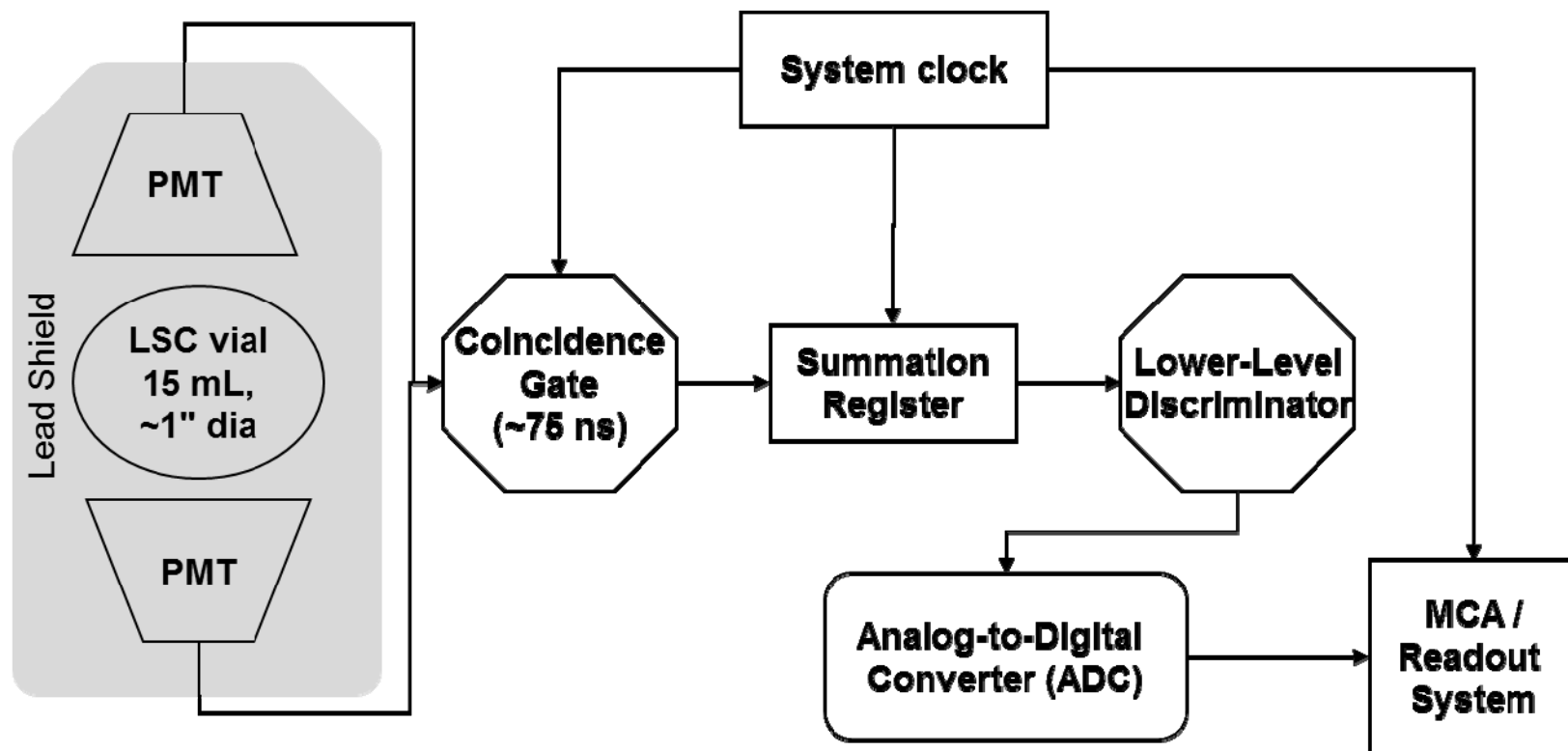
# Advantages of Liquid Scintillation (LSC)

- When a sample is surrounded by the "detector" the counting configuration we call it a $4\pi$ geometry

- LSC detects beta (and alpha) particles with high efficiency
  - Nearly all charged decay particles will be stopped within the scintillation vial (~20 mL volume)
  - The sample is intimately mixed with scintillation cocktail which acts as the primary radiation detector
  - The decay particles will interact with the "detector" almost 100% of the time!

# Liquid Scintillation Spectrometry
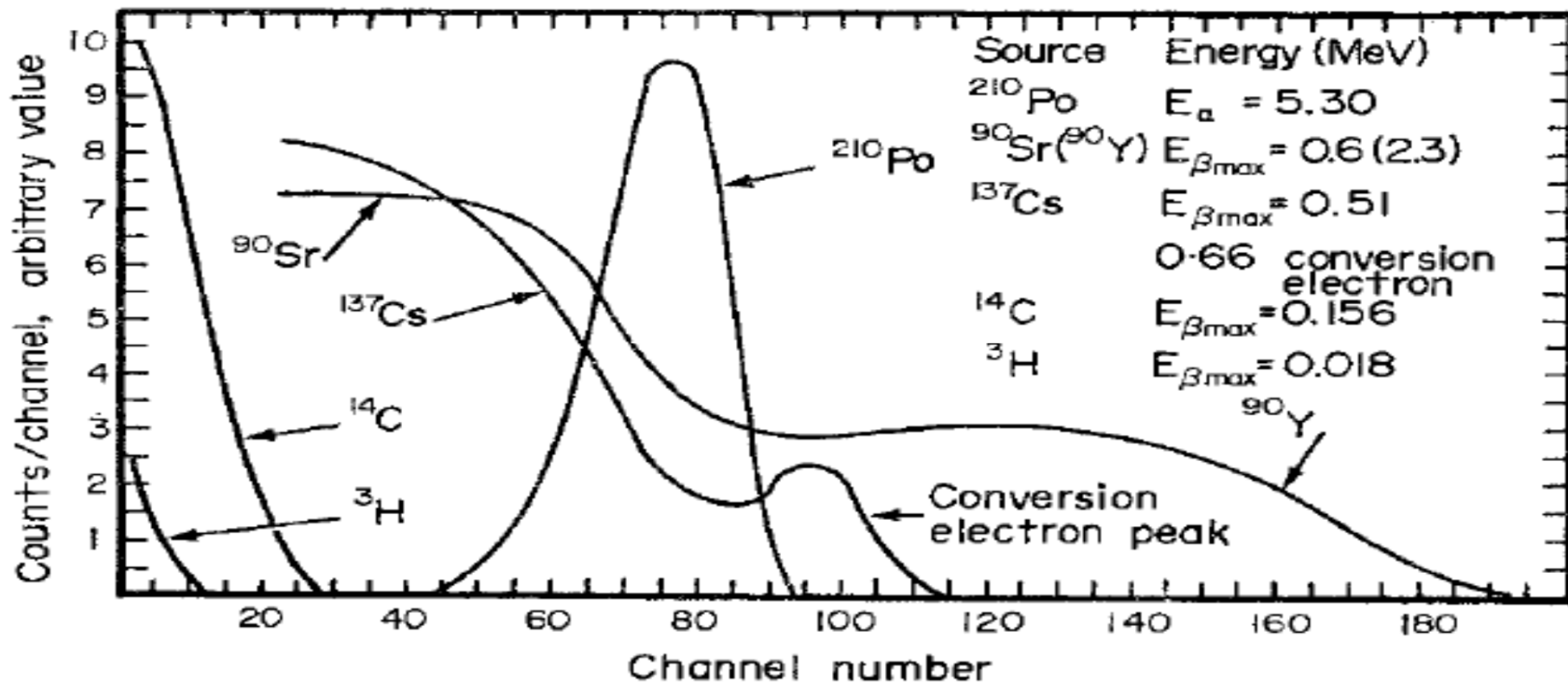
# Beta Particle Distribution

**T Beta Energy Distribution**

Population

$E_{\beta avg} = \sim 1/3\ E_{\beta max}$

Energy, kev
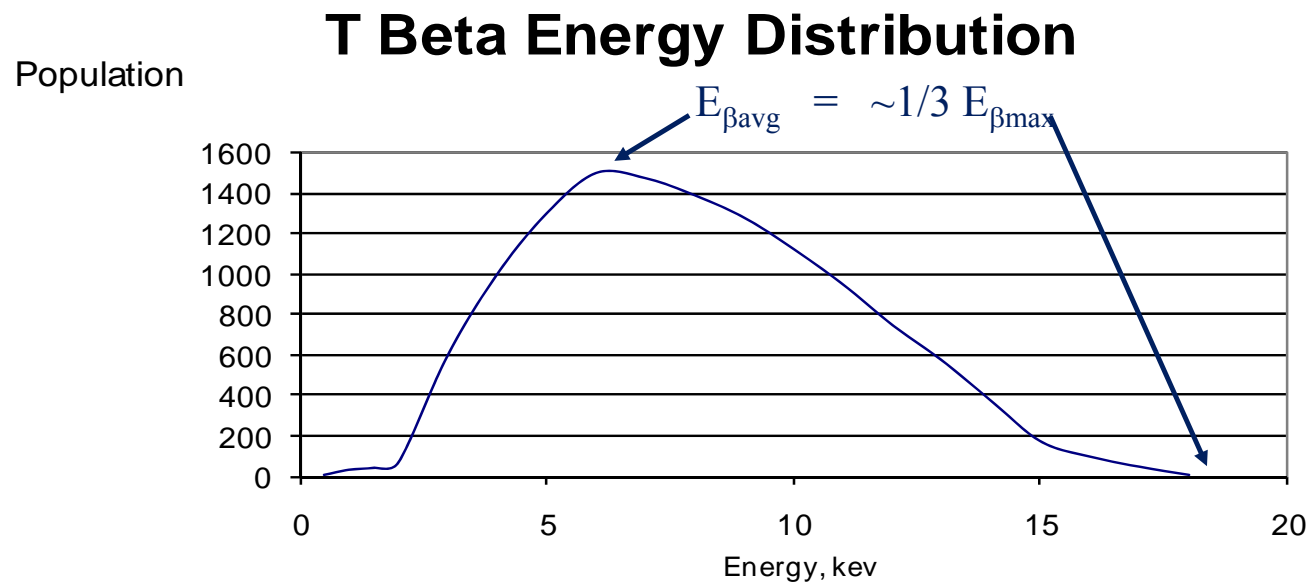
# Background Counts

"Background" refers to the response of the detector when no sample is present.

Background can arise from:

1. Ambient radiation

    corrected for using coincidence circuitry

2. Luminescence of excimers or fluor

    Minimized by "dark adapting" the samples

3. Contaminating radionuclides

    Identified by counts outside the ROI

# Correcting for Background

Background counts significantly controlled or minimized:
- Contamination of sample test source
- Response to ambient sources of radiation
- Radioactive contaminants in reagents and vials
- Static electricity
- Heat (i.e., laboratory temperature)

Background counts only minimally controlled:
- Noise from power or electromagnetic sources
- Photo- and  chemi-luminesence (dark adapt)
- Cosmic radiation (shielding)
- Thermal 'noise in PMTs (dark counts)

# Correcting for Background: Coincidence Circuits

- LSC units have 2 photomultiplier tubes (PMTs) placed at 180$^o$ from each other

- Many UV photons will result from beta decay interaction in the cocktail

- These photons will be emitted in all directions

- PMTs will receive a photon - essentially *simultaneously.*

- Cosmic radiation interacts with the individual PMTs - unlikely that such events occur *simultaneously* in *two different* PMTs.

- Coincidence circuit – holds open a circuit 'gate' for a short period of time (20-70 nanoseconds)

  - *Signal in both PMTs leads to count*

  - *Signal in only one PMT is eliminated..*

Tritium

# LSC – Basic Diagram
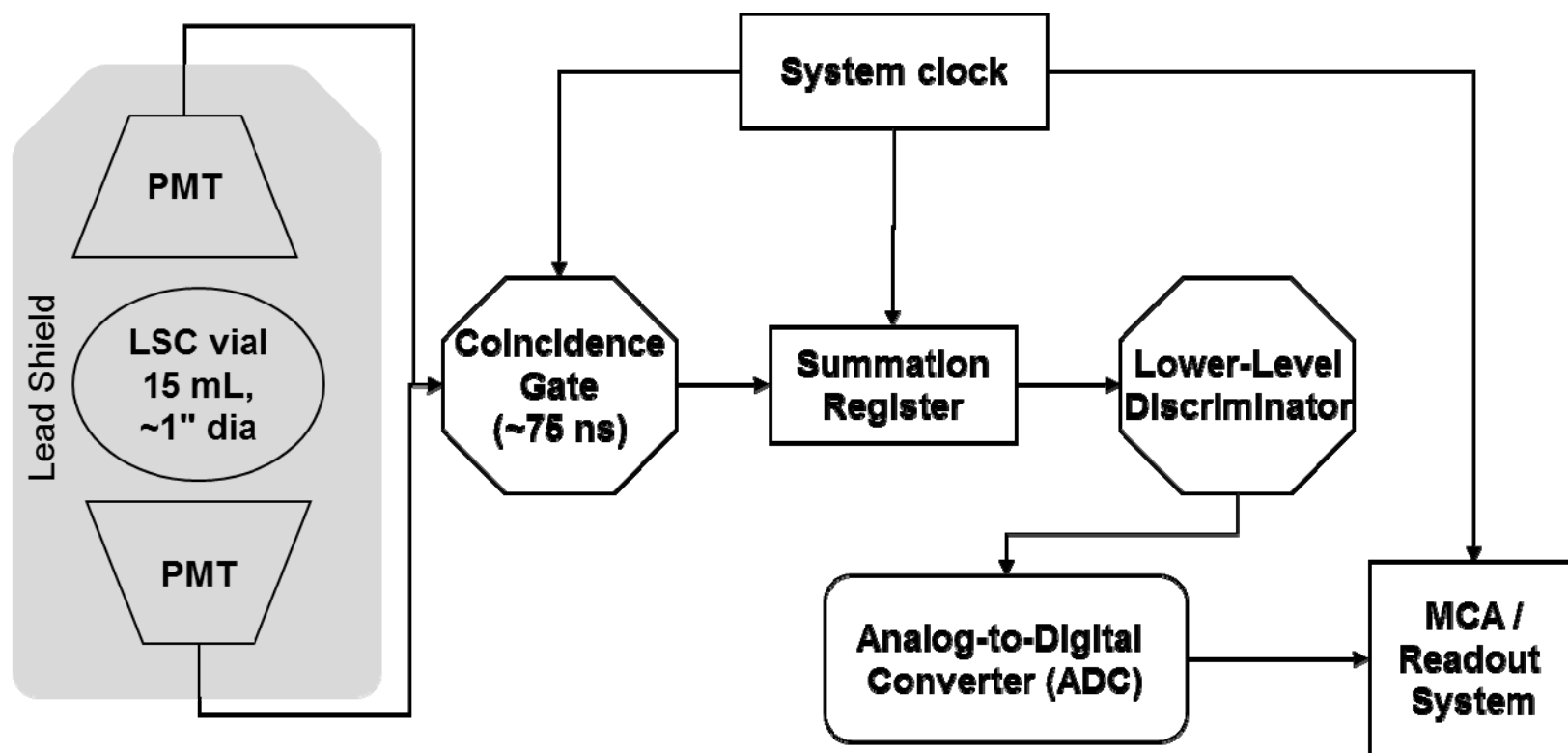
# Background: Luminescence

Scintillation cocktails can be stimulated to fluoresce by
 chemicals, ambient light (visible and UV), and by heat.

•This excitation, termed "chemi-luminesence" or "photoluminescence," can persist for a long period of time and can result in false positive counts.

•The de-excitation time frame is influenced by:
  • the formulation of the cocktail
  • the chemical makeup of the sample
  • the type, intensity and duration of exposure to the light
  • the temperature

# Background: Dark Adapting

- To minimize photoluminescence, LSC samples should be "dark adapted" before counting.

- To achieve dark adaptation:
  - Minimum of 30 minutes
  - May need longer depending on:
    - contaminants
    - solution make-up, and
    - cocktail formulation, or
    - contractual or method imposed requirements,
  - Same dark adaption protocol for calibrations, background, samples and QCs

# About Background in Water Analysis

- Backgrounds should be:
  - Determined free of analyte
  - representative of the sample test source
    - that matches the cocktail formulation/lot
    - the chemical and physical makeup of the test source
    - the type and levels of quench
  - Adequate precision to meet uncertainty requirements
  - Subtracted from sample count activity

# Quench

- Most prevalent interference in LSC
- Anything which results in the loss of conversion of radionuclide decay energy to a signal at the PMT.
  - Chemical quenching
  - Color quenching
  - Opacity quenching

# Effect of Quenching

• Quench, reduces the total number of scintillation events (photons) received by the PMTs
• Shifts the distribution of the events to lower energy.
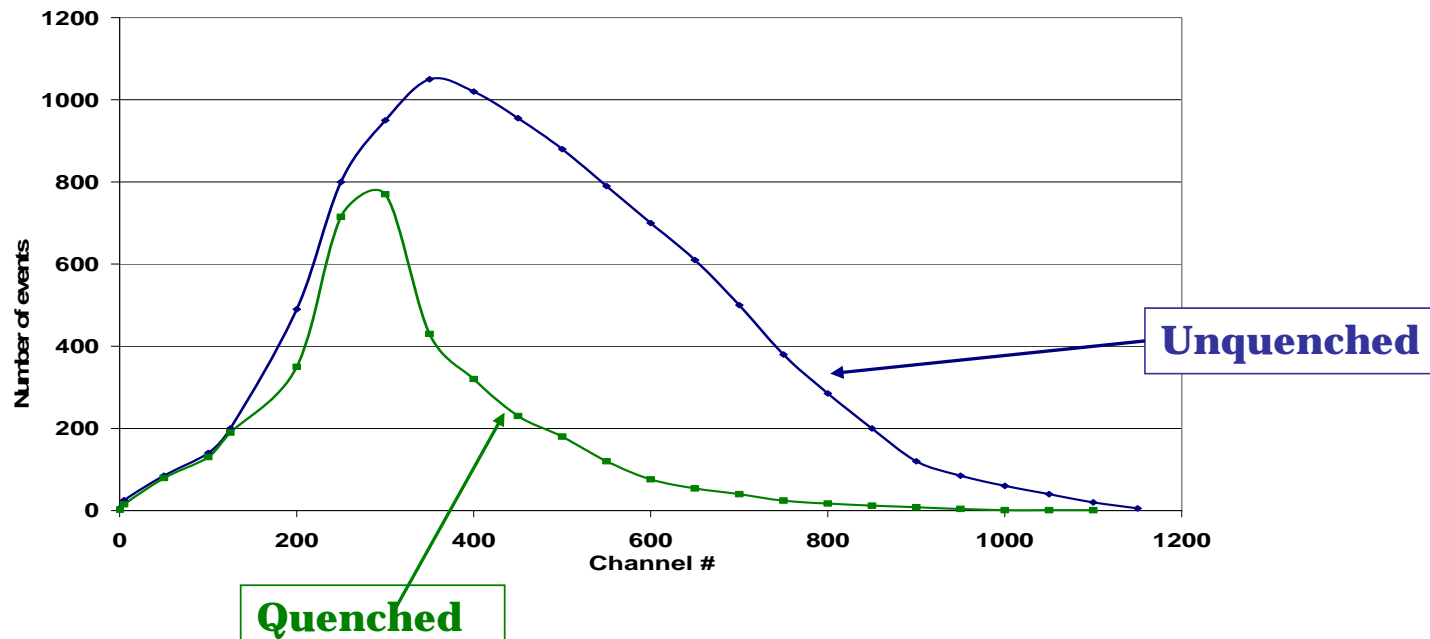
# Quench Indicating Parameters (QIPs)

Measures the amount of quench in a sample

- Initially QIPs included:
  - channels ratio
  - external standard
  - internal standardization

- LSC now contain software to calculate QIP
  - H Number
  - Spectral Index of the Sample (SIS)
  - Transformed Spectral Index of the External Standard (tSIE)

# Types of QIPs (usually instrument specific)

- The "H Number"
  - Quench-induced reduction of $^{137}$Cs beta energy at a single point of the energy spectrum compared to an unquenched $^{137}$Cs standard
    - Expressed as the number of channels the single point of the energy spectrum has down-shifted

- The Spectral Index of the Sample (SIS)
  - SIS is the most accurate QIP but should only be used for samples containing significant activity of the analyte
  - Generally not used for radiochemical analysis of drinking water

- The transformed Spectral Index of the External Standard (tSIE)
  - Uses the energy distribution of the *entire energy spectrum* as generated by an external $^{133}$Ba standard

# The H Number



Quench Measurement Using Cs-137
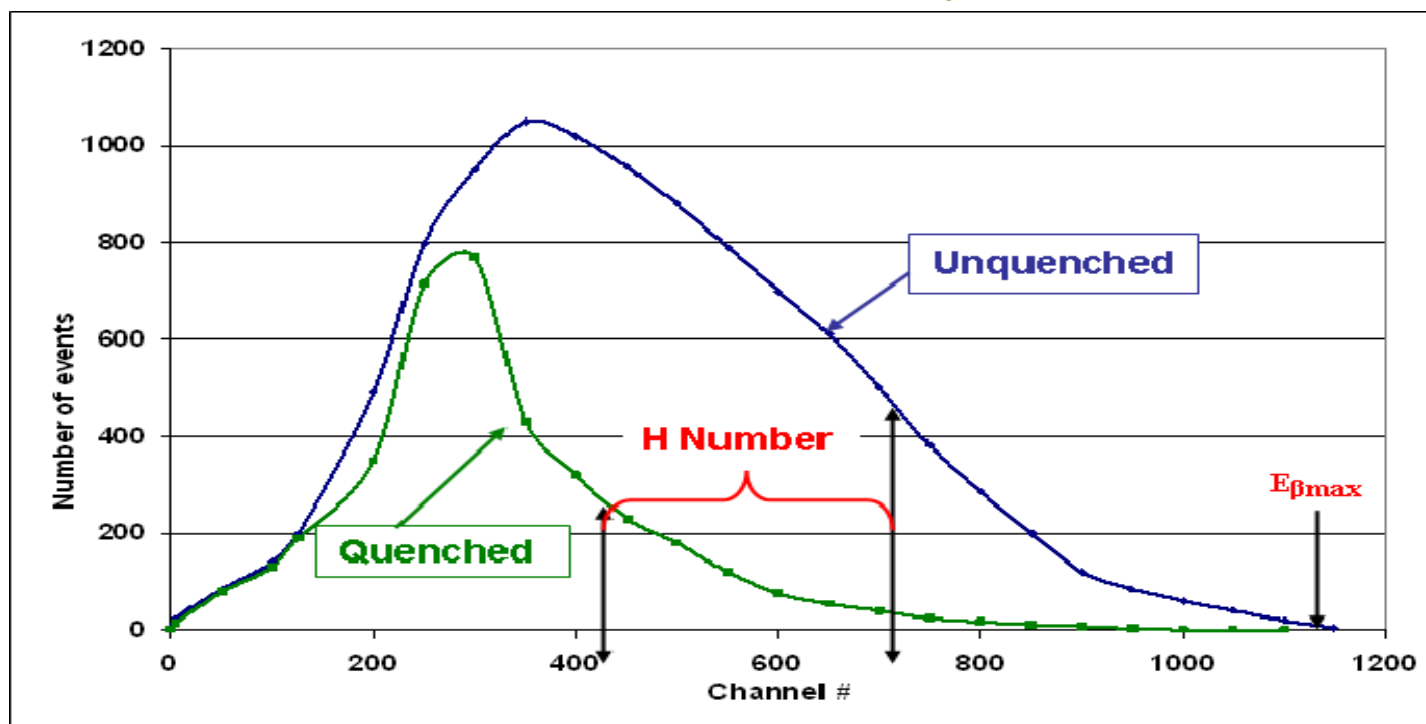
# Correlating Quench Values to Counting Efficiency (Slide 1/2)

EPA Method 906.0 (Tritium Analysis) efficiency be determined using a "quench curve"

- Prepare a series of calibration standards (CS) all containing the same amount of activity (pCi) of the radionuclide in question.
- Add increasing amounts of a quenching agent such as Eriochrome Black T or Nitromethane to each vial.
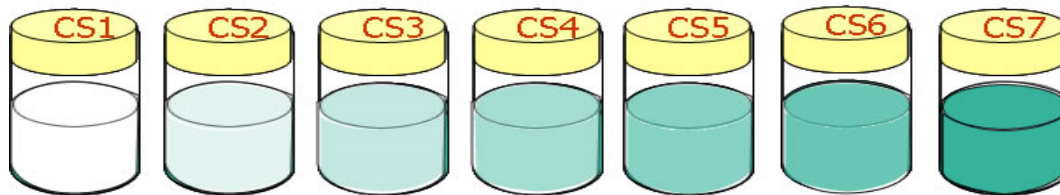


- Count each sample.

# Typical Quench Curve

The maximum efficiency for tritium is 65% because it takes a certain energy of the decay particle to excite the fluor. Only about 65% of all tritium beta particles have enough energy to do this.



Quench Curve
(QIP vs. Efficiency)
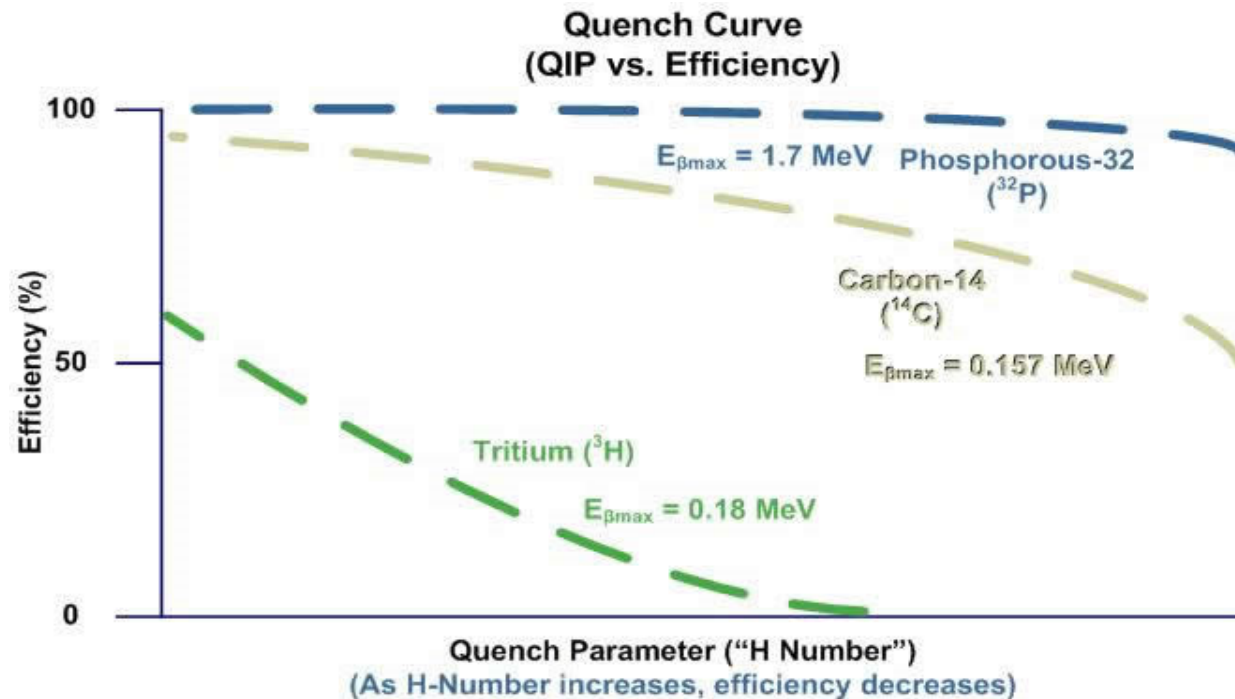
# Quench Indicating Parameters — tSIE
# Transformed Spectral Index of the External Standard

- Induce a Compton electron spectrum using an external standard of $^{133}$Ba

- Perform mathematical transformation on spectrum (reverse summation)

- Fit a line between the points at the high energy end of the curve that correspond to 10% and 20% of the transformed counts

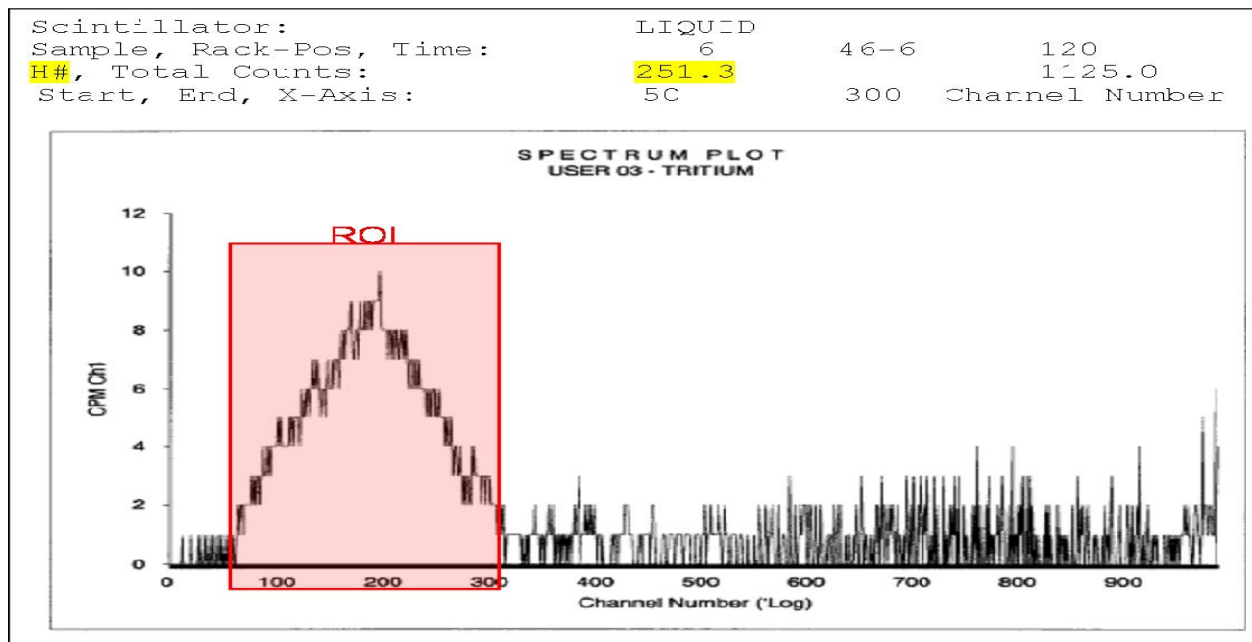- The tSIE for the sample is where the line intercepts the x-axis
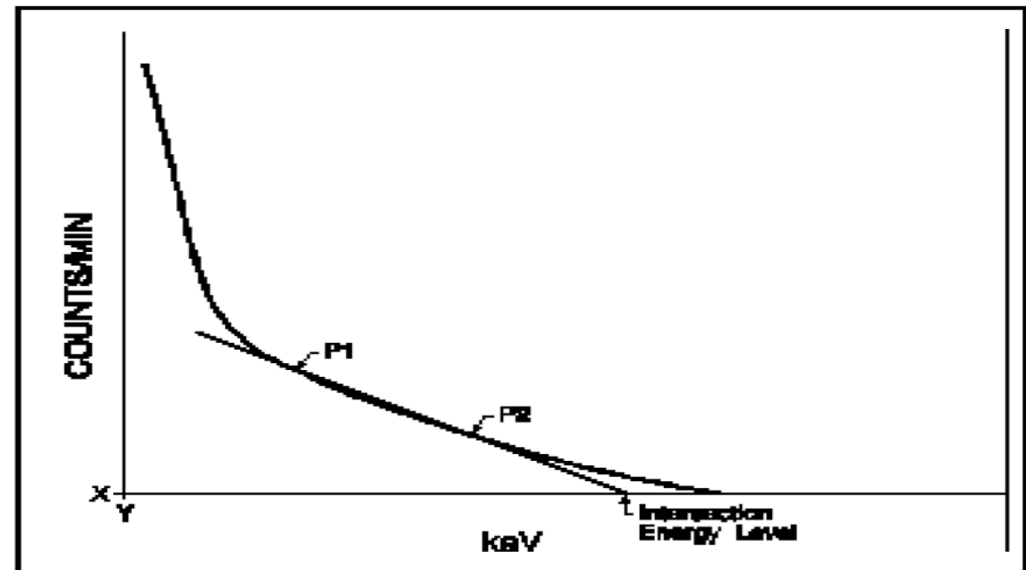
# Liquid Scintillation Spectrum Plot

- Typical LSC Plot is shown below.
- The H Number highlighted in yellow
- Region of interest (ROI, red box): pre-determined channel numbers corresponding to tritium energy levels. Only counts within the ROI are summed.
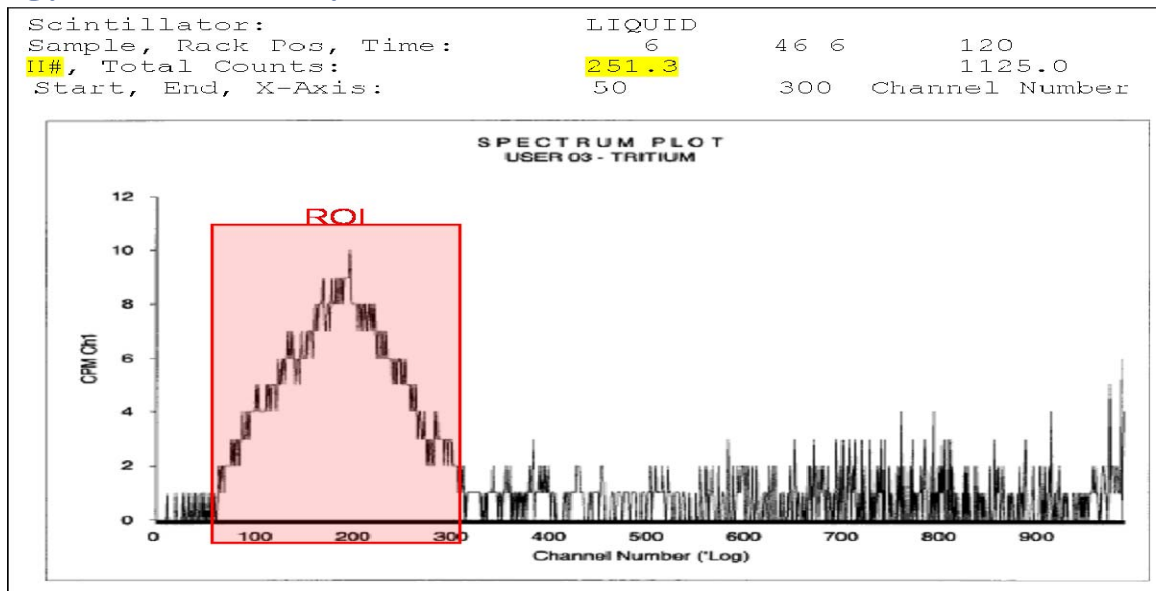
# Liquid Scintillation Spectrum Plot

- An LSC Plot is shown below.
- The region of interest (ROI) -channel numbers corresponding to tritium energy levels.



```
Scintillator:                      LIQUID
Sample, Rack-Pos, Time:              6          46-6          120
H#, Total Counts:                  251.3                     1125.0
Start, End, X-Axis:                 50          300   Channel Number
```

SPECTRUM PLOT
USER 03 - TRITIUM

# Spectrum Plot Indicating Contamination

•Note the presence of above-background counts in the higher-energy channels.



SPECTRUM PLOT
USER 03 - TRITIUM

Note potential high energy contaminants
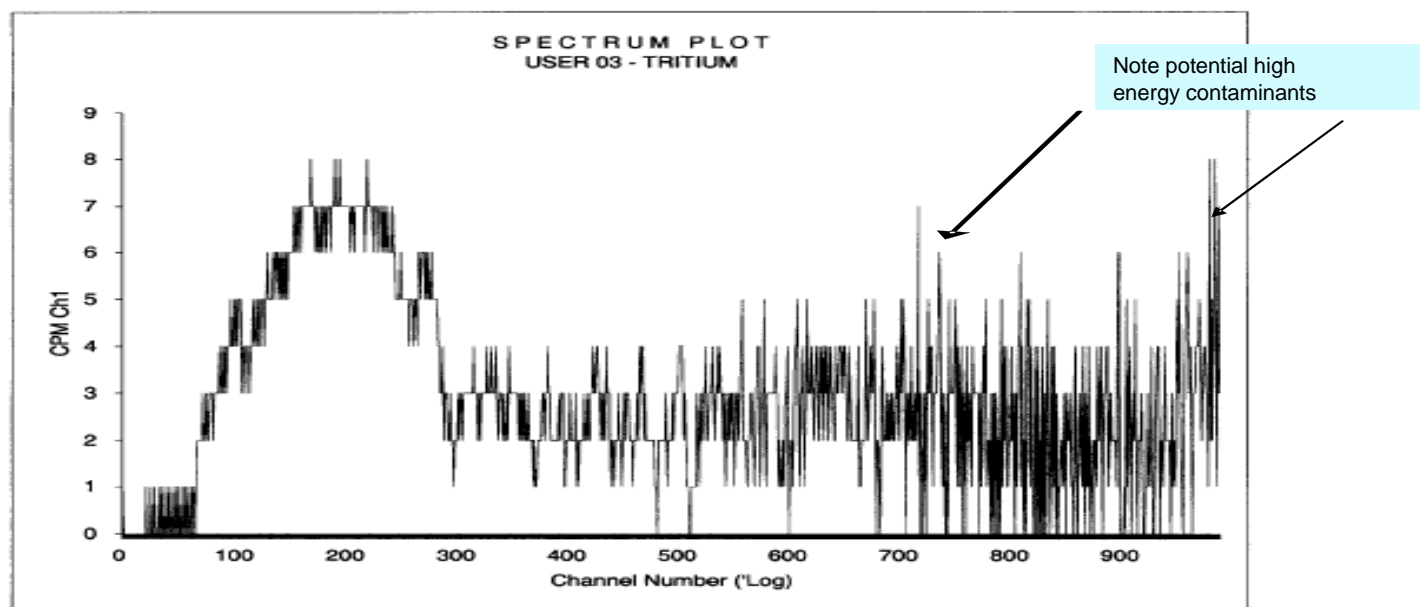
# Pulse-Shape Discrimination (PSD)

- Many LSCs are equipped with PSD capabilities
  - Alpha pulses decay more slowly than beta pulses
  - By analyzing the length of pulses one can discriminate between alpha and beta particles

- Alpha/Beta discrimination can be used for
  - Rapid screening highly radioactive liquid samples
  - Identifying an alpha component in the presence of beta activity
  - Eliminating spectral overlap when chemical separations are not 100% effective

# Result Bias and Background Levels of Tritium in the BSC

**Result Bias vs. Activity**
*(for background correction with water @50 pCi/L)*
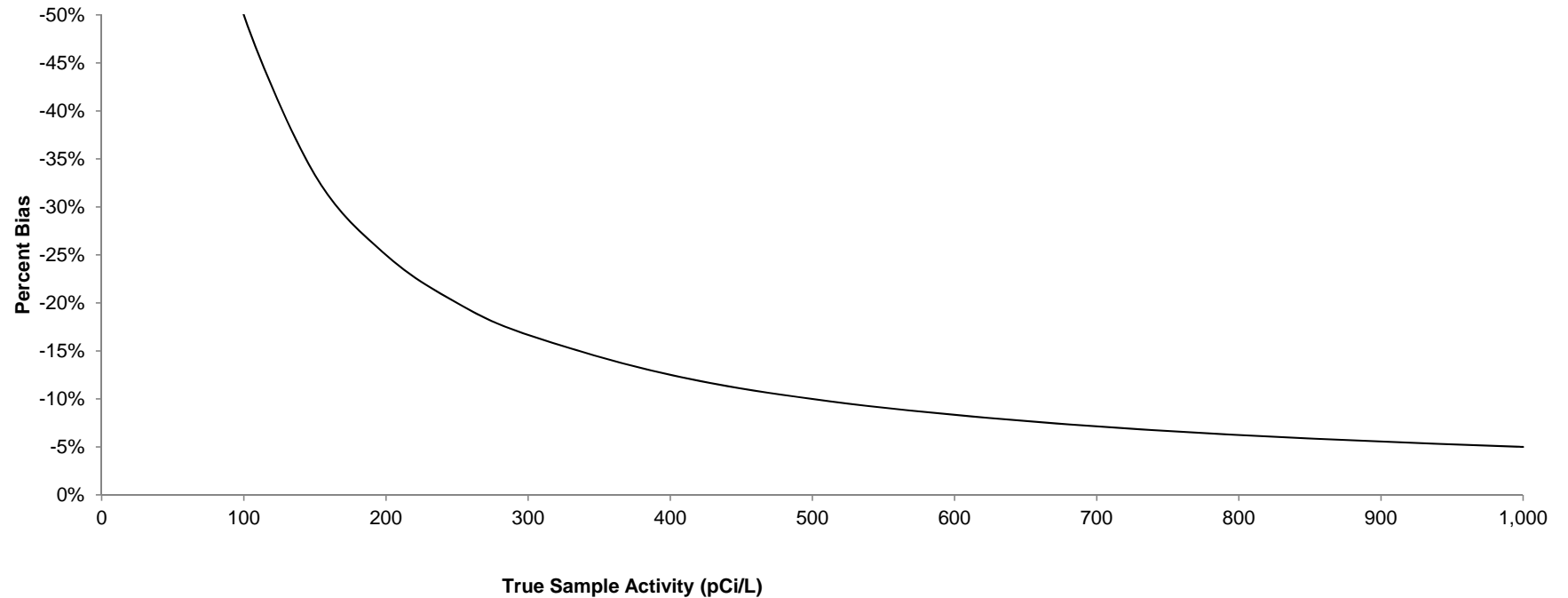
# Sample Issues

- Sampling and preservation must be performed:
  - Liquid samples
    - Sampling equipment adequately purged with *sample*
  - Solids taken
    - Ensuring no *loss* of water
    - Ensuring no water *enters* sample
    - Solids must be preserved as taken
  - Containers sealed - prevent oxidation of sample and $^3$H exchange with non-sample $^1$H

# Sample Preparation Techniques (I)

- Distillation process
  - Minimizes interference from other radionuclides
  - Commonly used for liquids
  - May yield low bias results for some solids
  - Need to ensure that carryover of other materials is minimized to reduce quench
- Freeze drying
  - Provides good alternative for solids
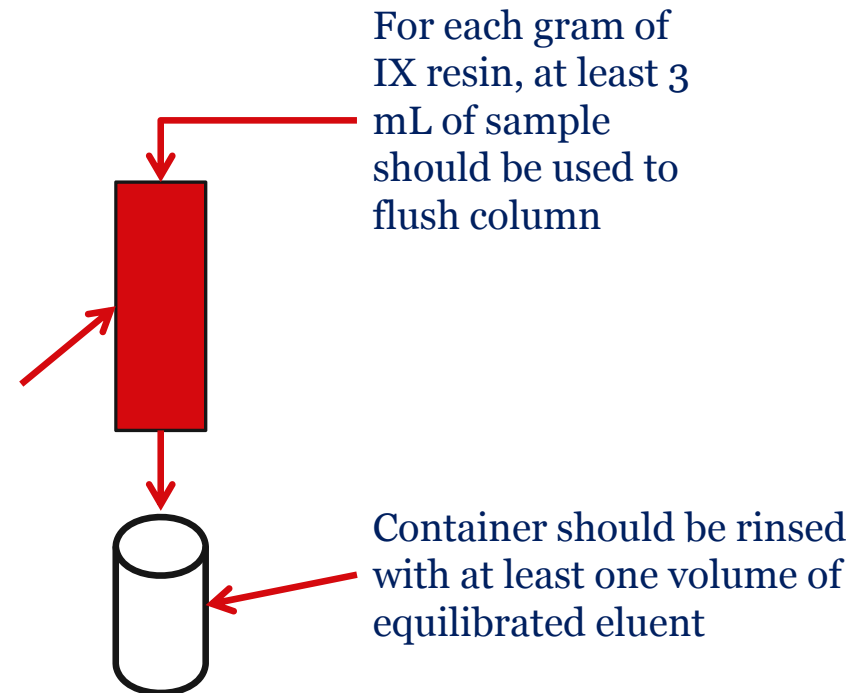  - Minimizes destructive distillation issues

# Lyophilization

Sample is frozen to below 273 K, then pressure is reduced to less than 0.006 atm. The temperature of the sample – raised to room T.
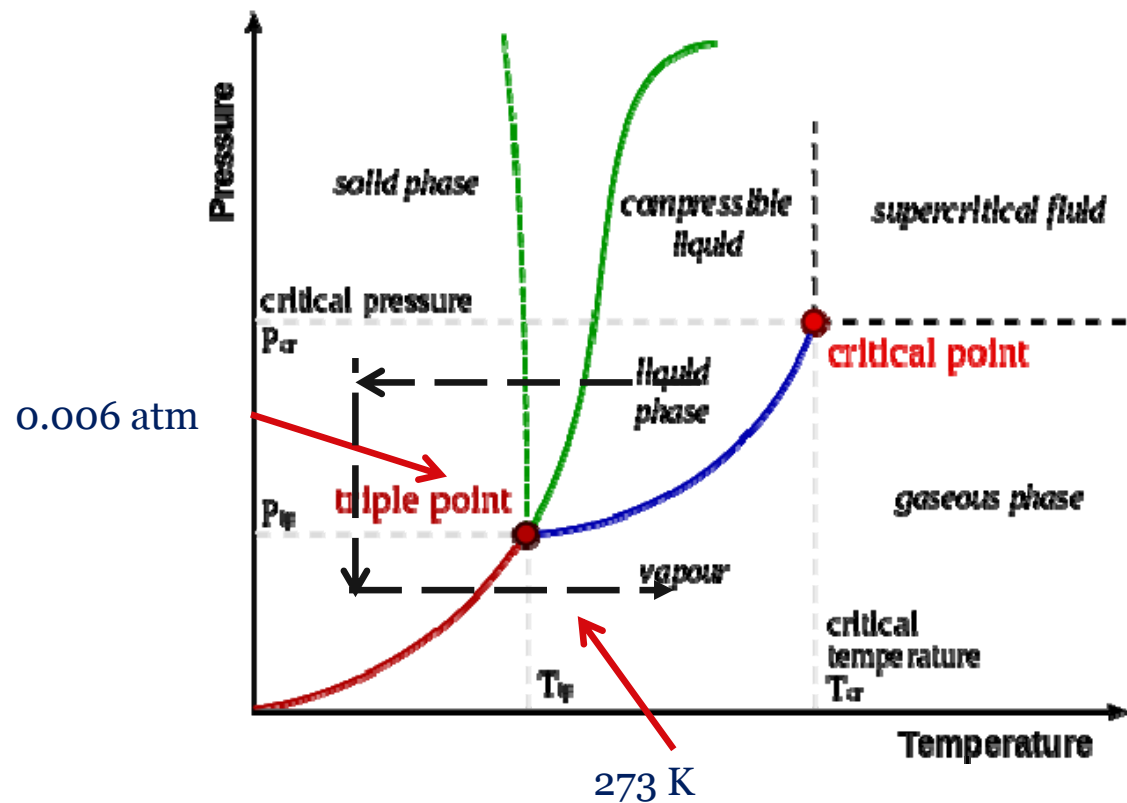
# Sample Preparation Techniques (II)

- Ion Exchange
  - Removes ionic contaminants
  - Does not remove organics
  - Need to ensure sufficient FCV of sample equilibrated with resin

For each gram of IX resin, at least 3 mL of sample should be used to flush column

Normal IX resins are about 50% water

Container should be rinsed with at least one volume of equilibrated eluent

# Sample Preparation Techniques (III)

- Electrolysis
  - Pre-concentration for very low $^3$H analysis (<100 pCi/L)
  - Very time consuming (up to 2 weeks)
  - Water is converted into hydrogen and oxygen gas
  - Cell voltage must be carefully controlled
    - H-O-T electrolyzes at a slightly higher potential than H-O-H
    - H-O-T enriches in the cell residual liquid
  - Need to ensure no interaction with environment during electrolysis

# Acronyms

- BSC = Background Subtract Count
- BWR = Boiling Water reactor
- FCV = Free Column Volume
- GPC = Gas Proportional Counting
- HTO or HOT = Tritiated Water
- LSC = Liquid Scintillation Counter
- MCL = Maximum Contaminant Level
- PMT = Photomultiplier Tube
- PSD = Pulse Shape Discrimination
- PWR = Pressurized Water Reactor
- QIP = Quench Indicating Parameter
- RCS Reactor Coolant System
- ROI = Region of Interest
- SFP = Spent Fuel Pool
- tSIE = Transformed Spectral Index of the External Standard
- TU = Tritium Unit

# Questions Welcomed!

T!

# Upcoming Webinars

Tritium

- Iodine-129 (gaseous fission products—capture and immobilization)
- Xe/Kr (capture and immobilization)
- Cesium

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