Liquid Scintillation counting of H-3 and C-14

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Eckert & Ziegler Analytics

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H-3

\[ E_{\text{max}} = 18.6 \text{ keV} \]
\[ T_{1/2} = 12.43 \text{ y} \]
\[ 1 \text{TU (tritium unit)} = 1 \text{ atom of H-3 per } 10^{18} \text{ atoms of H-1} \]
\[ 1 \text{TU} = 7.19 \text{ dpm/L} = 0.118 \text{ Bq/L} = 3.19 \text{ pCi/L of H}_2\text{O} \]

Natural activity in precipitation – about 25TU at high altitudes, about 4TU in the equatorial zone
C-14

- $E_{\text{max}} = 156.48$ keV
- $T_{1/2} = 5700$ y
- $pMC$ - percent modern carbon, proportion of C-14 activity in the sample compared to the C-14 standard activity.
- Standard activity - define as 74.59% of activity of oxalic acid SRM 4990C.
- 100 pMC = 13.56 dpm/g = 0.226 Bq/g = 6.108 pCi/g C
Liquid Scintillation

- Emulsifier
- Solvent (e.g. DIN)
- Fluor (e.g. PPO)
Scintillation

- Flash of light with 375-430 nm wavelength range
- Beta pulse decay time – 2-10 ns
- Alpha pulse decay time – 40-50 ns
- The intensity of light flashes is directly proportional to the original nuclear decay energy dissipated in the cocktail
- 10 photons per 1 keV energy absorbed in LSV
LS Analysis

- LS Counter
- Vials
- Cocktails
- Sampling
- Sample preparation for counting
- Counting
- Data evaluation
LS Counters

• LSC should be able to:
  – Detect light flushes from LS vial
  – Determined number of light flushes and their intensity
  – Process automatically different type of samples
LS Counters

Schematic diagram of modern LSC (TriCarb)
300 SL - Hidex

- Each other. These three PMT’s enable triple to double coincidence ratio counting-TDCR.
- Optimal lead shield design with a minimum of 70mm shielding in all directions provides good shielding and minimizes instrument weight.
- Lead shutter provides optimal shielding from cosmic radiation.
- Copper shielding eliminates x-rays from lead shield.
- Measurement chamber with high reflective opaque paint maximizes light collection.
- Robotic loading arm removes the need for a complex elevator mechanism. Shielding both on top and bottom of detector cavity results in the biggest reduction of background effects.
- Three low background PMTs provide optimal measurement geometry and facilitate TDCR counting.
Schematic diagram of TDCR LSA

FIGURE 5.49  The counting system of a three-phototube liquid scintillation analyzer with link to a personal computer. The components are similar to those found in a conventional dual-phototube LSA including amplifiers, pulse height discriminators, summation circuitry ($\Sigma$), electronic gates, coincidence circuit, and scalers. (From Cassette and Vatin, 1992, reprinted with permission Elsevier Science.)
TRIATHLER MULTILABEL COUNTER

Specifications:

- Sample Types: LSC vials, Microtubes, Test Tubes
- Detector: Single-Photon Counting PMT
- Display: 2 x 16 character alpha-numeric LCD
- Energy Range: 2 keV – 2000 keV
- Counting Time: 0.1 seconds – 99999 minutes
- Output: RS-232C to PC or thermal printer
- Power: 110-240V AC, 12V DC
- Dimensions: 33 L x 25 W x 19 H cm
- Weight: 9 kg

Liquid Scintillation Counting:

- Sample size: LSC Vials, Microtubes, Test Tubes
- Max. Count Rate: 2,000,000 CPM
- Beta Efficiency: up to 48% for 3H
- Direct 32P Efficiency: up to 75% in Plastic Scintillator Adapter Tube
Vials

• Glass vials- low potassium borosilicate glass
  – Provide advantage of transparency for cocktail

• Plastic vials – polyethylene vials
  – Unbreakable, less expensive, lower background than glass vials
  – Permeable to benzene, toluene and xylene based cocktails
  – Resistant to diffusion with environmentally friendly cocktails(Ultima Gold, Opti-Fluor etc.)
Nahle O. et al. light trapping in glass vials

1-plastic vial, 2- glass vial with scotch tape, 3-glass vial
Figure 5 Intensity profiles of a glass vial (solid), a polyethylene vial (dashed), and an etched vial (dotted) in a side view. The meniscus area is highlighted as a hatched rectangle. To the right, the profile of a typical glass vial is shown.
# Performance Vials

## Table 5.11 Tritiated Water in Ultima Gold LLT Scintillation Cocktail in Glass and Plastic, Large and Small Vials, Performance Comparison

<table>
<thead>
<tr>
<th>Vial size (mL)</th>
<th>Vial material</th>
<th>Water (%)</th>
<th>Efficiency&lt;sup&gt;a&lt;/sup&gt; (%)</th>
<th>Background (CPM)</th>
<th>E&lt;sup&gt;2&lt;/sup&gt;/B</th>
<th>Counting Region 0.5–5.0 keV</th>
<th>Efficiency&lt;sup&gt;a&lt;/sup&gt; (%)</th>
<th>Background (CPM)</th>
<th>E&lt;sup&gt;2&lt;/sup&gt;/B</th>
</tr>
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<td>103.9</td>
<td></td>
</tr>
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<td>0.5</td>
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<td>10.15</td>
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<td>29.31</td>
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<td></td>
</tr>
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<td>7</td>
<td>Plastic</td>
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<td>30.10</td>
<td>7.82</td>
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<td>28.10</td>
<td>2.58</td>
<td>306.1</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>% Counting efficiency = (CPM/DPM)(100).
LS Cocktails

• Cocktail is a media that holds sample during the analysis process
  – Emulsifying or aqueous cocktails (Safer)
    • Organic aromatic solvent
    • Scintillator
    • Emulsifier
  – Organic or non-aqueous cocktails (Classical)
    • Organic aromatic solvent
    • Scintillator
LS Cocktails-Solvents

LSC Solvents
Evolution Time Line

Flash Point (°F)


USA = 100°F
ROW = 149°F

T. DeVol et al.
LS Cocktails-Scintillators

• Scintillators
  – 2,5-diphenyloxazole (PPO) and
  – p-bis-(methylstyryl)benzene (bis-MSB)

is the most popular combination
LS Cocktails-Surfactants

- Surfactants form micro emulsion “oil-in-water” (~ 10nm droplet size) to ensure energy transfer:
  - Nonionic – alkyl phenol ethoxylates are the most popular surfactants found in most cocktails
  - Anionic
  - Cationic
  - Amphoteric
FIGURE 6.9  Example of cocktail performance evaluation.
# LS Cocktails for H-3

## TABLE 8.3  Cocktail Selection for Low Ionic Strength Samples (Based on the Use of 10 mL of Cocktail)

<table>
<thead>
<tr>
<th></th>
<th>Safer cocktail</th>
<th>Classical cocktail</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low sample</td>
<td>Ultima Gold, MV, AB, LLT, Opti-Fluor, Emulsifier Safe</td>
<td>Insta-Gel Plus (Insta-Gel XF), Pico-Fluor 15 and 40, and other equivalent cocktails.</td>
</tr>
<tr>
<td>volume (0–2.5 mL)</td>
<td>(Poly-Fluor), and other equivalent cocktails.</td>
<td></td>
</tr>
<tr>
<td>High sample</td>
<td>Ultima Gold, XR, AB, LLT, Opti-Fluor, and other</td>
<td>Insta-Gel XF, Pico-Fluor 40 and other equivalent cocktails.</td>
</tr>
<tr>
<td>volume (&gt; 2.5 mL)</td>
<td>equivalent cocktails.</td>
<td></td>
</tr>
</tbody>
</table>
LS Cocktails for C-14

• CarboSorb E, Optisorb-1(PE), Carbo-Trap (Baker), Carbomax Plus (Lumac), Carbomate-2 (N.D.), Zintol-II (Zinsser)
  \[ \text{CO}_2 + \text{amine} \rightarrow \text{carbamate} \]

• Permafluor E, Optisorb S(PE), 14C-Fluor (Baker), Oxosol-306(N.D.), Zintol-X (Zinsser)
## LS Cocktails for C-14

### TABLE 8.20 Reference Table for CO₂ Trapping and LSC Counting

<table>
<thead>
<tr>
<th>CO₂ absorber</th>
<th>mm CO₂ per mL</th>
<th>mL Reqd for 1 mM CO₂</th>
<th>mL Reqd for 5 mM CO₂</th>
<th>mL Reqd for 10 mM CO₂</th>
<th>LSC cocktail</th>
<th>Cocktail volume (mL)</th>
<th>mL of Absorber</th>
<th>Max CO₂ capacity (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH (0.1 M)</td>
<td>0.05</td>
<td>20.0</td>
<td>-</td>
<td>-</td>
<td>Emulsifier safe</td>
<td>15.0</td>
<td>3.0</td>
<td>0.15</td>
</tr>
<tr>
<td>NaOH (0.5 M)</td>
<td>0.25</td>
<td>4.0</td>
<td>-</td>
<td>-</td>
<td>Opti-Fluor</td>
<td>14.0</td>
<td>7.0</td>
<td>0.35</td>
</tr>
<tr>
<td>NaOH (1.0 M)</td>
<td>0.50</td>
<td>2.0</td>
<td>10.0</td>
<td>-</td>
<td>Ultima-Flo AF</td>
<td>10.0</td>
<td>10.0</td>
<td>2.50</td>
</tr>
<tr>
<td>Hyamine hydroxide</td>
<td>0.50</td>
<td>2.0</td>
<td>10.0</td>
<td>-</td>
<td>Hionic-Fluor</td>
<td>14.0</td>
<td>7.0</td>
<td>3.50</td>
</tr>
<tr>
<td>(in methanol)</td>
<td>0.50</td>
<td>2.0</td>
<td>10.0</td>
<td>-</td>
<td>Insta-Fluor</td>
<td>12.0</td>
<td>9.0</td>
<td>4.50</td>
</tr>
<tr>
<td>Ethanolamine</td>
<td>8.10</td>
<td>0.12</td>
<td>0.62</td>
<td>1.23</td>
<td>Emulsifier Safe</td>
<td>15.0</td>
<td>4.5</td>
<td>2.25</td>
</tr>
<tr>
<td>Carbo-Sorb E</td>
<td>4.80</td>
<td>0.21</td>
<td>1.04</td>
<td>2.08</td>
<td>Hionic-Fluor / Methyl cellosolve</td>
<td>10.0</td>
<td>3.0</td>
<td>24.3</td>
</tr>
<tr>
<td>of... Permafluor E+</td>
<td>10.0</td>
<td>10.0</td>
<td>10.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
LS Cocktails

• Aupiasis J. et al.
  – Elaborated discussion on energy transfer within the cocktail
Counting interferences factors

- Quench
- Background
- Luminescence
- Static electricity
- Wall effect
Quench in LSC

- A reduction of the light reaching the photomultiplier tube
- Quench alters the light production and transmission process.
- IT DOES NOT ALTER THE ENERGY OF THE PARTICLE.
- Types of Quench
  - Self Absorption
  - Color (Optical)
  - Chemical
Quench in LSC

• Self-absorption quench occurs when radiation emitted from a sample remains undetected due to entrapment in a non-scintillating media
Quench in LSC

- Chemical quench—interference with production of photons in the scintillator (compounds scavenge the excitation energy from the solvent, interfere with energy transfer from solvent to solute)
- Chemical quench is loss of energy
Quench in LSC

- Color quench is the result of absorption of the scintillation photons before they are detected by the photomultiplier tube.
- Color quench is the loss of light.
FIGURE 5.24 Liquid scintillation pulse height distributions of chemical- and color-quenched $^{14}$C samples. Both samples have identical activity and counting efficiencies (From Takiue et al., 1991a, reprinted with permission from Elsevier Science).
FIGURE 5.12 Color and chemical quench correction curves based on the external standard channels ratio (From Takiue et al., 1983, reprinted with permission from Elsevier Science).
Quench in LSC

**FIGURE 5.19** Quench correction curves for $^3$H ($E_{\text{max}} = 18.6$ keV), $^{14}$C ($E_{\text{max}} = 156$ keV), and $^{32}$P ($E_{\text{max}} = 1710$ keV) using tSIE as the external standard quench-indicating parameter with a Packard 2700TR LSA. The optimum counting efficiencies for the unquenched samples of $^3$H, $^{14}$C, and 5% water-quenched $^{32}$P were 67.6, 96.9, and 98.1%, respectively. (L'Annunziata, 1996, unpublished work.)
Quench in LSC
Quench correction

- Internal Standard Method
- Sample spectrum characterization methods
- Direct DPM methods
Quench correction - Internal Standard

- Internal Standard Method

\[ E = \frac{(C_{s+i} - C_s)}{A_i} \]

\[ A_s = \frac{C_s}{E} \]

- \( C_s \) – count rate of sample
- \( C_{s+i} \) – count rate of sample after addition of internal standard
- \( A_s, A_i \) – activity of sample and internal standard
- \( E \) – counting efficiency
Quench correction – Spectrum characterization

• Sample spectrum characterization methods

  – H# - Beckman
  – SQP – Wallac, Hidex
  – G# -
  – SIS- PE
  – tSIE-PE
Quench correction – Direct DPM counting

- Direct DPM methods
  - Efficiency tracing with C-14
  - Triple-to-double coincidence ratio (TDCR)
  - NIST/CIEMAT efficiency tracing
Quenching correction -Color

• Color quench:
  – Decolorized (bleaching or oxidation)
  – Use color correction software of the instrument
  – Count separate set of standards for color quenching correction
Quenching effects

- Komosa A, Slepecka K.

- 9 commercial cocktails, two type of vials – low potassium glass vial and low diffusion Teflon coated PE vial
Komosa A, and Slepecka K. Quenching Effects..

Table 5  Figures of merit (FOM) for $^{14}$C and $^{3}$H standard solutions and various cocktails (volume 10 cm$^3$) using the high-performance glass and the low-diffusion polyethylene (LD-PE) vials, without quenching agent addition.

<table>
<thead>
<tr>
<th>Cocktail</th>
<th>$^{14}$C Glass vials</th>
<th>$^{14}$C LD-PE vials</th>
<th>$^{3}$H Glass vials</th>
<th>$^{3}$H LD-PE vials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Insta Gel</td>
<td>1609</td>
<td>2370</td>
<td>228</td>
<td>1241</td>
</tr>
<tr>
<td>Insta Fluor</td>
<td>2750</td>
<td>4952</td>
<td>174</td>
<td>1198</td>
</tr>
<tr>
<td>Permablend</td>
<td>2895</td>
<td>6063</td>
<td>239</td>
<td>1785</td>
</tr>
<tr>
<td>Butyl-PBD</td>
<td>2691</td>
<td>5065</td>
<td>252</td>
<td>1918</td>
</tr>
<tr>
<td>Ultima Gold AB</td>
<td>2160</td>
<td>3942</td>
<td>233</td>
<td>1760</td>
</tr>
<tr>
<td>Ultima Gold LLT</td>
<td>2027</td>
<td>3650</td>
<td>254</td>
<td>1444</td>
</tr>
<tr>
<td>HiSafe 2</td>
<td>1695</td>
<td>2891</td>
<td>231</td>
<td>1266</td>
</tr>
<tr>
<td>Hionic Fluor</td>
<td>1061</td>
<td>1377</td>
<td>196</td>
<td>636</td>
</tr>
<tr>
<td>HiSafe 3</td>
<td>1990</td>
<td>4348</td>
<td>266</td>
<td>1320</td>
</tr>
</tbody>
</table>
Background

• Counts from sources external to the sample
  1. Instrument -10%
  2. Crosstalk - 22%
  3. Vial and PMT face - 37%
  4. Scintillator - 31%
Figure 2-31. Backgrounds.
Background

• Background count rates are determined by counting a blank samples

• The majority of background counts are found in 0-5 keV energy range
FIGURE 5.67  The calculated LLD or MDA in Bq L$^{-1}$ as a function of sample background in CPM for 4 different sample and background counting times: 100, 250, 500, and 1000 minutes for $^3$H tritium analysis with a counting efficiency of 35% or 0.35 and sample volume of 10 mL.
# Background Reduction, Vial material and size

## TABLE 5.11 Tritiated Water in Ultima Gold LLT Scintillation Cocktail in Glass and Plastic, Large and Small Vials, Performance Comparison

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<th>Vial material</th>
<th>Water (%)</th>
<th>Efficiency(^a) (%)</th>
<th>Background (CPM)</th>
<th>(E^2/B)</th>
<th>Counting Region 0.5–5.0 keV</th>
<th>Efficiency(^a) (%)</th>
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</tr>
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\(^a\)% Counting efficiency = (CPM/DPM)(100).

Michael F.L'Annunziata "Handbook of ...."
Background Reduction - Region optimization

FIGURE 5.66 Pulse height spectra of a $^{14}$C sample (above) and a background or blank sample (below). For this particular sample and blank, chemical composition, sample load, cocktail, and vial type the LL (left) and UL (right) discriminator settings of 9.0–73.5 were found to provide region optimization. In this example, the reduced counting region produced a sacrifice of 18% in the $^{14}$C counting efficiency but a reduction of 54% in the background counts. Region optimization is specific to radionuclide, sample-cocktail chemistry or quench level, and vial type and size (L’Annunziata, 1996, unpublished work).
K-40 contribution, Gonen R.et al.
4.27 0.98% in H-3 spectrum

Figure 1 Equivalent $^3$H spectra of different background contributions
Background Reduction

- **Temperature control**
  - Cooling used to minimize thermal noise from PMT. In contemporary LS counters cooling optimizes sample chemistry

- **Shielding**
  - Passive (lead)
  - Active (BGO guard detector)

- **Pulse Discrimination Electronics**
## Background Reduction

### Pulse Discrimination Electronics

<table>
<thead>
<tr>
<th>Amount of pulse index discrimination</th>
<th>Detector guard</th>
<th>$^3$H efficiency (%)</th>
<th>Background (CPM)</th>
<th>Figure of Merit ($E^2/B$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>No</td>
<td>26.50</td>
<td>18.45</td>
<td>38</td>
</tr>
<tr>
<td>Normal TR-LSC</td>
<td>No</td>
<td>26.24</td>
<td>12.75</td>
<td>54</td>
</tr>
<tr>
<td>High-sensitivity TR-LSC</td>
<td>No</td>
<td>24.68</td>
<td>9.25</td>
<td>66</td>
</tr>
<tr>
<td>Low-level TR-LSC</td>
<td>No</td>
<td>22.59</td>
<td>3.33</td>
<td>153</td>
</tr>
<tr>
<td>Ultra-low-level TR-LSC + BGO Active Guard</td>
<td>Yes</td>
<td>20.01</td>
<td>1.00</td>
<td>400</td>
</tr>
</tbody>
</table>

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*a* The optimized counting region is 0.5–5.0 keV with various level of TR-LSC pulse index discrimination applied to the pulse event. Courtesy of Perkin Elmer Life and Analytical Sciences.
## Background Reduction—Pulse Discrimination Electronics

<table>
<thead>
<tr>
<th>Scintillator&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Radiocarbon Dating Samples as 3.5 mL Benzene with PPO/POPOP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount of pulse index discrimination</td>
<td>Detector guard</td>
</tr>
<tr>
<td>None</td>
<td>No</td>
</tr>
<tr>
<td>Normal TR-LSC</td>
<td>No</td>
</tr>
<tr>
<td>High-sensitivity TR-LSC</td>
<td>No</td>
</tr>
<tr>
<td>Low-level TR-LSC</td>
<td>No</td>
</tr>
<tr>
<td>Ultra-low-level TR-LSC + BGO Active Guard</td>
<td>Yes</td>
</tr>
</tbody>
</table>

<sup>a</sup>The optimized counting region is 10–102 keV with various levels of TR-LSC pulse index discrimination applied to the pulse events. Courtesy of PerkinElmer Life and Analytical Sciences, Boston.
Luminescence

- Luminescence refers to emission of light photons due to energy absorption and concomitant molecular excitation from origins other than nuclear radiation. Contribute to the background through random coincidence effects in PMT that view the sample
  - Photoluminescence
  - Chemiluminescence
Photoluminescence

- Result of the exposure of the sample to UV light
- Single photon event and decays in 10-15 minutes
- Light emitting substance can be repeatedly activated
Chemiluminescence

- One time event when mixing cocktail and sample due to chemical reaction
- Single photon event
- The majority of the counts are in 0-6 keV region
- Two counting regions can be used to detect chemiluminescence
Chemiluminescence

FIGURE 5.30 Pulse height distributions of $^3$H and $^{14}$C scintillation pulses and of chemiluminescence pulses, and channel settings for the analytical measurement of each activity and chemiluminescence count rate (From Takiue et al., 1985, reprinted with permission from Elsevier Science).
Luminescence control

• Chemical methods – neutralization with nonoxidizing acid, neutralization before adding a cocktail, use of special cocktails (Hionic-Fluor).

• Temperature control – cooling slows down the reaction, heating up to 40°C drives reaction to its endpoint.

• Counting region setting

• Delayed coincidence counting
Static

- Electrostatic discharge is photon-producing event of random nature
- Methods for reducing or eliminating static:
  - Electrostatic controller
  - Selection of vials (antistatic plastic vials)
  - Antistatic wipes
  - Humidification of sample preparation and counting areas
Wall effect

• Applies to plastic vials and traditional cocktails:
  – Cocktail penetrates plastic vial and causes scintillation.
  – Quench indicating parameter would be erroneous, providing wrong counting efficiency, and as result wrong activity of the sample.
Sampling and counting of H-3

• Samples should be sealed in airtight containers (glass or HD plastic)
• When samples are exposed to outside air. It should be assumed that contamination is possible and monitoring is required.
• Purification of water samples is recommended if (1) color is visible, (2) organics are present or (3) sample history is unknown
Sampling and counting of H-3

• Sample purification/Extraction techniques
  – Filtering
  – Ion exchange
  – Freeze drying
  – Azeotropic distillation
  – Distillation
Sampling and counting of H-3

- Madruga M.J et al. Determination of H-3 in waters
  - Distillation and Electrolytic enrichment
  - 8/12 UG LLT
  - 20 ml glass vial
Sampling and counting of H-3

- Z. Tosheva et al.
  - Comparison of Distillation (ISO-9698) and chromatographic (Eichrom OTWO2) methods for H-3 determination:
    - 250 ml sample for distillation – up to 7 hours
    - 25 ml sample for chromatography – 30 min
  - Comparison of 6 cocktails:
    - UG LLT, UG XR, Pico Fluor LLT, OptiPhase HiSafe 2 with added Triton X100, OptiPhase HiSafe 3 and OptiPhase TriSafe for efficiency, background and MDA
Sampling and counting of H-3

• Gudelis et all.
  – Water from the wells around Waste Storage facility:
  – Water and soil
  – MDA - 0.8 Bq/l for 2800 min 12+8 ratio
  – H-3 range up to $10^5$ Bq/l
Sampling and counting of H-3

- Pujol L. et al.
  - National network
  - No distillation, UG LLT 10/12
  - MDA 1.5-2.3 Bq/L
  - Background – 0.8-2.6 cpm
  - Counting efficiency - ~ 20%
  - Detailed discussion of H-3 level in “nuclear” vs “non-nuclear” rivers
Sampling and counting of H-3

• Gonen R. et all (OBT in Urine)
  – Biological half-life of OBT is 4 times greater than for HTO
  – OBT determination is time consuming
  – Direct determination:
    – (HTO+OBT)- from analysis of total urine,
      2ml urine+14ml UG XR+ 4 ml water
    – HTO – after filtration through charcoal, 20 ml of urine + 3g active charcoal, 2ml of filtrate+14ml UG XR+4ml water
Gonen R. et al (OBT in Urine)

- Chemi- and photoluminescence are discussed, chemiluminescence's spectrum overlaps both H-3 and C-14 spectra
- K-40 contribution is considered
- ANSI-N13.30 HPS 1996 – recommendations
- MDA for 45 min counting – 0.058Bq/sample (Quantulus 1220)
Baglan N. et al, OBT round-robin exercise

• 11 laboratories were participating in CETAMA (Comite d’ETAbliissement des Methodes d’Analyse) organized round-robin exercise
Sampling of C-14

- Benzene synthesis
  - Most accurate, used in dating
- Direct counting
  - Limited application
- CO$_2$ Absorption
  - Sample preparation is less time-consuming
  - Limited amount of carbon can be absorbed (0.7g vs 10g for benzene)
Sampling and Counting of C-14

Figure 1  Schematics of CO$_2$ absorption line (see text below for label abbreviations).
### Sampling and Counting of C-14

#### TABLE 8.18 Trapping Capacity of Suitable Reagents for Carbon Dioxide

<table>
<thead>
<tr>
<th></th>
<th>mM CO₂ per mL</th>
<th>mL Required for 1 mM CO₂</th>
<th>mL Required for 5 mM CO₂</th>
<th>mL Required for 10 mM CO₂</th>
<th>Flash point</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium hydroxide 0.1 M</td>
<td>0.05</td>
<td>20.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium hydroxide 1.0 M</td>
<td>0.50</td>
<td>2.0</td>
<td>10.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hyamine hydroxide 1.0 M (in methanol)</td>
<td>0.50</td>
<td>2.0</td>
<td>10.0</td>
<td></td>
<td>11°C</td>
</tr>
<tr>
<td>Ethanolamine</td>
<td>8.10</td>
<td>0.12</td>
<td>0.62</td>
<td>1.23</td>
<td>93°C</td>
</tr>
<tr>
<td>Carbo-Sorb E</td>
<td>4.80</td>
<td>0.21</td>
<td>1.04</td>
<td>2.08</td>
<td>27°C</td>
</tr>
</tbody>
</table>
Svetlik I et al., C^{14}O_2 in grab samples

- Samples were collected in high pressure (200 atm) SS bombs – 30 min, 150-350L
- Samples were stored for 1 month to reduce background from short-lived radionuclides
- Samples were transferred to low pressure gas bags with 2 outlets
- Gas was pumped from the gas bag through gas meter to series of traps (washing - 1% H_3PO_4, absorbing – 3M NaOH and condensation trap – 1% H_3PO_4 ) and back to the gas bag.
Svetlik I et al., C^{14}O_{2} in grab samples

- 1 sorption cycle – 33-36% of CO_{2}
- 13 cycles – above 98%
- Finally system was purged with N_{2}
- 8g out of total ~ 50g of Na_{2}C^{14}O_{3} were used to prepare duplicate final samples 5 g each with pH~9.3
  Diluted H_{2}SO_{4} was used to adjust the pH
- 15 ml of Hionic-Fluor (PE) were added
- Counting efficiency – 32-34%
- Background – 6.5 cpm
- Counting time – 60 min
- For the total combustible C-14 – CuO catalyst (at 700^\circ C) was inserted between gas bag and gas meter
Figure 1 A comparison of $^{14}$C activities (Bq/m$^3$) determined in stack air from continual and grab sampling in NPP Temelin, reactor HVB1.
• Precipitation of dissolved inorganic carbon as carbonate
• Acidification and release of CO₂
• Direct absorption of CO₂ in tertiary amine
• Addition of scintillation solution and counting
Saxen R. and Hanste U. M, C-14 in foodstuff

- Automatic oxidizer Model 307 (PE)
- CO$_2$ is absorbed by CarboSorb E
- Permafluor E cocktail added to the sample
- 2000-2007 ~ 125 Bq/kg C in mixed diet
- Annual dose ~ 10μSv/yr (12 μSv/yr – “natural level”)
- No increase due to discharge from NPPs
C-14 Vartii V-P, Optimizing counting

• CarboSorb is a strong quenching agent, background sample should be adjusted to match the same quench as in the sample
• 10 ml of CarboSorb can take up 48 mmoles of C, that limits sample size to 1g
• It very challenging to prepare representative sample
Molnar et al., Refining the CO$_2$ absorption …

- Carbosorb (PE) – 11 ml, Mean absorbed amount of CO$_2$ – 1.98g (82% saturation), 0.54g of C
- Permafluor E (PE) – 11 ml
- Counting time – 1020 min
- TriCarb 3170, 7-52 channels, FM=2283
  FM=$E^2/B$, Bkg. 1.869 .020 cpm
Table 3  Results of the $^{14}\text{C}$ activity concentrations in environmental samples from the vicinity of the Finnish NPPs in 2006–2007.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Place</th>
<th>Reference date</th>
<th>$^{14}\text{C}$ Bq/kg (dry weight)</th>
<th>± % (2σ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rosehip</td>
<td>Olkiluoto</td>
<td>7.9.2006</td>
<td>72</td>
<td>20</td>
</tr>
<tr>
<td>Blueberry twigs and leaves</td>
<td>Olkiluoto</td>
<td>7.9.2006</td>
<td>127</td>
<td>26</td>
</tr>
<tr>
<td>Leaves of black alder</td>
<td>Olkiluoto</td>
<td>7.9.2006</td>
<td>90</td>
<td>20</td>
</tr>
<tr>
<td>Blueberry twigs and leaves</td>
<td>Loviisa</td>
<td>31.8.2006</td>
<td>77</td>
<td>18</td>
</tr>
<tr>
<td>Leaves of black alder</td>
<td>Loviisa</td>
<td>31.8.2006</td>
<td>82</td>
<td>20</td>
</tr>
<tr>
<td>Pine needles</td>
<td>Loviisa</td>
<td>30.8.2007</td>
<td>122</td>
<td>60</td>
</tr>
<tr>
<td>Grass</td>
<td>Loviisa</td>
<td>30.8.2007</td>
<td>123</td>
<td>76</td>
</tr>
<tr>
<td>Leaves of birch</td>
<td>Loviisa</td>
<td>30.8.2007</td>
<td>146</td>
<td>18</td>
</tr>
<tr>
<td>Leaves of birch</td>
<td>Olkiluoto</td>
<td>17.7.2007</td>
<td>116</td>
<td>12</td>
</tr>
<tr>
<td>Grass</td>
<td>Olkiluoto</td>
<td>17.7.2007</td>
<td>119</td>
<td>50</td>
</tr>
<tr>
<td>Pine needles</td>
<td>Olkiluoto</td>
<td>17.7.2007</td>
<td>152</td>
<td>36</td>
</tr>
</tbody>
</table>
Do-Sung Kim et al. Retrieval estimation of gaseous C-14 discharged..

- CANDU – PHWR 700MWe x 4
- Retrieval of discharge rates for H-3 and C-14 from pine trees rings
- Rings were separated, ground and dried. $\alpha$-Cellulose was extracted, dried and burned
- Water was used for OBT determination
- $CO_2$ was absorbed by $NH_4OH$ and precipitated as $CaCO_3$
- Nitric acid was added and $CO_2$ trapped in LS vial
- Samples were counted for 600 min (30 min x 20)
Do-Sung Kim et al. Retrieval estimation of gaseous C-14 discharged..

Figure 2 OBT concentrations of pine tree rings in 3 different sampling locations
Do-Sung Kim et al. Retrieval estimation of gaseous C-14 discharged.

Figure 3 $^{14}$C concentrations of pine tree rings in 3 different sampling locations.
Do-Sung Kim et al. Retrieval estimation of gaseous C-14 discharged.

Figure 6 The estimated gaseous $^{14}$C discharge rate of the Wolsung NPP
Noakes J. et al., A comparison of analytical …

- ASTM D 6866-05 for USDA Biobased products:
  - Accelerator mass-spectrometry (AMS)
  - Benzene synthesis
  - LSC of CO$_2$
Noakes J. et al., A comparison of analytical …

- 20 ml vial, 10 ml Carbosorb E, 10 ml Permafluor
- 10 ml Carbosorb E – 1L CO$_2$ at STP
- Amount of CO$_2$ determined by weight
- Linearity of absorption is verified
- 1L CO$_2$ – 0.45 g C
Noakes J. et al., A comparison of analytical ...

- 56-66% efficiency
- Background – 2.53 - 4.08 dpm/g
- Preparation time – 3 h
- Analysis time – 1300 m
- Analysis cost - $250
- Instrument cost – $100,000
Culp R. et al., Further development of ASTM 6866-06

![Flowchart](image)

Figure 7 Present ASTM 6866-06a analytical protocol, with UGA pricing

- Biobased Material
  - Liquid
    - Carbonate Determination
      - Absent
        - % Carbon Determination
          - High
            - Sample Size Determination
              - >5 g
                - \(^{14}\text{C by LSC}\) $275
              - <5 g
                - \(^{14}\text{C by AMS}\) $400
            - Low
              - \(^{14}\text{C by AMS}\) $450
  - Solid
    - Carbonate Determination
      - Present
        - \(^{14}\text{C AMS Determination}\)
          - >97% pMC
            - \(^{14}\text{C AMS Determination on acid extracted CO}_2\)
            - Differential
              - \(^{14}\text{C by AMS}\) $900
          - <97% pMC
            - \(^{14}\text{C by AMS}\) $450
Resources

• Michael F. L’Annunziata

• Michael J. Kessler,
Resources

- Series of “Advance in Liquid Scintillation Spectrometry”, Radiocarbon, The Univ.of Arizona, Tucson, Arizona, USA.
- ISO –9698 - distillation method for H-3
- Eichrom H-3 column method (Ref.#OTWO2)
Resources

• www.lsc-international.org
Reference - vials

- Nahle O. et al, Study of light emission processes for the design of LS counters, LSC 2008, Advance in Liquid Scintillation Spectrometry, pp87-95
Reference - cocktails

- Komosa A., Slepecka K., Study of quenching effects for C-14 and H-3 measurement parameters using a Quantulus spectrometer, LSC 2008, Advance in Liquid Scintillation Spectrometry, pp161-172
Reference - H-3


Reference H-3


Reference C-14


4. Svetlik I et al., Determination of CO$_2$ in grab samples of stackair from NPPs., LSC 2005, Advance in Liquid Scintillation Spectrometry, p417-422


• 7. Varlam C et al., Optimization of C-14 measurement in aqueous samples using the direct absorption method and LSC, LSC 2005 Advance in Liquid Scintillation Spectrometry, p423-428


• 10. Vartii Vesa-Pekka, Optimizing the counting conditions for C-14 for the sample oxidizer-liquid scintillation counter method, LSC 2008 Advance in Liquid Scintillation Spectrometry, p293-298