NAMP

Savannah River National Laboratory

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Radiochemistry Webinars

Carbon-14: Sample Collection, Preservation and Analysis

NWP Nuclear Waste Partnership LLC

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Meet the Presenter…

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 28 years.

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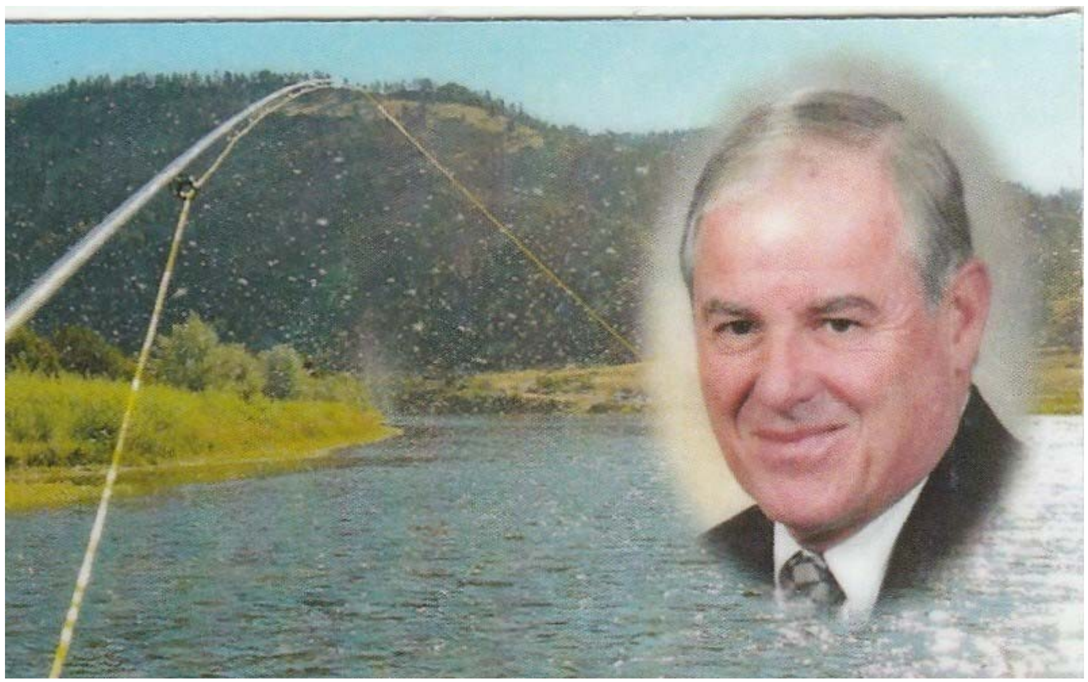
EMS

In Memoria
David McCurdy (1944-2017)
Friend, Scientist, Mentor, Colleague



^{14}C in the Environment

- Naturally formed - upper atmosphere
  - $^{14}N(n, p)^{14}C$
  - $^{17}O(n, \alpha)^{14}C$
- Atmospheric Transport
  - $^{14}CO_2$
  - $^{14}CH_4$ +other short chain hydrocarbons
- Environmental "Sinks"
  - Bodies of water as carbonate
  - Organics in vegetation through photosynthesis

Anthropogenic Formation of ^{14}C

- Activation in power or research reactors:
  - $^{17}O(n, \alpha)^{14}C$ (cross section decreases:10 b to 0.05 b in thermal region)
  - $^{16}O(n, ^{3}He)^{14}C$ (no documented b value but very small)
  - $^{14}N(n, p)^{14}C$ (cross section decreases:100 b to 0.1 b in thermal region)
  - $^{13}C(n, \gamma)^{14}C$ (1.4mb in thermal region)
- These reactions take place in the-
  - coolant,
  - fuel,
  - metal components
- Formed as a fission product (very, very small %)
- Accelerator produced

Radioactive Decay of ^{14}C

C-14 is a beta-only emitter

$$^{14}C \rightarrow {}^{14}N + \beta^- + \bar{\upsilon}$$

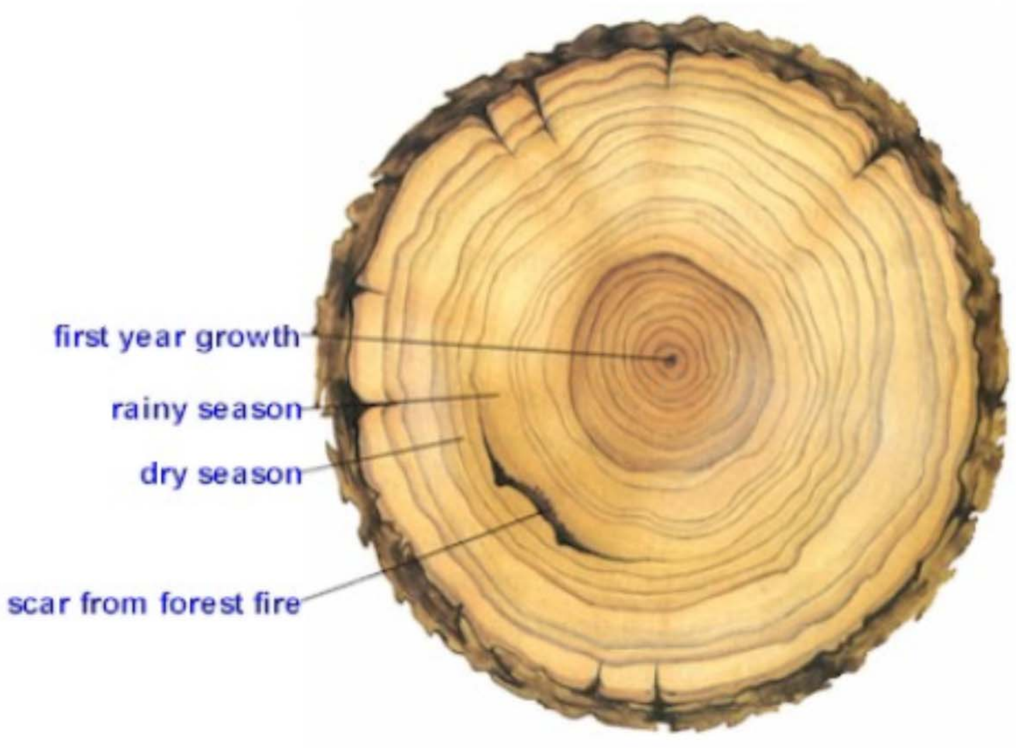
Half-life is 5715 years

Maximum beta particle energy is 0.157 MeV

Mean beta particle energy is 0.050 MeV

Its neutron capture cross-section is < 1 μb

Detection of ^{14}C Over the Ages



Tree Ring Sampling for ^{14}C is a Well Established Technique

From, "C-14 Environmental Pathways to Man", by J. Key, 20th Annual RETS-REMP Conference, San Jose, CA (2010)

Concentration in the Environment

- CRC Handbook: Constituents of Air
  - CO_2 Volume Fraction = 3.3×10^{-4}
  - CO_2 Mass Fraction = 5.0×10^{-4}
- CO_2 in air = 0.65 g CO_2/m^3 air
  = 0.18 g C/m^3 air
- ^{14}C in air = 1.2 pCi $^{14}C/m^3$ air (varies with altitude, longitude etc.)
  = 0.044 Bq $^{14}C/m^3$ air
- In organic matter
  - 6 pCi/g of carbon

Anthropogenic Contributions

- Nuclear Weapons Testing
  - Neutron activation of atmospheric O and N
  - Doubled the natural ^{14}C content in the atmosphere by the '70s
    - Back to background values in atmosphere
- Nuclear Power Plant Effluents
  - Principally from ventilation of reactor building and waste gas systems
- Spent Nuclear Fuel
  - Mostly contained within the fuel
- Tracers in inorganic and organic molecules
  - Very small environmental contribution

^{14}C Dose Limits

Child dose by pathway – mrem/yr

Pathway	RG-1.109		ICRP-72
	Bone	Other	EDE
Inhalation	4.4E-02	8.2E-03	1.8E-04
Fruit+Veg	5.3E+00	1.1E+00	1.6E+00
Leafy Veg	2.6E-01	5.3E-02	8.0E-02
Meat	6.4E-01	1.3E-01	2.0E-01
Milk	2.0E+00	4.0E-01	6.1E-01
Total	**8.2E+00**	**1.6E+00**	**2.5E+00**

Total doses shown here are ~100 times greater than contributions from nuclear power plant effluents

From "Naturally-occurring Carbon-14 and Implications to Power Plant Dose Assessment", K. Sejkora, 20th Annual RETS-REMP Conference, San Jose, Ca (2010)

Production of ^{14}C in Reactors

- Fuel
  - ^{17}O activation of oxygen in the UO_2 (3.5 Ci per year - 1,000 MWe)
  - Fuel also has some nitride (15 Ci per year - 1,000 MWe)
  - Nitrogen in Fuel clad (30 Ci per year - 1,000 MWe)
    - What happens in the spent fuel pool (SFP)?
- RCS
  - ^{17}O and ^{16}O activation of oxygen in water

Sampling and Analysis for C-14

- Air
  - Prevalent chemical forms
  - Direct and indirect analysis
- Water
  - Prevalent chemical form
  - Preservation
  - Separation and analysis
- Solid Media
  - Soils
  - Resins
  - Concrete

Air and Atmospheric Sampling

Power Plant Releases of ^{14}C

- Nominal gaseous release rate is 8 to 12 Ci
  - For a 1,000 MWe power plant in one year
- For BWRs
  - 90-95% released as CO_2; 5-10% organic (during the operating cycle)
  - 20-30 % released as CO_2; 70-80 % organic (during outages)
- For PWRs
  - 10-15 % released as CO_2; 85-90 %organic (during the operating cycle)
  - 85-95 % released as CO_2; 5-15 % organic (during outages)
- Dose assessment; only the CO_2 form is of interest to human dose

Significance – Principal Radionuclide

- Regulatory Guide 1.21, Rev 2
  - a radionuclide is considered a principal radionuclide if it contributes either
    - (1) greater than 1 percent of the 10 CFR Part 50, Appendix I, design ***objective dose*** for all radionuclides in the type of effluent being considered, or
    - (2) ***greater than 1 percent of the activity*** of all radionuclides in the type of effluent being considered.
  - Once principal radionuclides are identified…monitored in accordance with the sensitivity levels in the Offsite Dose Calculation Manual (ODCM)

Significance – Principal Radionuclide (cont'd)

- From RG 1.21 for ^{14}C
  - Because the production of C-14 is expected to be relatively constant at a particular site,
    - If sampling is performed for C-14 (instead of estimating C-14 discharges based on calculations from a normalized source term), the sampling frequency may be adjusted to that interval that allows adequate measurement and reporting of effluents.
    - If estimating C-14 based on scaling factors and fission rates, a precise and detailed evaluation of C-14 is not necessary. It is not necessary to calculate uncertainties for C-14 or to include C-14 uncertainty in any subsequent calculation of overall uncertainty.

^{14}C COMPOUNDS OF INTEREST
Atmospheric Releases

- Organic Carbon – primary form for PWRs
  - $^{14}CH_4$, $^{14}CH_3OH$ and other low MW hydrocarbons
- Inorganic Carbon – Primary form for BWRs
  - $^{14}CO_2$, ^{14}CO not formed in appreciable quantities
- Particulate Carbon
  - Associated with reactor CRUD
  - This is an extremely small fraction of the organic and inorganic carbon released as gases.

Gaseous Effluents- Sampling Locations Issues

Reactor Plants

- Plant Vent
  - Potentially high moisture
- Waste Gas System
  - Limited oxygen at most locations
  - Levels of hydrogen present safety concern
- Containment Building
  - Very high flow rate
- Spent Fuel Pool Area
  - Large surface area to sample from

Environmental Atmosphere

- Particulates
- SO_2, H_2S, humidity

^{14}C in Gaseous Effluents

ASTM D7938 – 15 "Standard Practice for Sampling of C-14 in Gaseous Effluents"

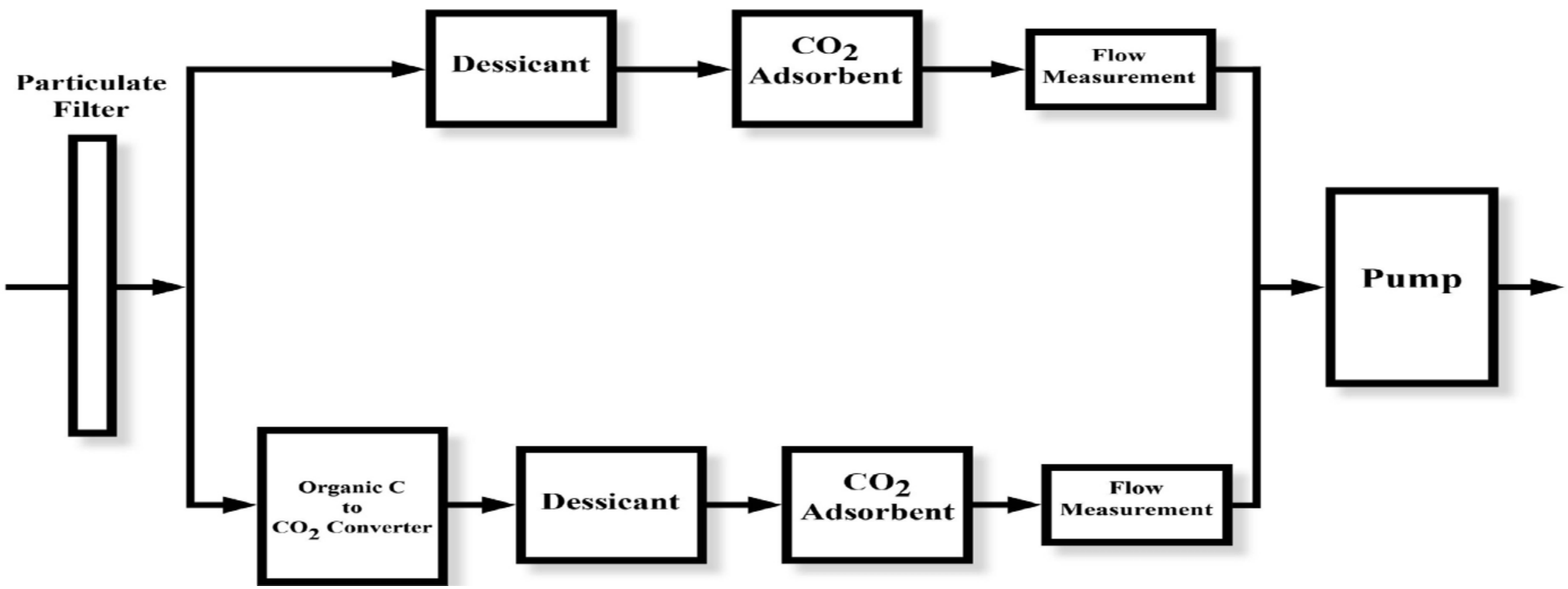
- Sampling methodology allows distinction between total ^{14}C and inorganic ^{14}C
  - *inorganic* ^{14}C —the gaseous, chemical form of ^{14}C as CO_2.
- Organic ^{14}C is obtained by the difference
  - organic ^{14}C —any gaseous, chemical ^{14}C form (including CO) that is not particulate and not CO_2.
- Specific organic compounds are not identified

ASTM Method Advantages for Sampling Gaseous ^{14}C

Successful preservation from gaseous samples

- Differentiation of Total, inorganic, and particulate carbon
- Large range of activity
- In situ preservation
- Potentially flammable gases are not an issue
- Relatively short Sample times
- Sample method and analytical separation minimizes interference by other radionuclides,
- Employs convenient and reliable hardware

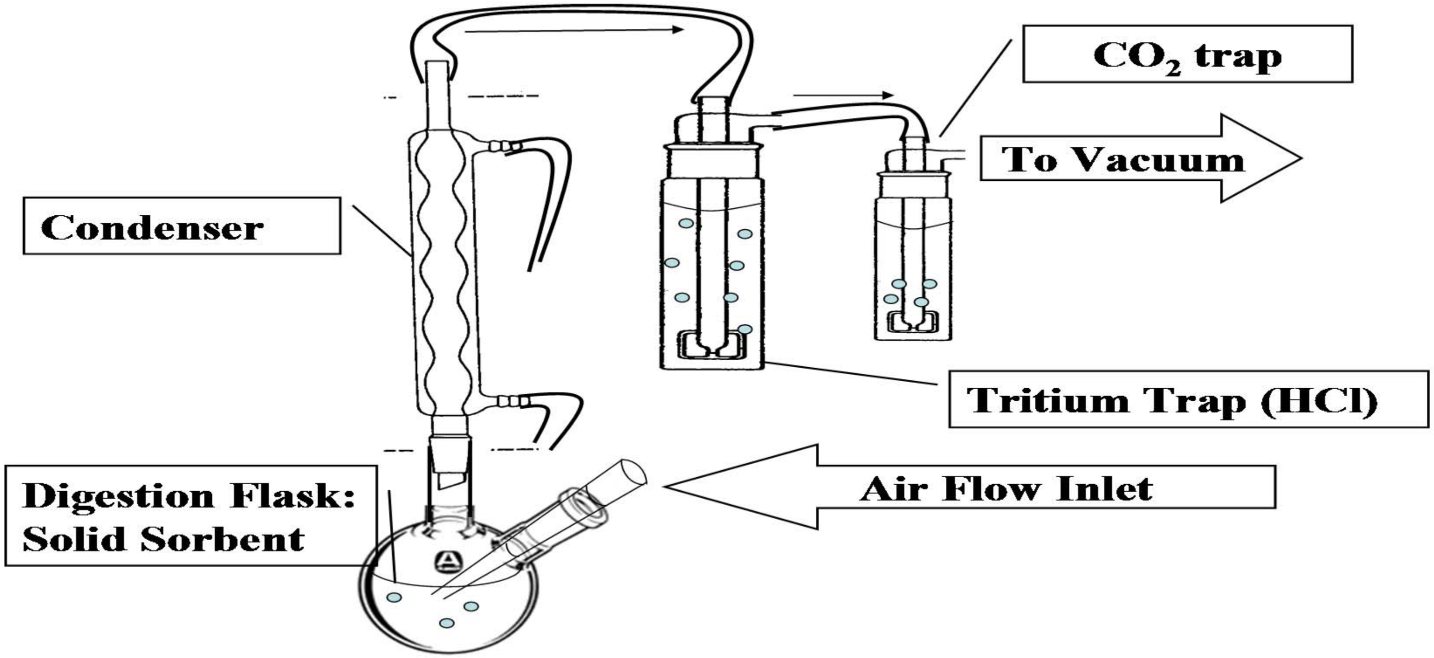
Diagram of Sampler



Wet Chemistry

- The Ascarite traps the carbon dioxide at an average efficiency of 95 %
- The Ascarite is treated with nitric acid, silver nitrate and potassium persulfate
  - Ensures conversion of all organic and inorganic to CO_2
  - Acid "boils off" the carbon dioxide
- Carbon dioxide - trapped in special cocktail for LSC

Diagram of Separation Process



Analytical QC Data

Power Pant Sampling

QC	Filter blank, pCi/mL	Ascarite Blank (T)	Ascarite Blank (I)	Laboratory Control Sample (LCS)	LCS-Dup
Lab	$-3 \pm 4.1 \times 10^{-8}$	$-2.9 \pm 7.8 \times 10^{-8}$	$-3 \pm 8.8 \times 10^{-8}$	$1.11 \pm 0.08 \times 10^{-6}$	$1.11 \pm 0.07 \times 10^{-6}$
Plant		$1.1 \pm 11 \times 10^{-8}$	$-7.2 \pm 15 \times 10^{-8}$	$1.83 \pm 0.52 \times 10^{-6}$	$1.87 \pm 0.50 \times 10^{-6}$

Analytical Results - PWR

Location	Total, pCi/L [pCi/ft^3]	% Organic	% Inorganic	Annual flow, ft^3
Plant Vent	1.39 ± 0.18 [$(3.93 \pm 0.51)x10^1$]	99.3	0.7	$1.1x10^{11}$
Waste Gas #1	$(4.50 \pm 0.84)x10^6$ [$(1.27 \pm 0.24)x10^8$]	91.9	8.1	775 to 3192 for all three
Waste Gas #2	$(5.56 \pm 0.14)x10^6$ [$(1.57 \pm 0.040)x10^8$]	96.8	3.2	
Waste Gas #3	$(5.26 \pm 0.14)x10^6$ [$(1.49 \pm 0.040)x10^8$]	93.1	6.9	

Liquid Samples

Groundwater Samples

- Includes surface water, shallow aquifers and deep wells
  - Chemical form of ^{14}C depends on
    - depth of groundwater (oxygen content)
    - presence of oxidizing-reducing conditions (ORP)
    - pH
    - Bacteria
  - Sampling should take into account
    - Potential for presence of volatile $^{14}C_xH_y$ compounds (dissolved organic compounds, DOC)
      - Need to acquire sample with its head space (special sampling equipment and containers)
    - Presence of carbonate (dissolved inorganic carbon, DIC)
      - Samples should be preserved with NaOH (if other analyses are required separate samples should be taken) to a pH of ~10

Water Sample Preparation

In-situ generation:

- If only DIC exist in sample
  - *Sample pH lowered using HCl, H_2SO_4, or H_3PO_4*
  - *Circulation pump or sparger - pass exsoluted gas through*
    - *NaOH solution or*
    - *Solid CO_2 trap*
- *If both DIC and DOC exist*
  - *Oxygen or air purge first through a DIC trap*
  - *Pass effluent through a catalytic converter to convert all DOC to DIC*
  - *Pass through a DIC trap*

Water Sample Preparation

When concentrating from a large volume

- High pH; maintain as CO_3^{2-}
- Precipitate with either Sr^{2+} or Ba^{2+}, or
- Anion Exchange
- Dissolve or rinse with HCl
- Re-precipitate or ion exchange prior to final sample test source preparation

Soils and Solids

Types of Solid Matrices

- Loamy Soil
- Sandy Soil
- River or lake sediment
- Concrete
- Cement
- Vegetation
- Animal Matter

Preservation of Soil-like Samples

- Watery samples
  - Siphon/decant excess water (save for liquid analysis)
- For a short time frame (hours to 2-3 days)
  - Refrigerate to about 4 °C
  - Maintain under a nitrogen blanket
- For longer timeframes
  - Bring to 4 °C
  - Place under a nitrogen blanket
- These precautions minimize oxidation and bacterial attack of the carbon

Preservation/Preparation of Construction Materials

- Storage prior to analysis
  - Concrete
  - Drywall
  - Marble
    - In general, will be relatively dry
  - Stored in air tight containers
- Preparation
  - Freeze shattering
  - Avoid excessive temperatures
  - Digestion with nitric acid: sweep vapors through NaOH trap

Biological Sample Preservation/Preparation

- Immediately freeze under inert atmosphere
- Slice or use blender (while cold) to reduce sample size
- Digestion process starts in basic solution, or
- Freeze dry in acidic oxidizing medium and capture generated carbon dioxide

Most Common Detection Methods for ^{14}C Analysis

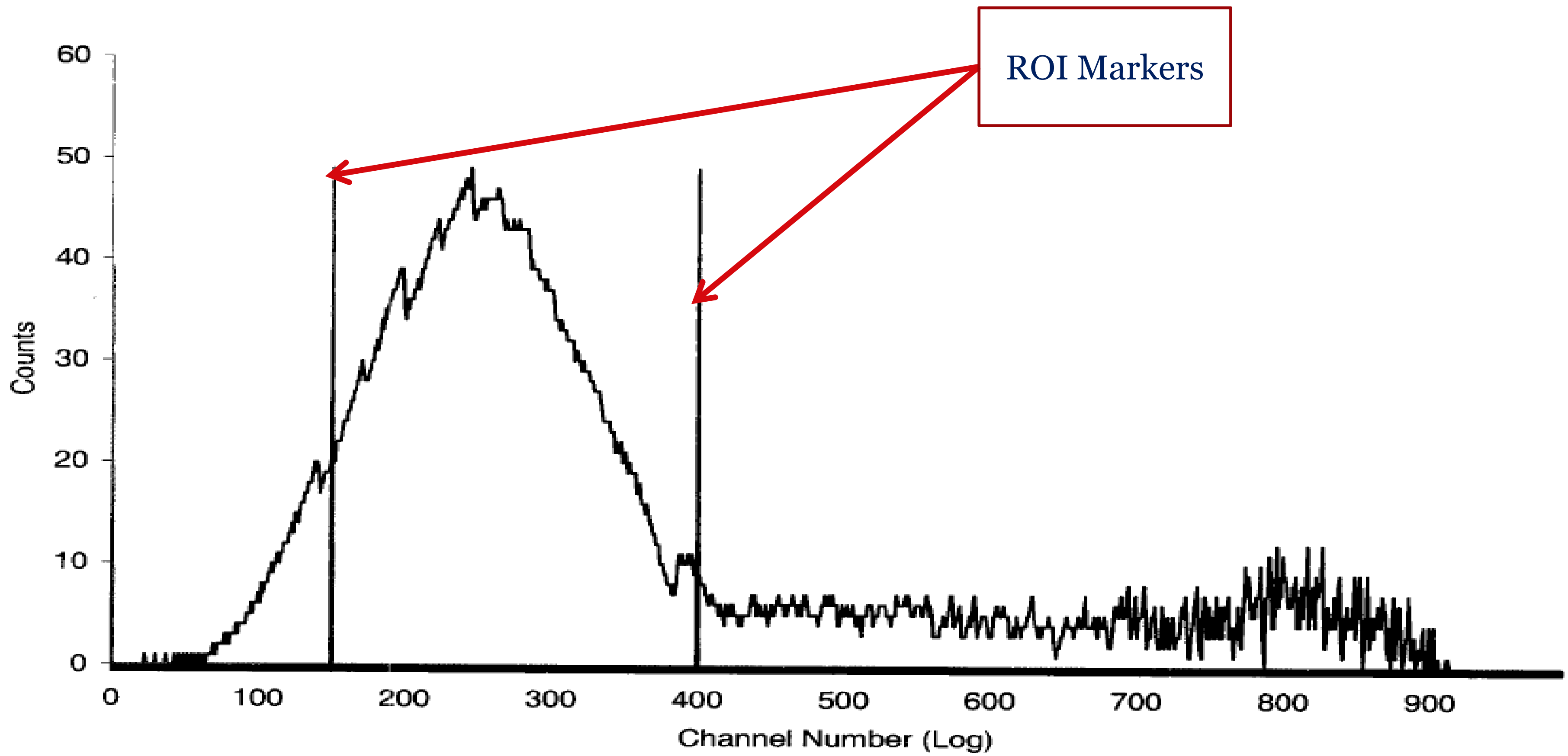
- Liquid Scintillation Counting (LSC)
  - Sample Preparation – removes radionuclide impurities
  - E_{max} = 156 keV
  - Detection Efficiency = ~95 %
  - Spectrum can give indications of radionuclide impurities
- Gas Proportional Counting (GPC)
  - Precipitation of $BaCO_3$: not as effective at contamination removal
  - No ability to assess contamination potential
  - Self absorption by sample test source is significant
- Accelerator Mass Spectrometry (AMS)
  - Sample test source must be a solid or sample preparation must make the material a solid.

Alternate CO_2 Capture for LSC

- Direct release of CO_2 - using acid
- Nitrogen sweep through a solution of ethanolamine cocktail
- Ethanolamine cocktail - limited capacity for CO_2
  - Limits sample size if stable carbon content is high

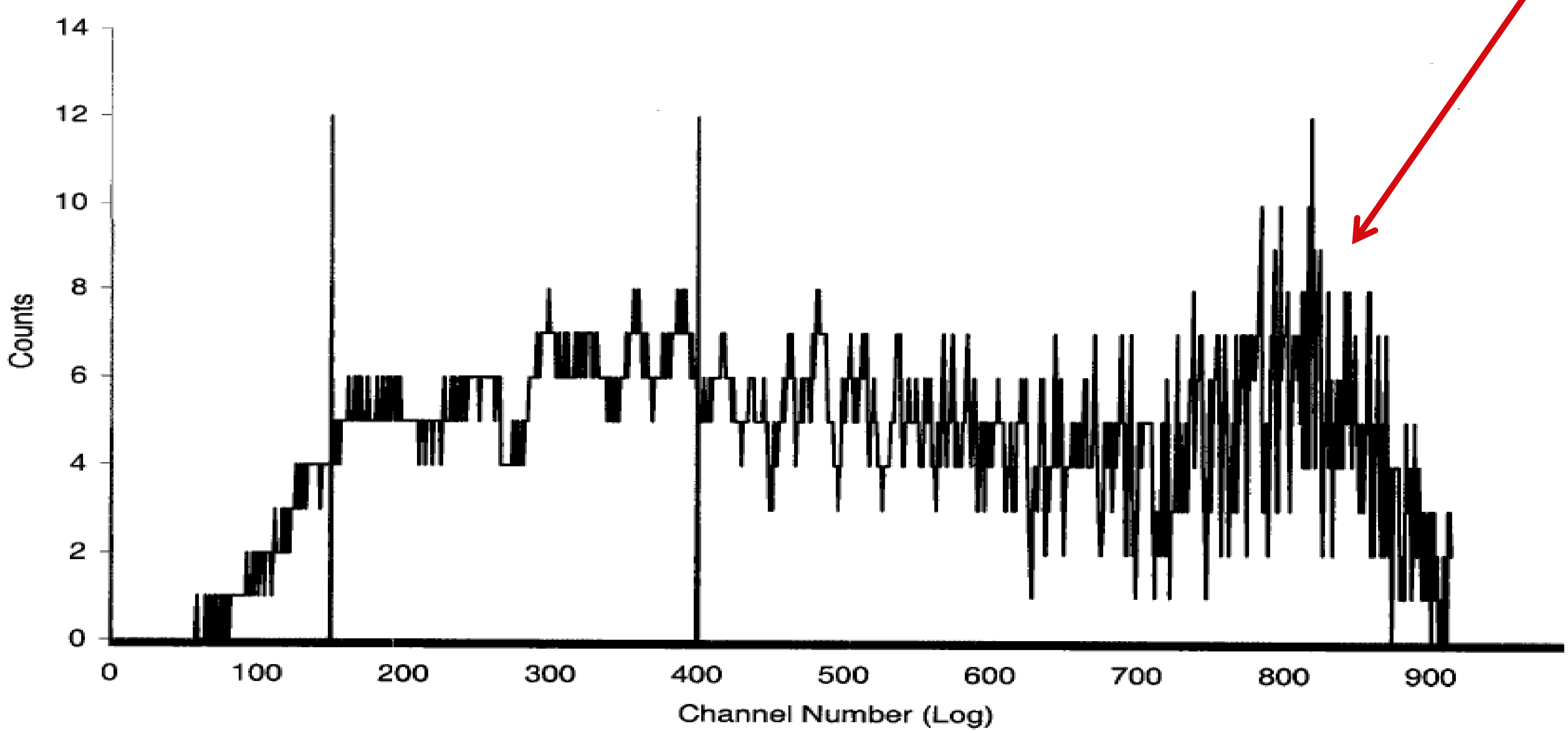
^{14}C Liquid Scintillation Spectrum –PWR Gaseous Effluent

(1.39 pCi/L, 36 L sample, 120 min count time)

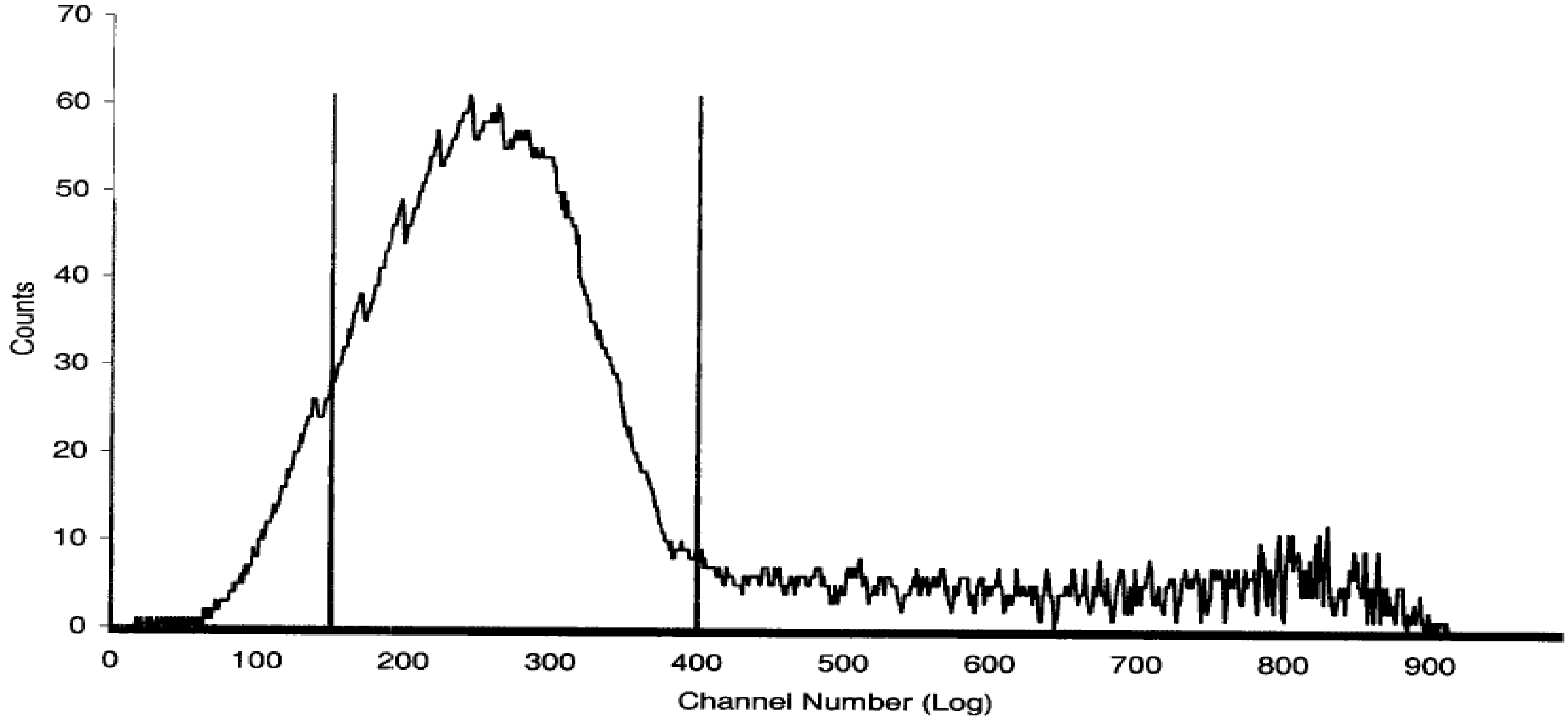


^{14}C Method Blank Spectrum

What could this be?



Laboratory Control Sample – Ascarite Spiked with ^{14}C Standard



Gas Proportional Counting

- Collection/preservation prior to counting
  - Maintains ^{14}C on the STS (planchet or filter)
- Relies on thorough chemical separation of all other beta emitters
  - No way to determine if interferences are present
  - (possibly by sample recount)
- Sample test source needs to be almost "massless"
  - Efficiency will only be about 40 % maximum

Accelerator Mass Spectrometry

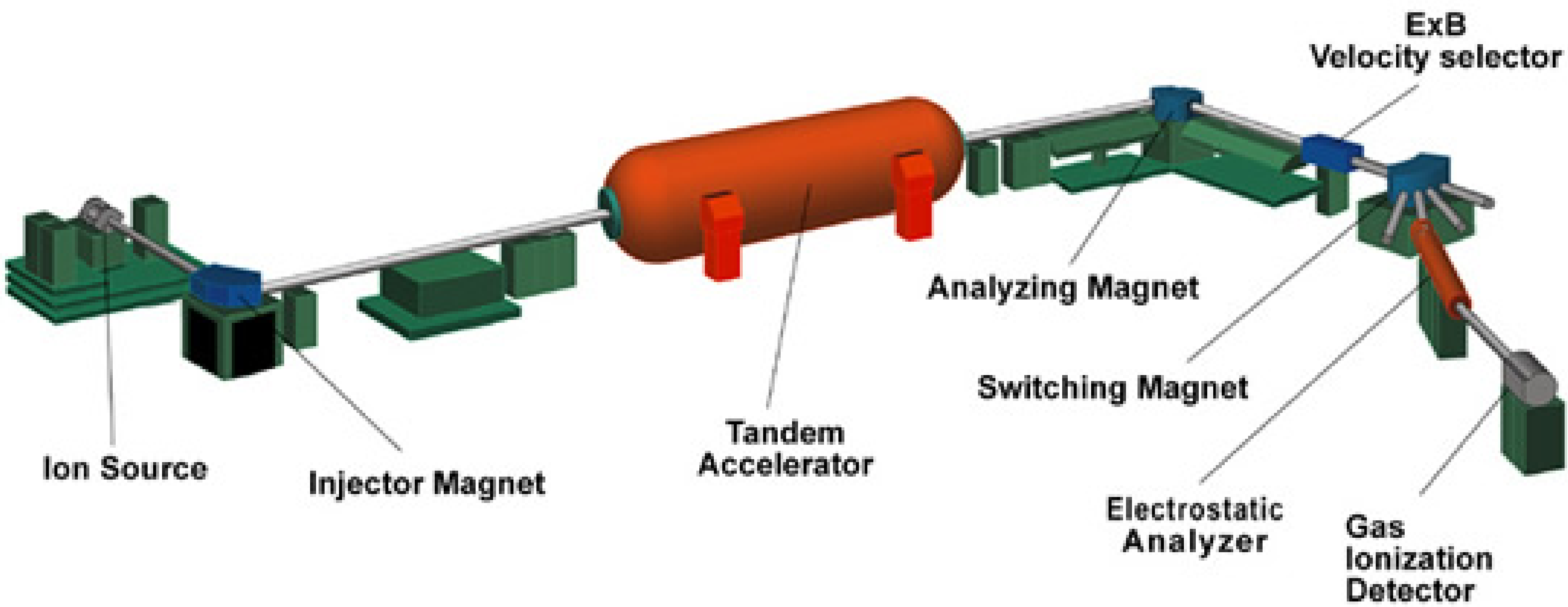


Figure taken from “https://www.physics.purdue.edu/ams/introduction/ams.html

AMS

- Used mostly for carbon dating of archeological samples
- Excellent sensitivity since it counts atoms vs decays
- Several labs place restrictions
  - Sample size requirements – can compromise representative sampling
  - Only naturally occurring ^{14}C (no samples that contain tracer ^{14}C)

Case Study 1- Standard Preparation

- A laboratory had requested a standard for ^{14}C on filter paper for calibration of their gas proportional counter.
- The efficiency calculated was much lower than anticipated
- Analysis of cross-check samples showed a high bias

Case Study 2 – ^{14}C in Concrete

- Decommissioning of a nuclear power plant
- Tritium was found in containment concrete; was ^{14}C also present
- Method to sample concrete required modification

Case Study 3 – ^{14}C interference by ^{3}H

- Contract laboratory received a GW sample for ^{14}C analysis
- Most of sample was used in initial sample preparation which was lost during a blunder.
- Remainder of sample was too small to perform analysis at the LLD requested. Remainder of sample was used directly in liquid scintillation analysis to get estimate of content

General References

- ORNL/NUREG TM-12, “Carbon-14 Production in Nuclear Reactors” (1977)
- GEOLOGICAL SURVEY CIRCULAR 480, “Preparation of Water Sample for Carbon-14 Dating” (1963)
- ORNL/CDIAC-104, “Carbon-14 Measurements in Surface Water CO_2 from the Atlantic, Indian and Pacific Oceans, 1965-1994” (1998)
- https://www.physics.purdue.edu/ams/introduction/ams.html

Dose References

- ICRP-60 "1990 Recommendations of the International Commission on Radiological Protection" (ICRP, 1991)
- ICRP-72 "Age-dependent Doses to the Members of the Public from Intake of Radionuclides – Part 5 Compilation of Ingestion and Inhalation Coefficients" (ICRP, 1995)
- ICRP Report 103 "The 2007 Recommendations of the International Commission on Radiological Protection" (ICRP, 2007)
- USNRC 10CFR20, Standards for Protection Against Radiation
- USNRC 10CFR50 Appendix I
- USNRC Regulatory Guide 1.109
- USNRC Regulatory Guide 1.111
- USNRC Regulatory Guide 1.113
- ICRP Publication 101a, "Assessing Dose of the Representative Person for the Purpose of the Radiation Protection of the Public" (ICRP, 2006)

Thanks for your attention.
Happy to address your questions!

Upcoming Webinars

- Technetium
- Gross Alpha and Gross Beta by LSC
- Northern Lights Exercise

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