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

Radiochemistry Webinars

Environmental/Bioassay Radiochemistry Series

Applications of Liquid Scintillation Counting

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Meet the Presenter…

Dr. Ralf Sudowe

Dr. Ralf Sudowe has extensive experience in the area of nuclear and radiochemistry, particularly in the development of radioanalytical separations for actinide and transactinide elements, as well as fission products. He is an Associate Professor of Health Physics and Radiochemistry at the University of Nevada Las Vegas. He received a M.S. degree in Chemistry from the Philipps-University Marburg in Germany in 1995, and a Ph.D. in Nuclear Chemistry from the same institution in 1999. Dr. Sudowe spent two years as Visiting Postdoctoral Fellow in the Nuclear Science Division at Lawrence Berkeley National Laboratory and then worked for five years as Staff Scientist in the Nuclear Science and Chemical Sciences Division at LBNL before joining the faculty at UNLV in 2006. He is a member of the American Chemical Society, the American Nuclear Society, and the Health Physics Society.

At UNLV, Dr. Sudowe teaches courses in radioanalytical chemistry, radiation detection, and environmental health physics and radiation biology, as well as laboratory courses in radiochemistry and radiation detection instrumentation. His research focuses on the development and optimization of advanced radioanalytical methods for environmental monitoring, nuclear forensics and safeguards, and emergency response. The goal is to make radioanalytical methods available that have lower detection limits for the radionuclides of interest, facilitate the fast analysis of a large number of samples, and allow assay of unusual sample matrices such as urban rubble and process streams. The research utilizes a variety of modern analytical tools to obtain better understanding of the fundamental properties of the separation process and to elucidate the role that interfering elements have on the technique. Dr. Sudowe also studies the chemical and nuclear properties of transactinide elements and is involved in target preparation and cross section measurements for stockpile stewardship science.

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Applications of Liquid Scintillation Counting

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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

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- Certain products and manufacturers are mentioned during this presentation for the purpose of fostering understanding.

- Reference to these commercial products and manufacturers in this presentation does not constitute recommendation or endorsement of the products.

Introduction

- The detection of ionizing radiation by scintillation light is one of the oldest techniques known.
- It still remains one of the most useful methods for radiation detection and spectroscopy.
- It is widely used for beta, alpha and neutron counting.
- It can be used for particle identification based on pulse shape analysis of the light pulse emitted.

Emission Processes

- Fluorescence
  - Prompt emission of visible radiation
- Phosphorescence
  - Emission at a longer wavelength
  - Occurs over a longer period of time
- Delayed fluorescence
  - Same emission wavelength as prompt fluorescence
  - Occurs over a longer period of time

Organic Scintillators

- The fluorescence of organic scintillators is based on electron transitions between different energy levels.

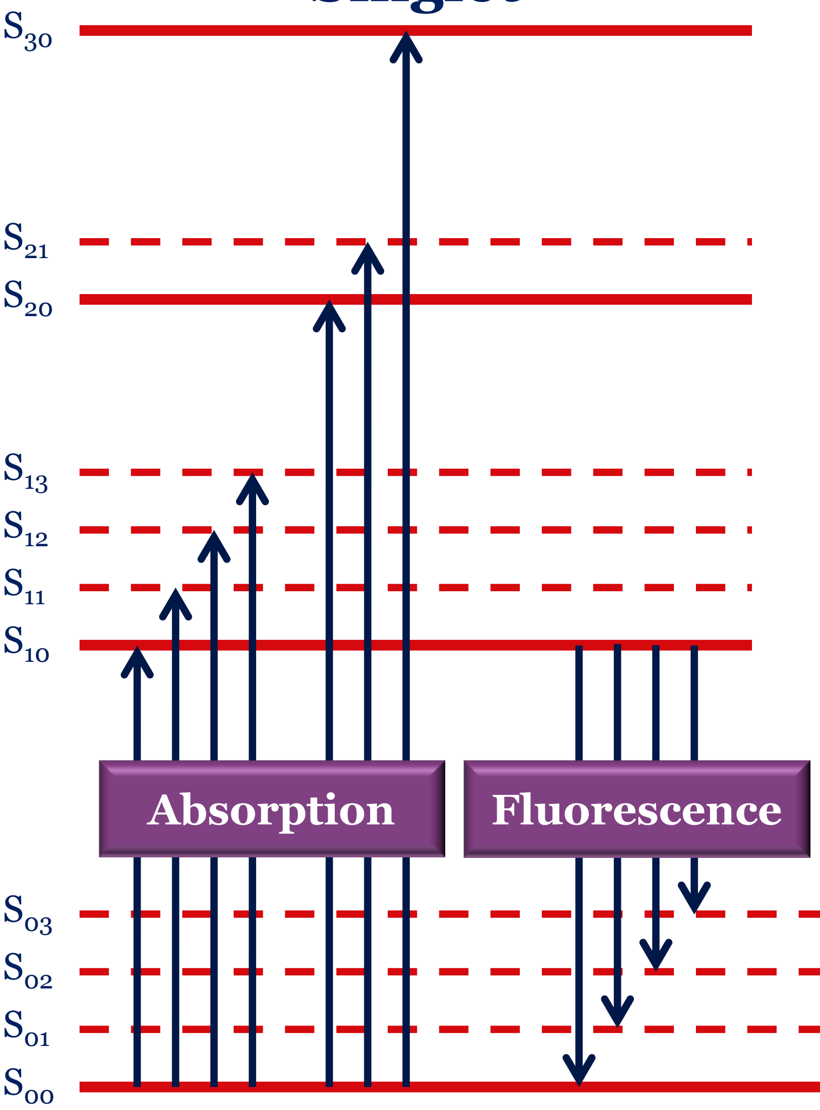
- This is a molecular property.

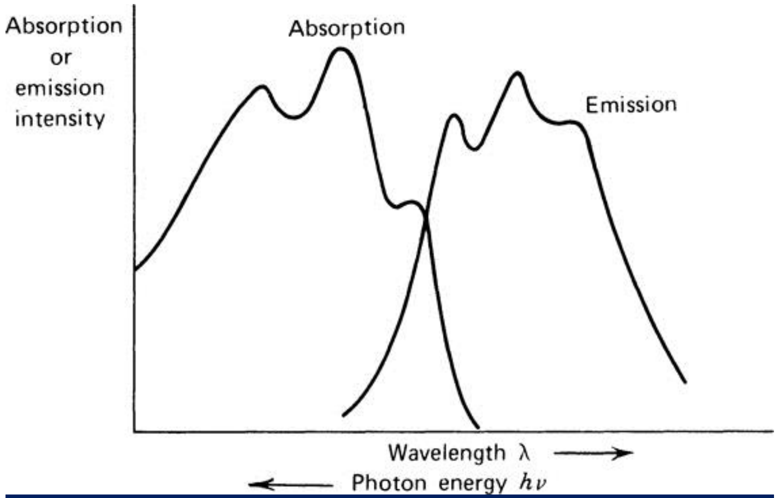
- It can be observed independent of the physical state.

Organic Scintillators

- Many organic scintillators are based on molecules with π-bonds.
- These are covalent chemical bonds involving p-orbitals (double bonds, aromatic rings).
- Energy can be absorbed by exciting an electron into a number of different excited energy states.

Singlet



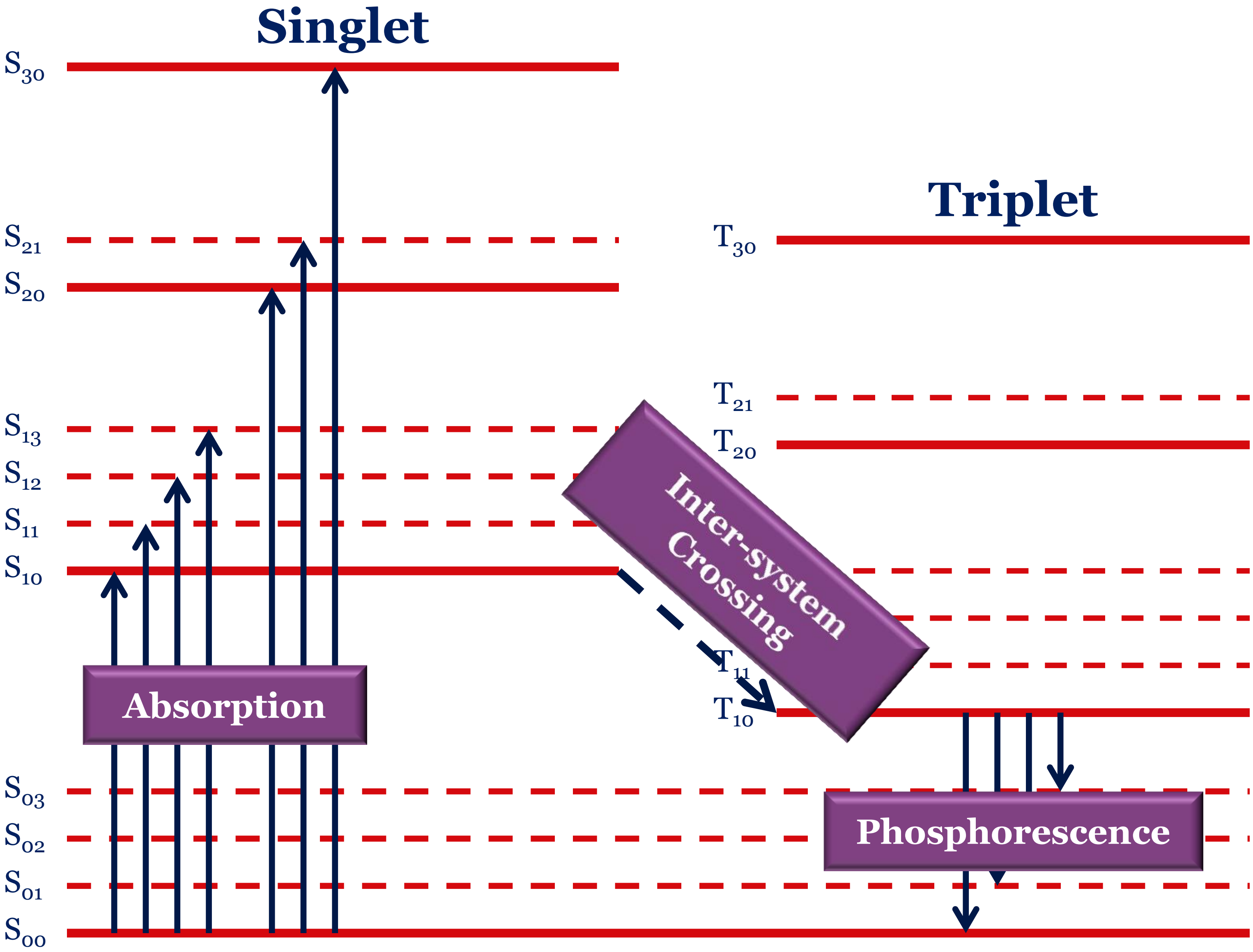


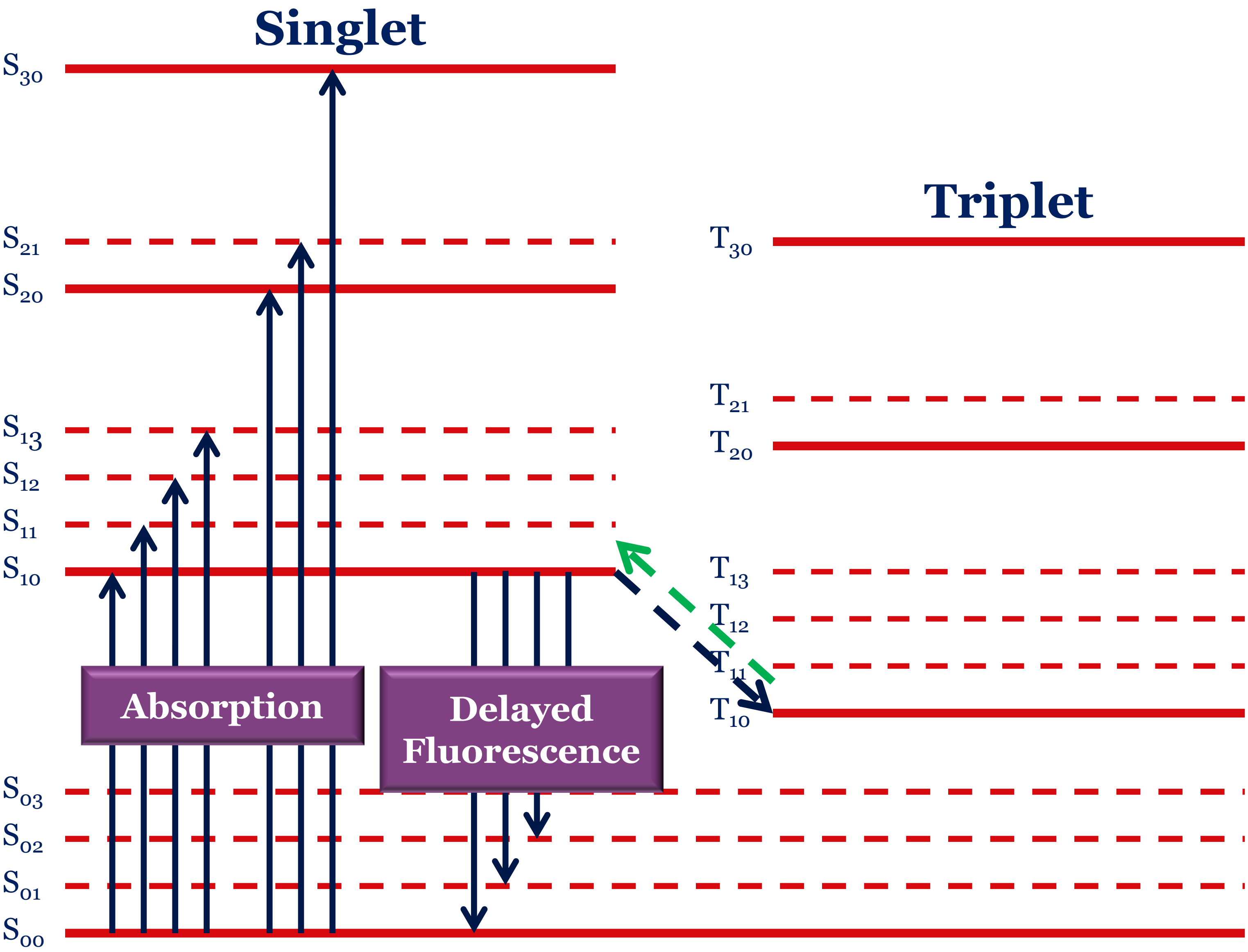
Optical absorption and emission spectra of a typical organic scintillator.

Source: Knoll, G. F., *Radiation Detection and Measurement*, 4th Edition, John Wiley (2010)

Wavelength & Absorption

- Fluorescence transitions have generally a lower energy than the excitation transitions.
- This means the absorption occurs at a shorter wavelength than the emission.
- There is little overlap between the absorption and the emission spectra.
  - Only little self-absorption of the fluorescence radiation by the scintillator material.
  - Scintillator is transparent to its own fluorescence.


Singlet
Triplet
S_{30}
S_{21}
S_{20}
S_{13}
S_{12}
S_{11}
S_{10}
S_{03}
S_{02}
S_{01}
S_{00}
T_{30}
T_{21}
T_{20}
T_{11}
T_{10}
Absorption
Inter-system Crossing
Phosphorescence


Singlet
Triplet
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S_{02}
S_{01}
S_{00}
T_{30}
T_{21}
T_{20}
T_{13}
T_{12}
T_{11}
T_{10}
Absorption
Delayed Fluorescence

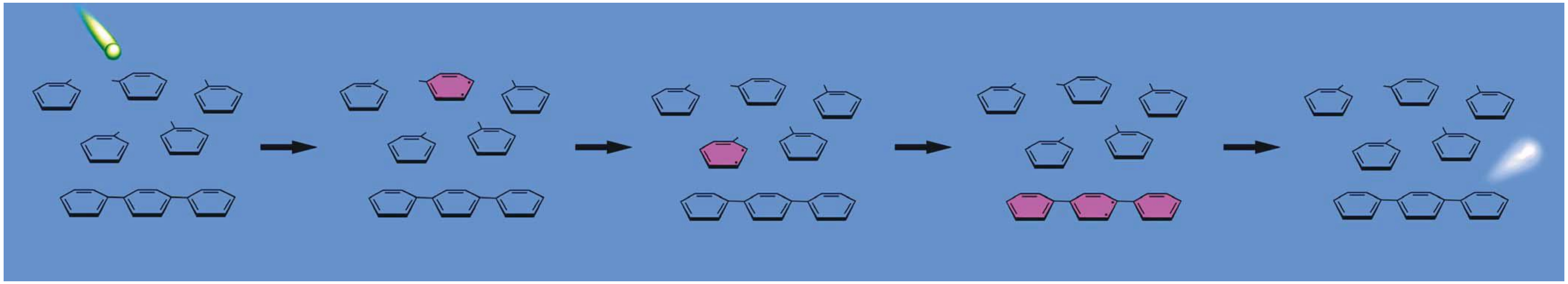
Multi-Component Scintillators

- Excitation energy can be transferred to other molecules through collisions before de-excitation occurs.
  - This is important for organic scintillators that involve more than one species of molecules.
- A small concentration of an efficient scintillator is typically added to a bulk solvent.
  - Energy taken up by the solvent molecules can be transferred to the scintillator through collisions.

Multi-Component Scintillators

- Once the energy has been transferred to a scintillator molecule, it can be emitted as light.
  - Binary organic scintillators are widely used both as liquid and plastic solutions.
- A third component is sometimes added to these mixtures to serve as a “waveshifter”.
  - It absorbs the light from the primary scintillator and reradiates it at a longer wavelength.
  - This improves the match between emission spectrum and photomultiplier tube.

Multi-Component Scintillators



Source: National Diagnostics, *Principles and applications of liquid scintillation counting* (2004)

LSC Cocktail Components

- Organic Cocktails:
  - Aromatic Solvent
  - Scintillator (0.3 – 1.0%)
- Aqueous (Emulsifying) Cocktails:
  - Aromatic Solvent
  - Scintillator (0.3 – 1.0%)
  - Emulsifier
- Both can also contain a secondary scintillator as a wave shifter.

Scintillation Solvents

- Traditional Solvents:
  - Toluene
  - Xylene
  - Pseudocumene

- Counting efficiency increases as:

Benzene > Toluene > Xylene > Pseudocumene

Scintillation Solvents

- Safer Solvents:
  - Di-isopropylnaphthalene (DIN)
  - Phenylxylylethane (PXE)
  - Dodecylbenzene (LAB)

- Counting efficiency increases as:

Benzene > LAB > Toluene > Xylene >
Pseudocumene > PXE > DIN

Scintillation Solvents

Solvent	Boiling Point	Flash Point	Vapor Pressure	Classification	Hazards
Toluene	110 °C	4 °C	28 mm Hg	Flammable	Inhalation Skin absorption Irritating to skin/eyes
Xylene	138 °C	25 °C	8 mm Hg	Flammable	Inhalation Skin absorption Irritating to skin/eyes
Cumene	152 °C	31 °C	5 mm Hg	Flammable	Inhalation Irritating to skin/eyes
Pseudocumene	168 °C	50 °C	2 mm Hg	Flammable	Inhalation Irritating to skin/eyes
LAB	300 °C	149 °C	< 1 mm Hg	Harmless	None
PXE	305 °C	149 °C	< 1 mm Hg	Harmless	None
DIN	300 °C	140 °C	< 1mm Hg	Harmless	None
Benzyl toluene	290 °C	135 °C	< 1 mm Hg	Harmless	None
Diphenyl ethane	290 °C	135 °C	< 1 mm Hg	Harmless	None

Primary Scintillators

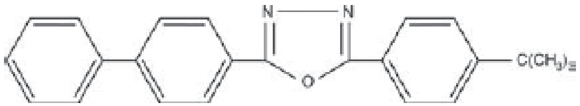
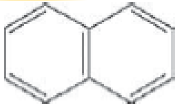
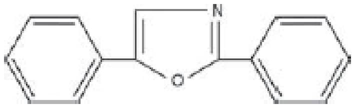
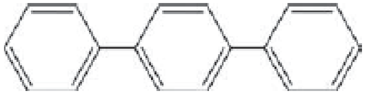
- Requirements for an ideal scintillator:
  - High fluorescence quantum efficiency
  - Spectrum matched to response of PMT
  - Short fluorescence decay time
  - Large Stokes' shift
  - Good solubility
  - Low sensitivity to quenching agents

Primary Scintillators

Acronym	Full Name
PPO	2,5-diphenyloxazole
PPD	2,5-diphenyl-1,3,4-oxadiazole
PBO	2-(4-biphenylyl)-5-phenyloxazole
PBD	2-phenyl-5-(4-biphenylyl)-1,3,4-oxadiazole
BBD	2,5-di-(4-biphenylyl)-1,3,4-oxadiazole
Butyl-PBD	2-(4-t-butylphenyl)-5-(4-biphenylyl)-1,3,4-oxadiazole
BBOT	2,5-bis-2-(5-t-butyl-benzoxazoyl) thiophene
TP	p-terphenyl

Primary Scintillators

Primary Scintillators

Scintillator	Structure	Emission Wavelength
Butyl PBD 2-[4-biphenylyl]-5-[4-*tert*-butyl-phenyl]-1,3,4-oxadiazole)		363nm
Naphthalene		322nm
PPO 2,5-diphenyloxazole		357nm
p-Terphenyl		340nm

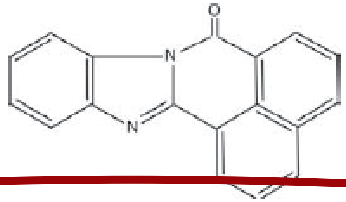
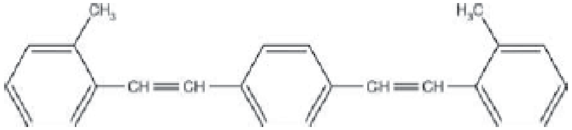
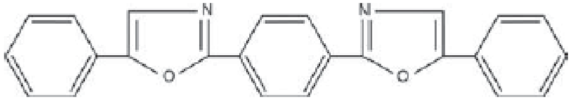
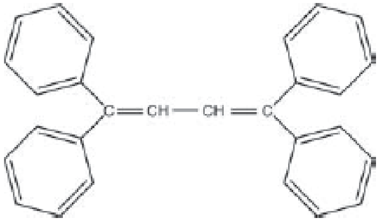
Source: National Diagnostics, *Principles and applications of liquid scintillation counting* (2004)

Wave Shifters

Acronym	Full Name
bis-MSB	p-bis-(o-methylstyryl)benzene
POPOP	1,4-bis-2-(5-phenyloxazolyl)benzene
Dimethyl POPOP	1,4-bis-2-(4-methyl-5-phenyloxazolyl)benzene
NPO	2-(1-naphthyl)-5-phenyloxazole
NPD	2-(1-naphthyl)-5-phenyl-1,3,4-oxadiazole
BBO	2,5-di(4-biphenylyl)oxazole
PBBO	2-(4-biphenylyl)-6-phenylbenzoxazole

Wave Shifters

Secondary Scintillators

BBQ (7H-benzimidazo[2,1-a]benz [de]isoquinoline-7-one)		477nm
Bis-MSB (1,4-bis[2-methylstyryl]-benzene)		420nm
POPOP (1,4-bis[5-phenyloxazol-2-yl]benzene)		410nm
TPB (1,1,4,4-tetraphenyl-1,3-butadiene)		455nm

Source: National Diagnostics, *Principles and applications of liquid scintillation counting* (2004)

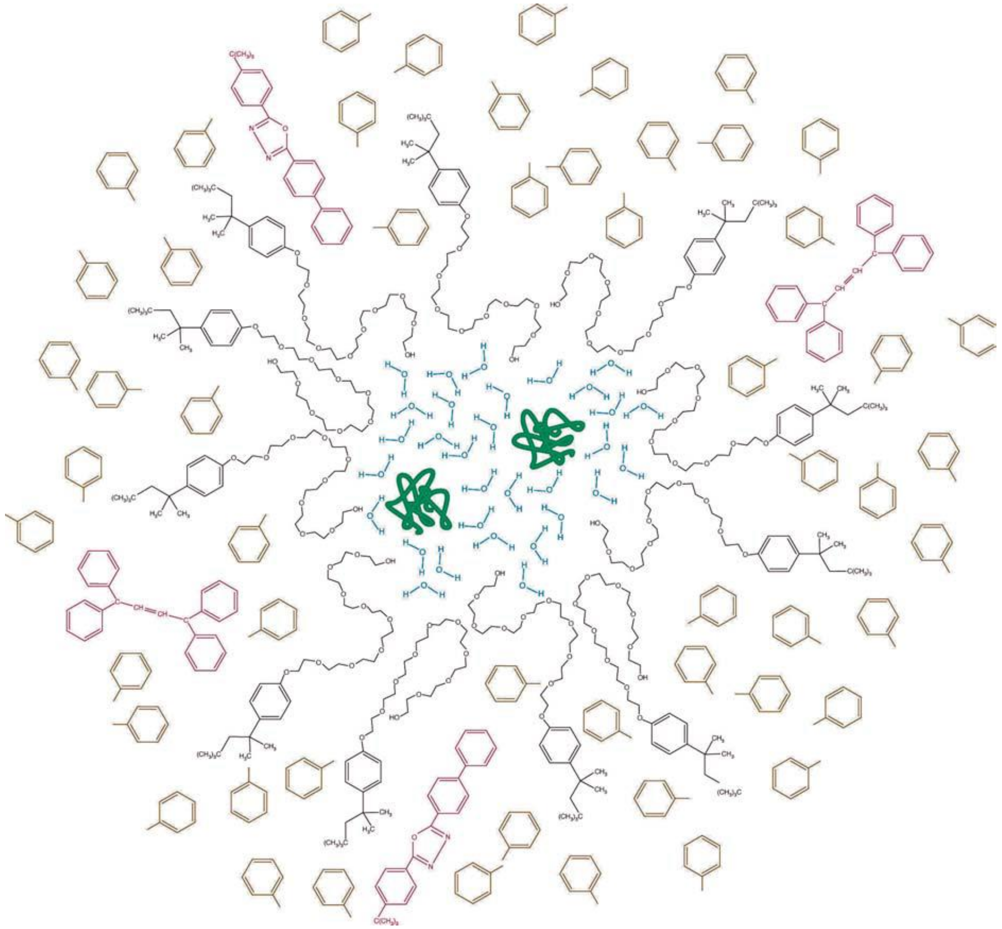
Emulsifier

- Aromatic organic solvents allow for the most efficient energy transfer between molecules.
- However, typically aqueous samples need to be analyzed.
- Such samples are generally not miscible with aromatic solvents.
- Emulsifiers are therefore used to bring the aqueous phase into close contact with the organic phase.

Emulsifier

- Use of surfactants results in the formation of micelles.
- These allow the dispersion of the aqueous phase in the form of very small droplets.
  - Radius of approximately 10 nm

Emulsifier



- Micellar structure in a scintillation cocktail.
- Hydrophilic proteins (green) and water (blue) are emulsified by Triton X-100 (black).
- Radioactive emissions from the labeled protein must pass through the micelle to encounter the toluene solvent (brown) before energy can be passed to the primary and secondary phosphors (red) and be reemitted as light.

Source: National Diagnostics, *Principles and applications of liquid scintillation counting* (2004)

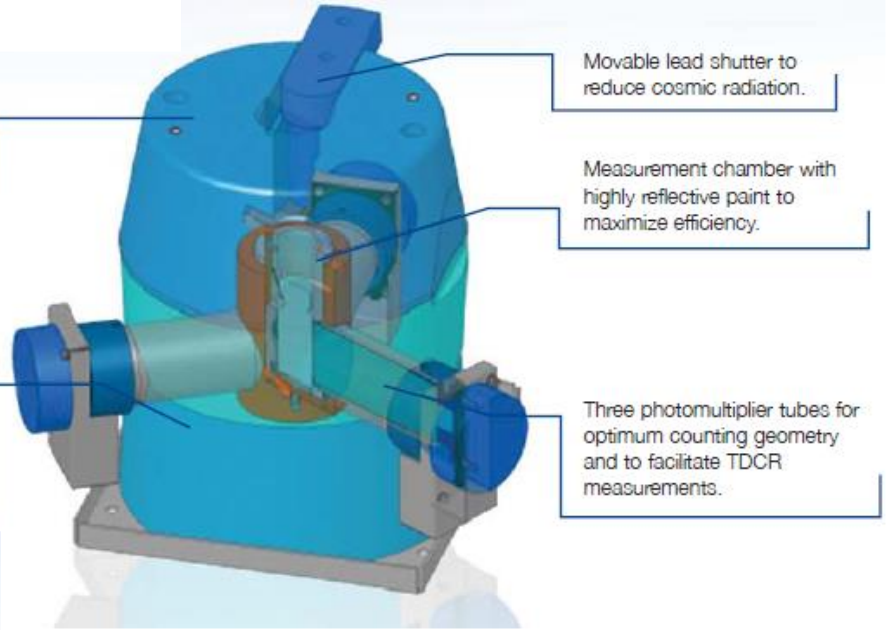
Emulsifier

- A number of detergents have been investigated for use in LSC cocktails.
- Detergents that have been successfully used can be categorized as:
  - Nonionics
  - Anionics
  - Cationics
  - Amphoterics

Instrumentation

Source: PerkinElmer , http://www.perkinelmer.com/catalog/family/id/tri%20carb%20liquid%20scintillation%20counters, Retrieved May 20, 2014

Instrumentation



Optimum lead shielding with a minimum 70mm depth to reduce background and keep the 300SL as light as possible.

A robotic loading arm is used instead of a conveyor to prevent vials from jamming. The lead shield beneath the counting chamber reduces background levels.

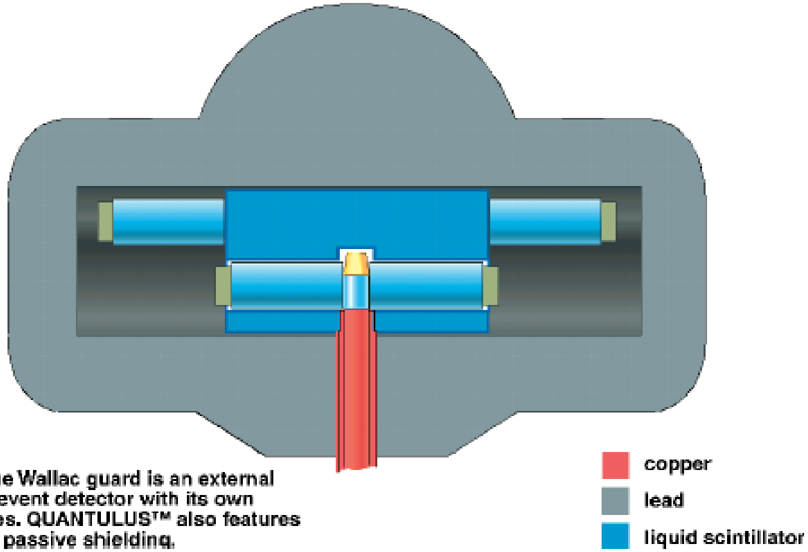
Movable lead shutter to reduce cosmic radiation.

Measurement chamber with highly reflective paint to maximize efficiency.

Three photomultiplier tubes for optimum counting geometry and to facilitate TDCR measurements.

Source: LabLogic Systems Limited, http://www.lablogic.com/display.asp?name=300SL, Retrieved May 20, 2014

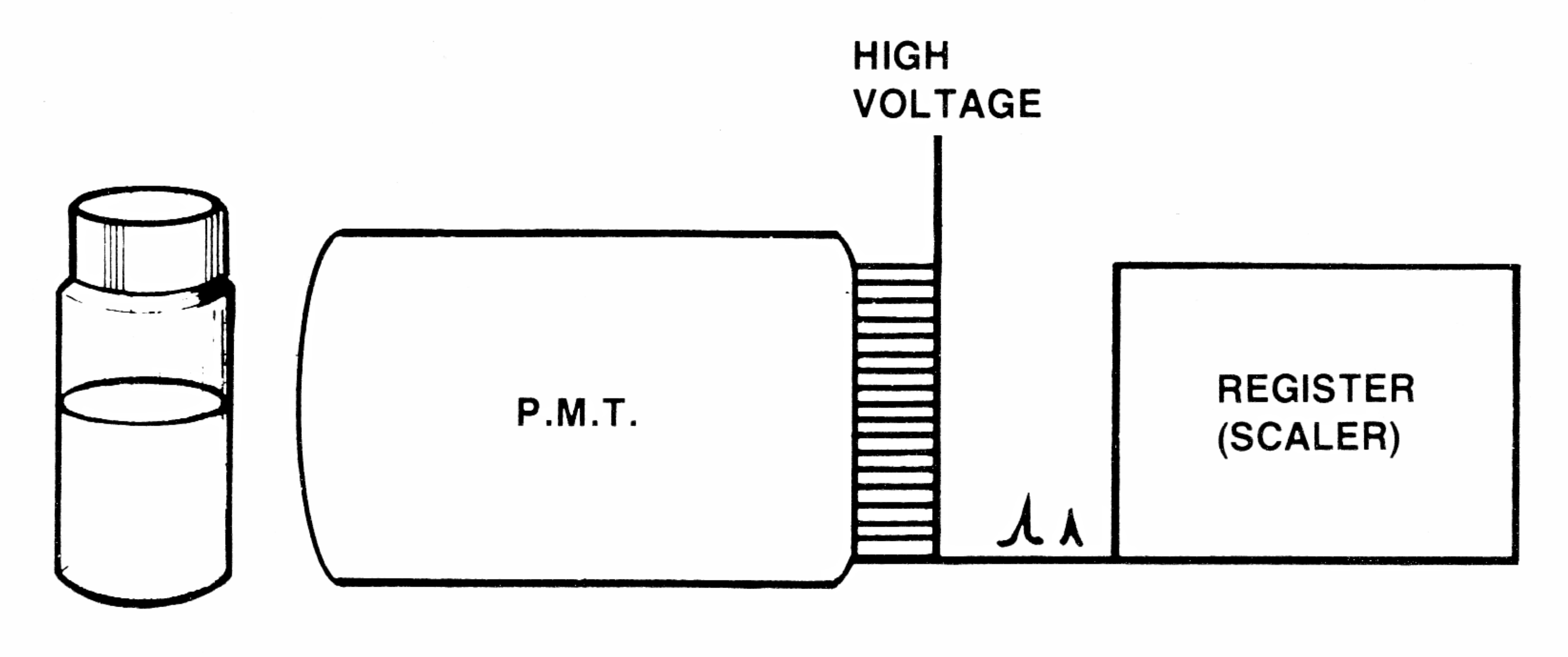
Instrumentation



The unique Wallac guard is an external radiation event detector with its own phototubes. QUANTULUS™ also features extensive passive shielding.

Source: PerkinElmer, http://www.perkinelmer.com/catalog/family/id/quantulus%20family, Retrieved May 20, 2014

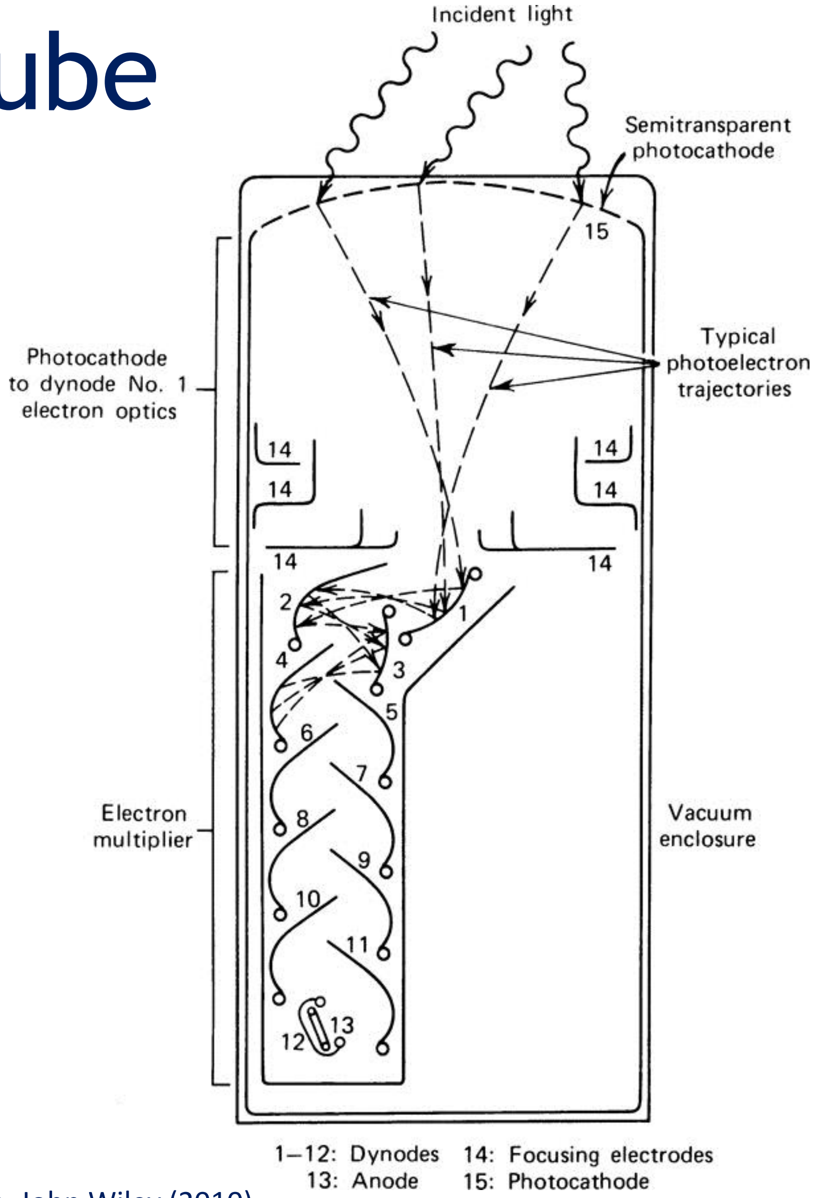
Simplified LS System



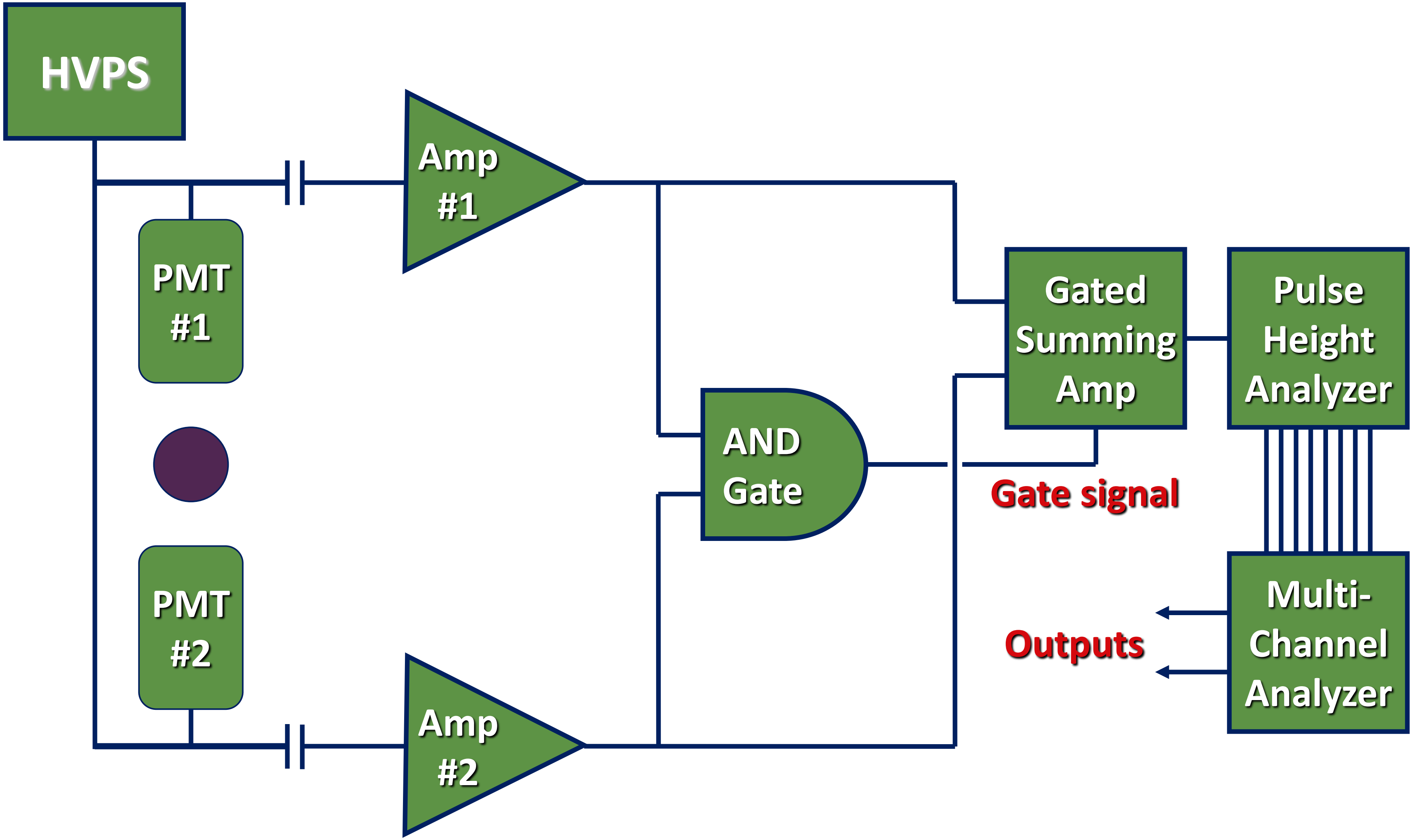
Source: Packard, *Liquid scintillation analysis – Science and Technology*, Packard Instrument Company (1989)

Photomultiplier Tube

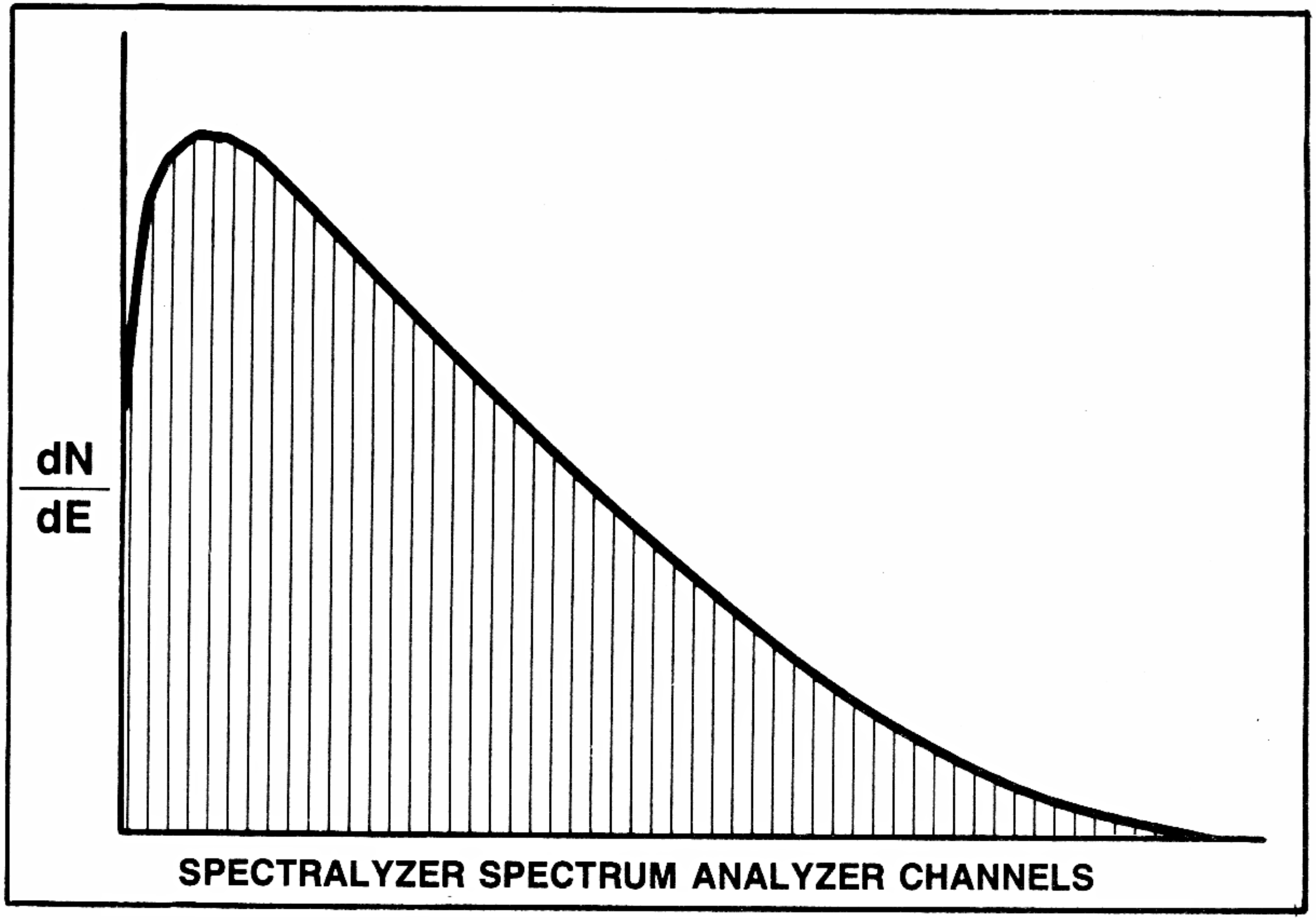
Basic elements of a PM tube



Source: Knoll, G. F., *Radiation Detection and Measurement*, 4th Edition, John Wiley (2010)

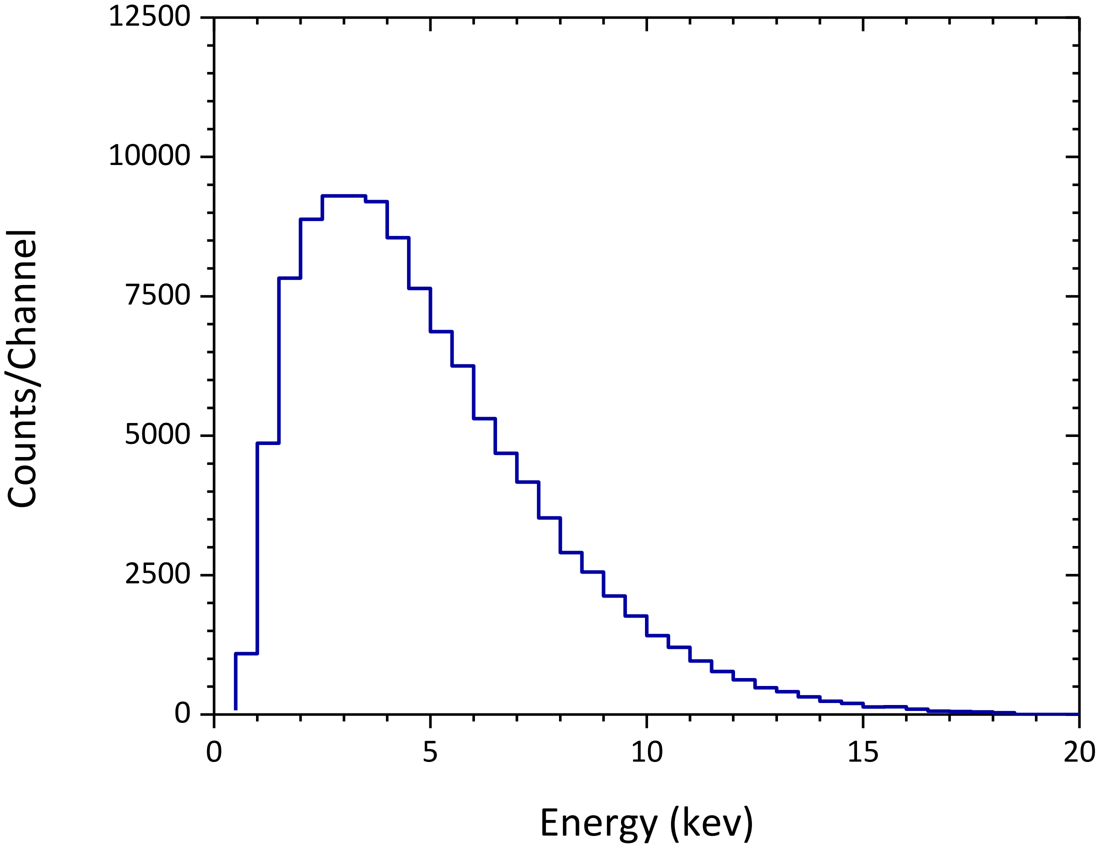

HVPS
PMT #1
PMT #2
Amp #1
Amp #2
AND Gate
Gated Summing Amp
Pulse Height Analyzer
Multi-Channel Analyzer
Gate signal
Outputs

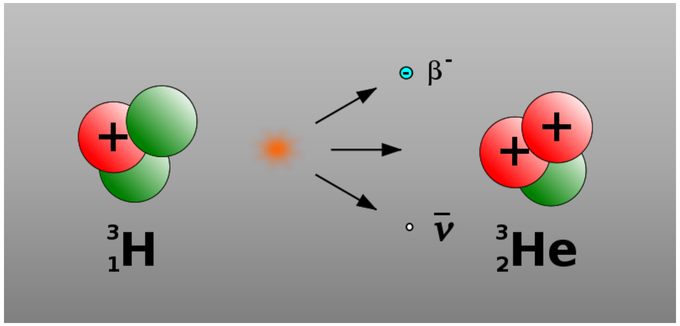
Sample Spectrum



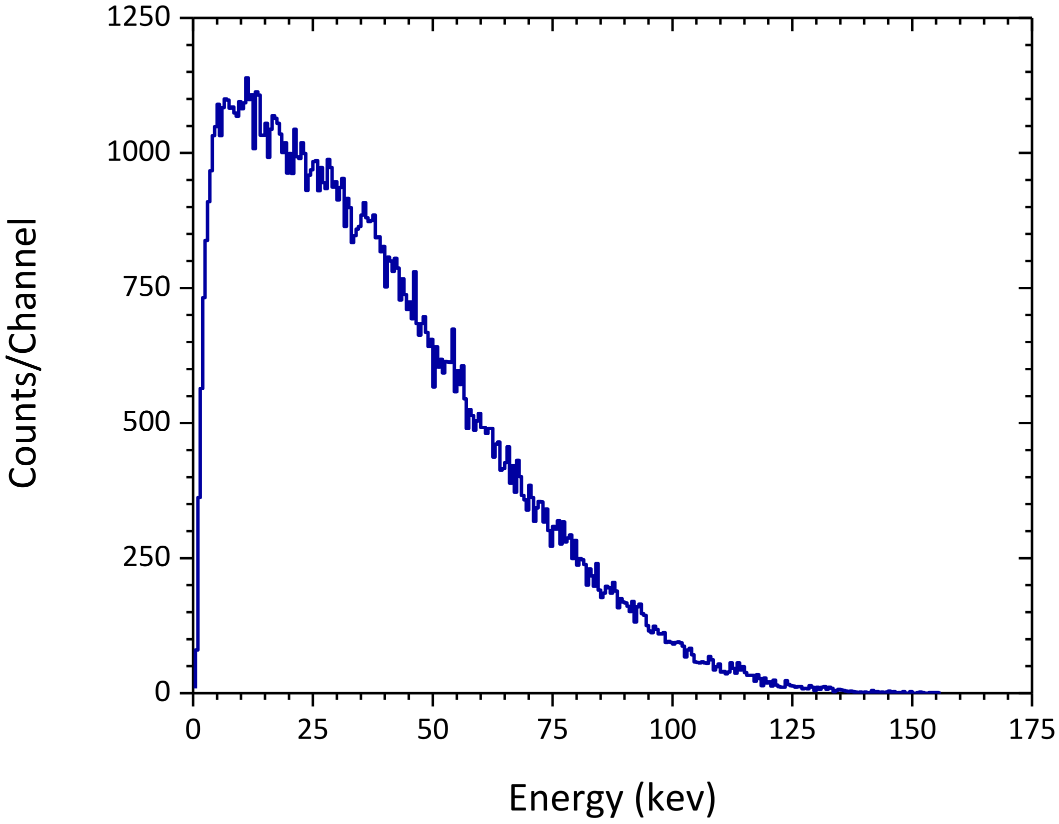
Source: Packard, *Liquid scintillation analysis – Science and Technology*, Packard Instrument Company (1989)

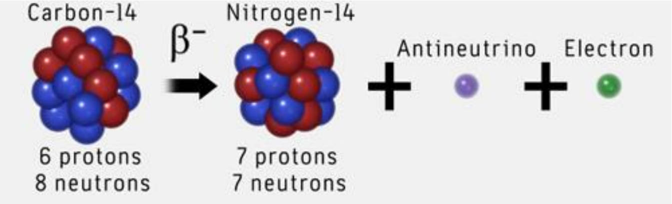
Beta Spectrum – H-3



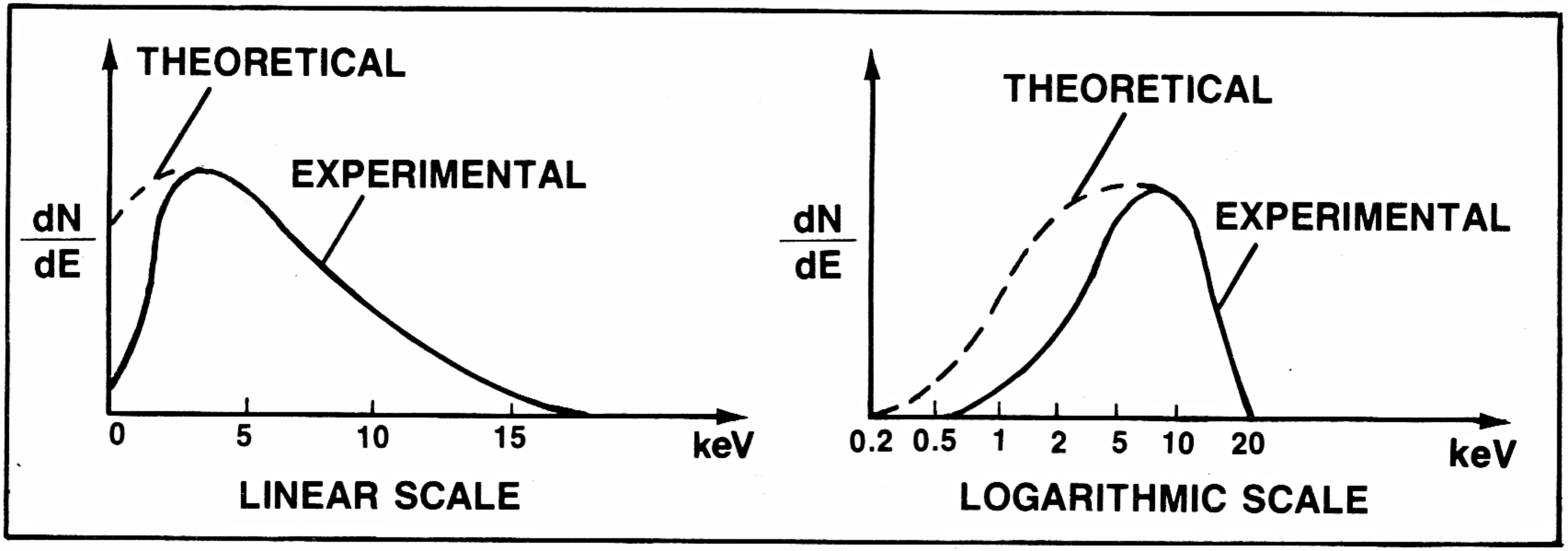


Beta Spectrum – C-14





Theoretical Vs. Actual Shape



Source: Packard, *Liquid scintillation analysis – Science and Technology*, Packard Instrument Company (1989)

Beta vs. Alpha Spectrum

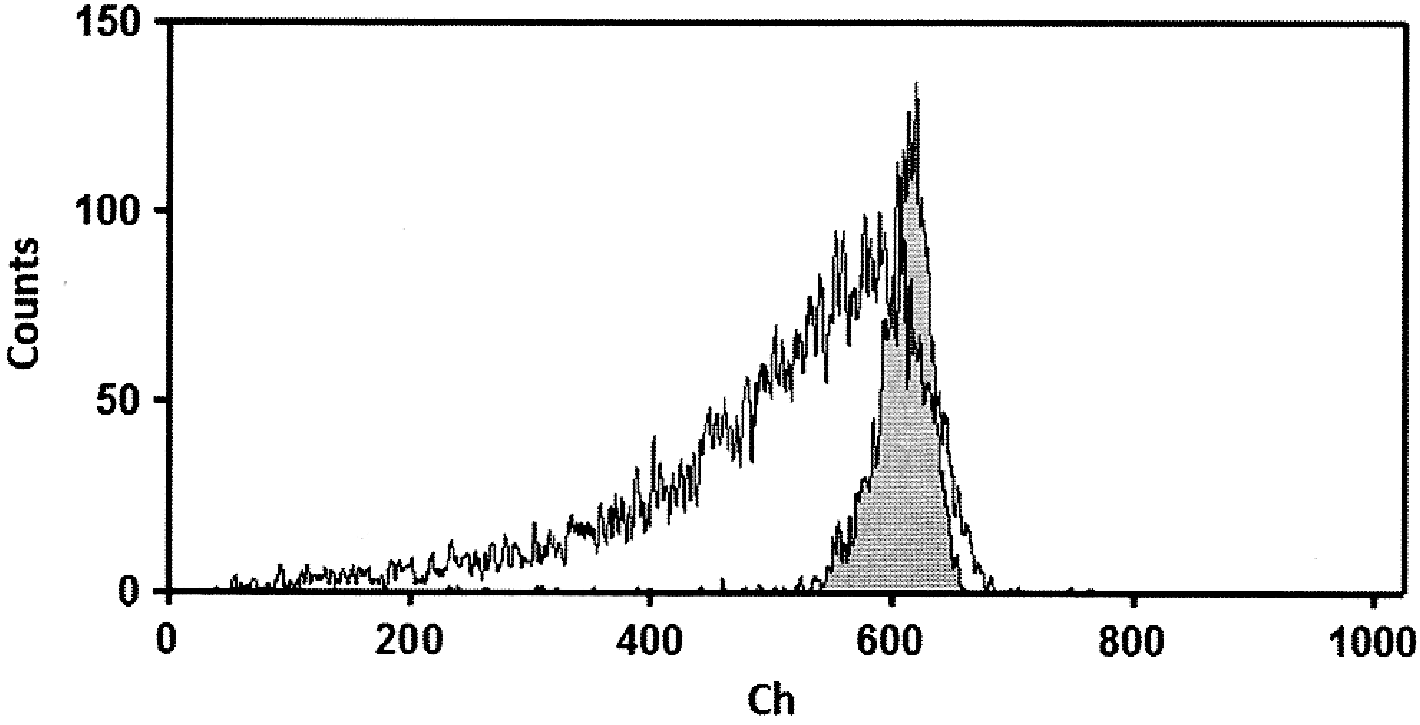
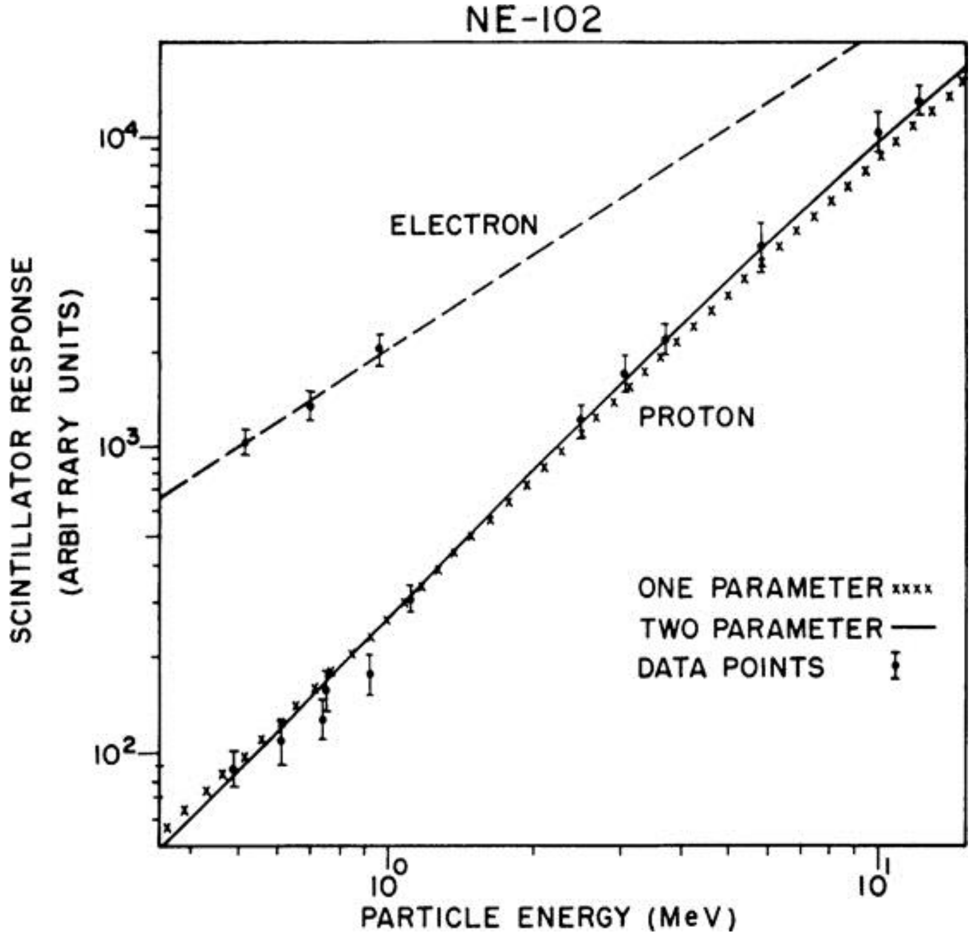


FIGURE 9.11 Logarithmic Quantulus Multi-Channel Analyzer display for ^{36}Cl and ^{241}Am (gray) spectra.

Source: L'Annunziata, M.F., *Handbook of Radioactivity Analysis*, 3rd Edition, Academic Press (2012)

Electron/Proton Light Output



The scintillation light yield for a common plastic scintillator (NE 102) when excited by electrons and protons.

Source: Knoll, G. F., *Radiation Detection and Measurement*, 4th Edition, John Wiley (2010)

Spectral Resolution for α-emitter

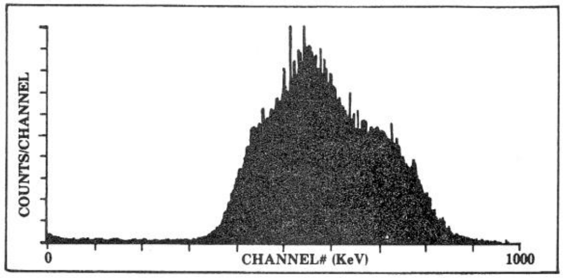


Figure 2-9. 15 ml SAMPLE CONTAINING ^{233}U and ^{241}Am.

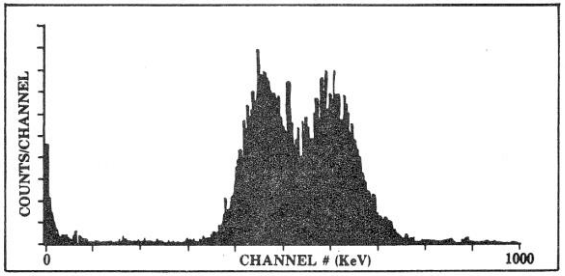


Figure 2-10. 6 X 50 mm SAMPLE CONTAINING ^{233}U and ^{241}Am.

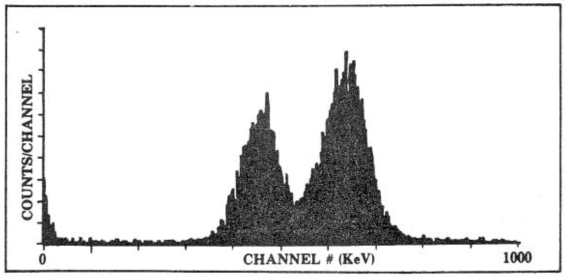


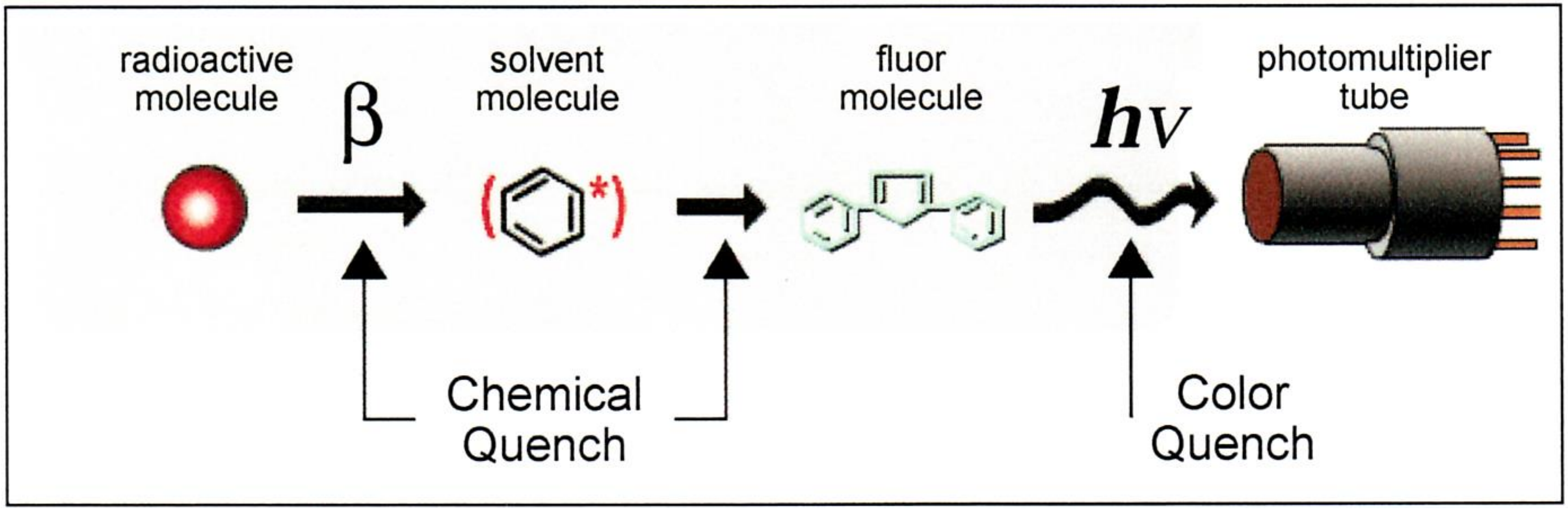
Figure 2-11. 6 X 50 mm SAMPLE CONTAINING ^{233}U and ^{244}Cm.

Source: Packard, *Liquid scintillation analysis – Science and Technology*, Packard Instrument Company (1989)

Quenching

- The fraction of all incident particle energy that is converted to light is called scintillation efficiency.
- It should be as large as possible.
- Any process that reduces the efficiency of the conversion of particle energy into light is called “quenching”.
- There are two types of quenching:
  - Chemical quench
  - Color quench

Quenching



Source: Thomson, J., *Use and preparation of quench curves*, Liquid Scintillation Counting Application Note P11399, PerkinElmer (2002)

Chemical Quench

- Chemical quench occurs during the transfer of energy from the solvent to the scintillator.
- It occurs if the excited molecules have alternate de-excitation modes available that do not involve the emission of light.
- In these cases the excitation energy is mainly converted to heat.

Chemical Quench

- Any chemical species that is electronegative will affect the energy transfer process.
- It does so by involving the π- electrons associated with the aromatic solvent.
- This reduces the availability of π-electrons necessary for efficient energy transfer.

Chemical Quench

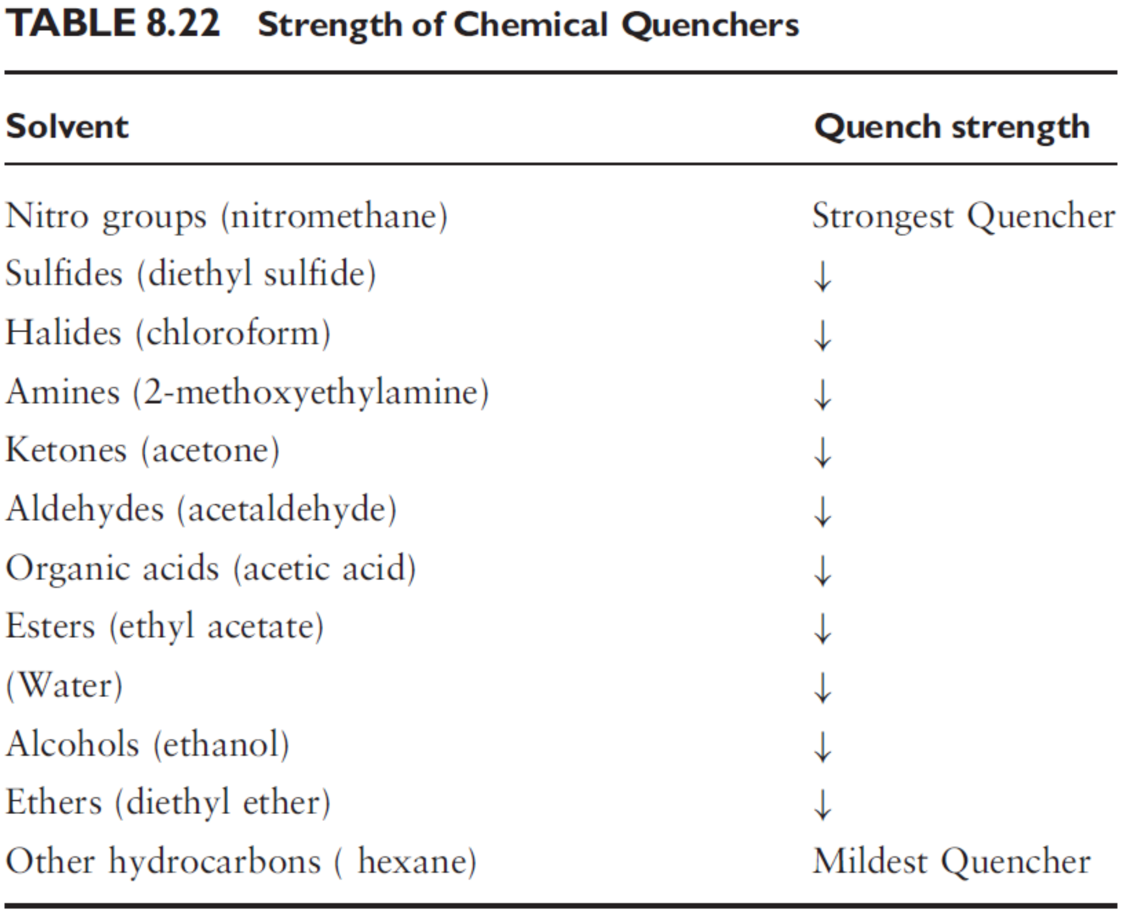


TABLE 8.22 Strength of Chemical Quenchers

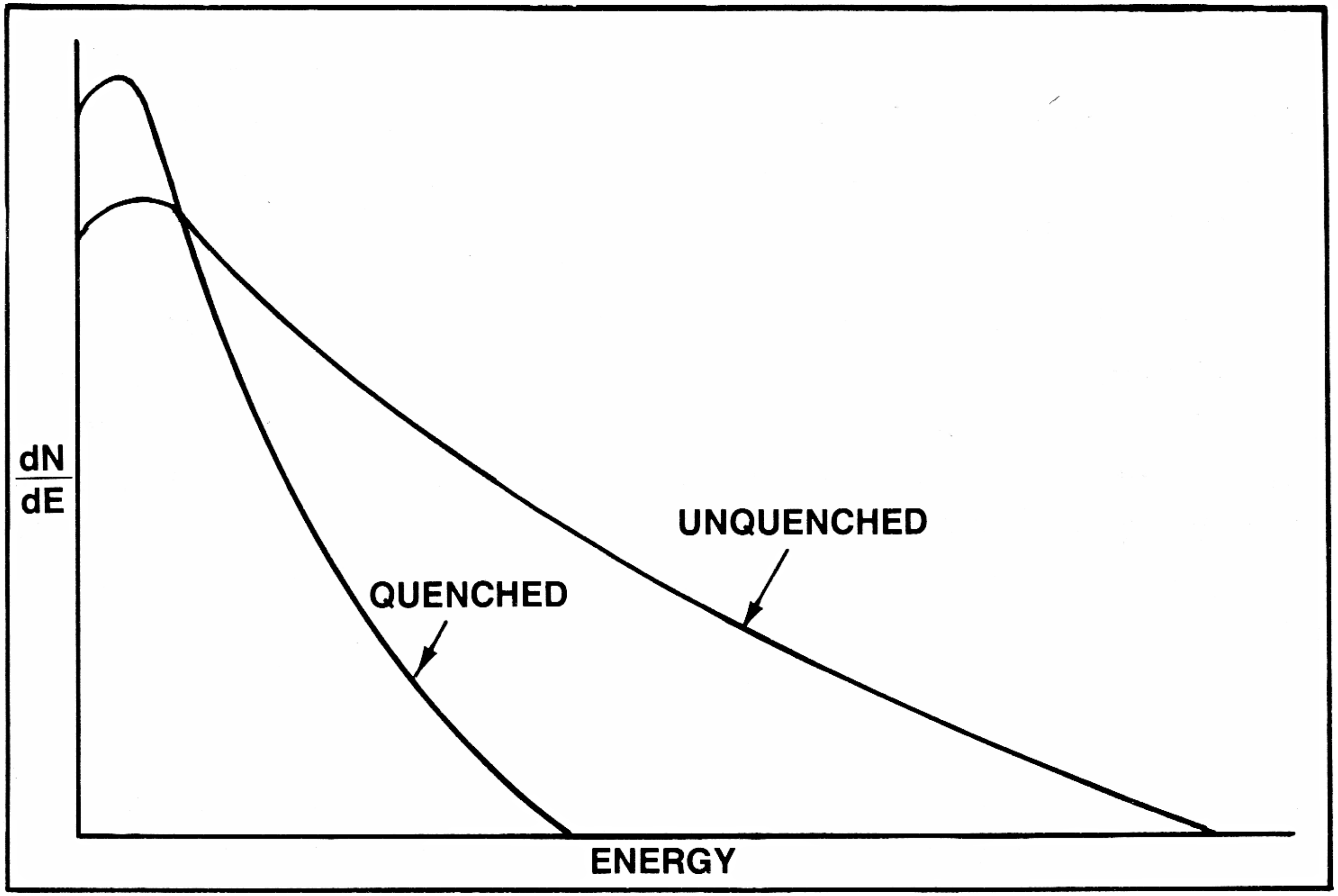
Solvent	Quench strength
Nitro groups (nitromethane)	Strongest Quencher
Sulfides (diethyl sulfide)	↓
Halides (chloroform)	↓
Amines (2-methoxyethylamine)	↓
Ketones (acetone)	↓
Aldehydes (acetaldehyde)	↓
Organic acids (acetic acid)	↓
Esters (ethyl acetate)	↓
(Water)	↓
Alcohols (ethanol)	↓
Ethers (diethyl ether)	↓
Other hydrocarbons (hexane)	Mildest Quencher

Source: L'Annunziata, M.F., *Handbook of Radioactivity Analysis*, 2nd Edition, Academic Press (2003)

Color Quench

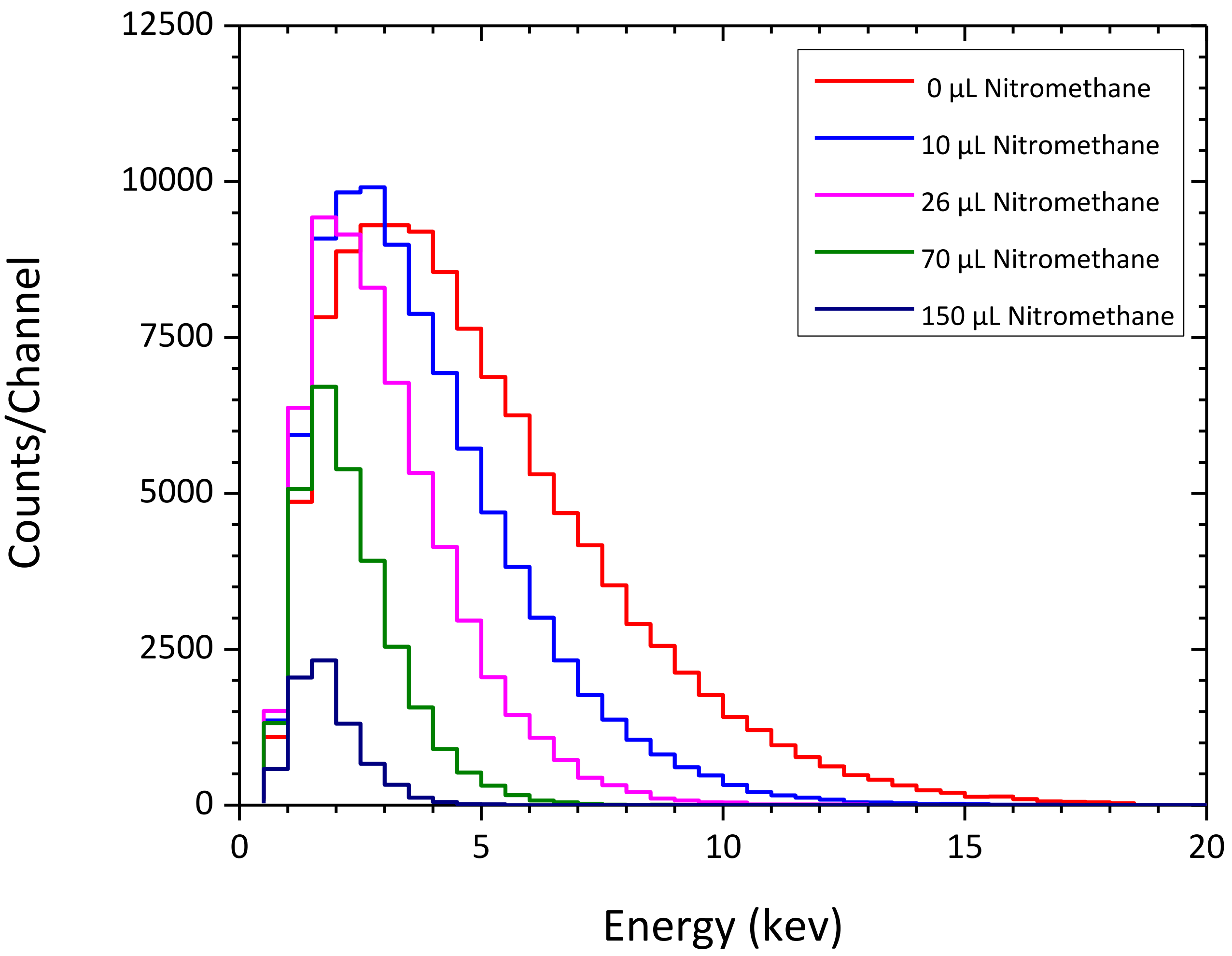
- Color quenching is caused if the photons emitted are prevented from being detected by the PMT.
- The photons produced are absorbed or scattered by the color in the solution.
  - If the wavelength of the photon is changed, the PMT may not be sensitive to it anymore.
- This results in a reduced light output available for measurement by the PMTs.

Quenched Spectra

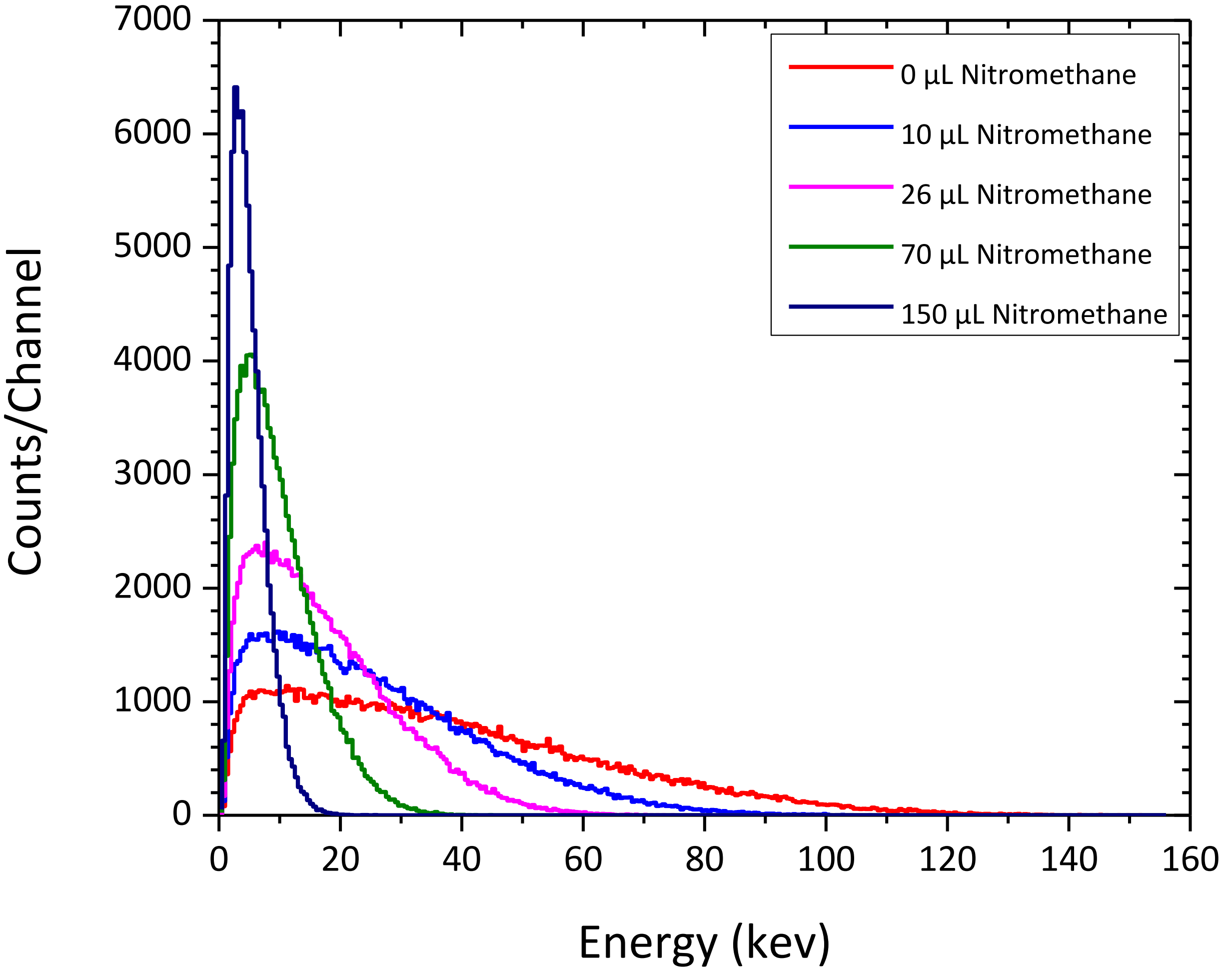


Source: Packard, *Liquid scintillation analysis – Science and Technology*, Packard Instrument Company (1989)

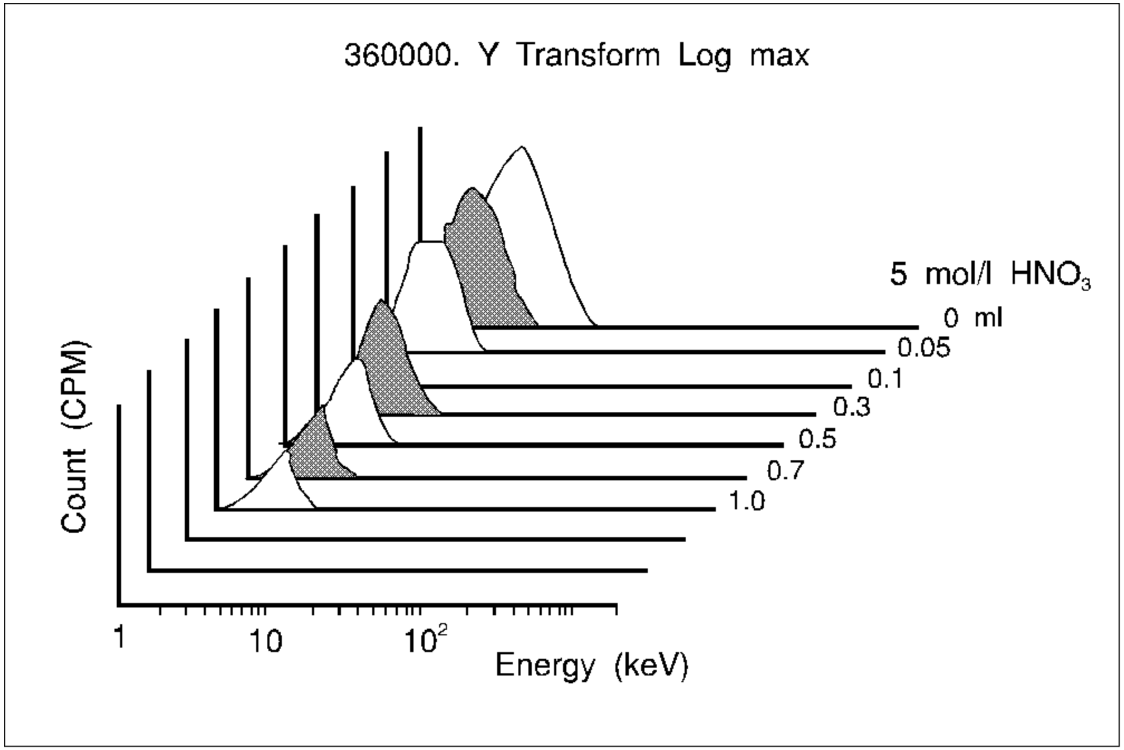
Effect of Quench on Spectrum

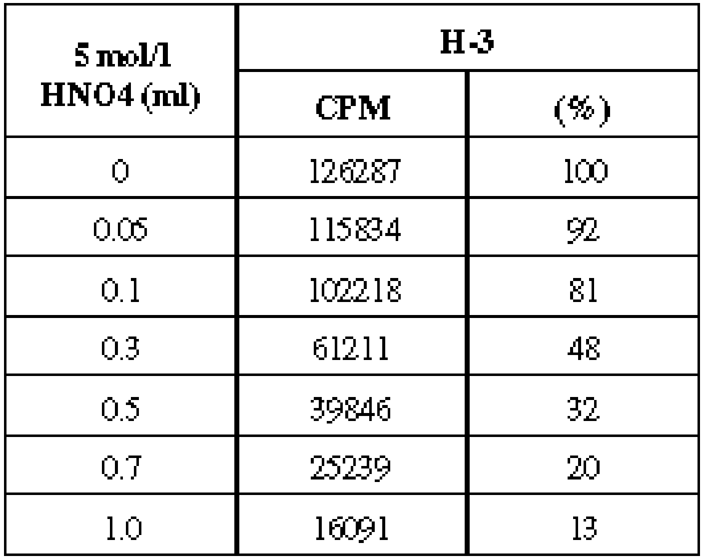


Effect of Quench on Spectrum



Effect of Quench on Spectrum

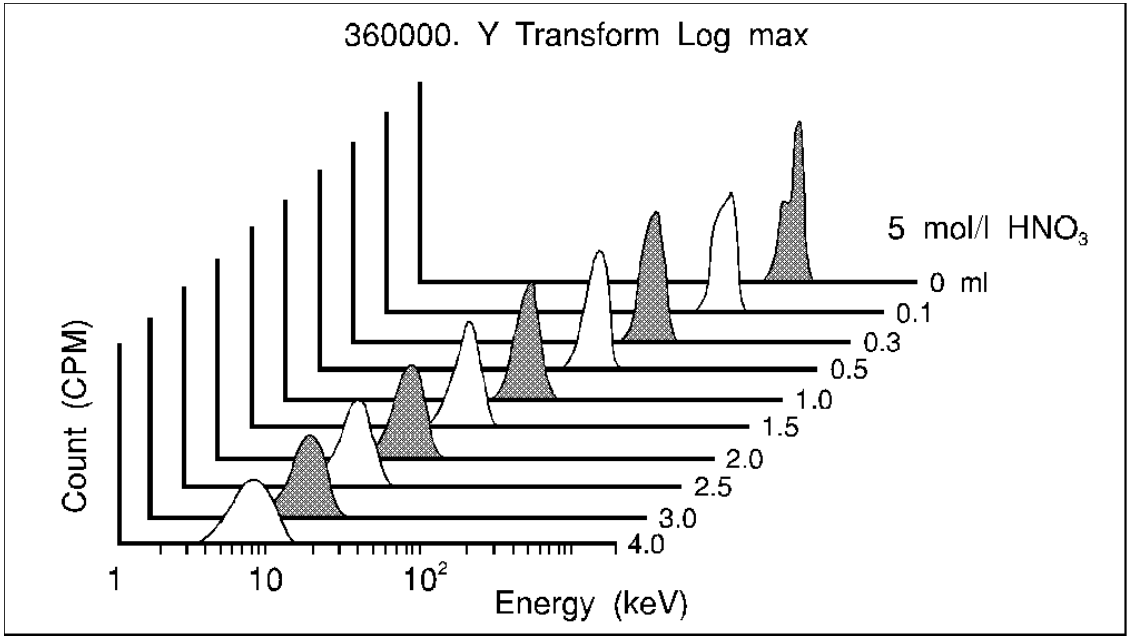


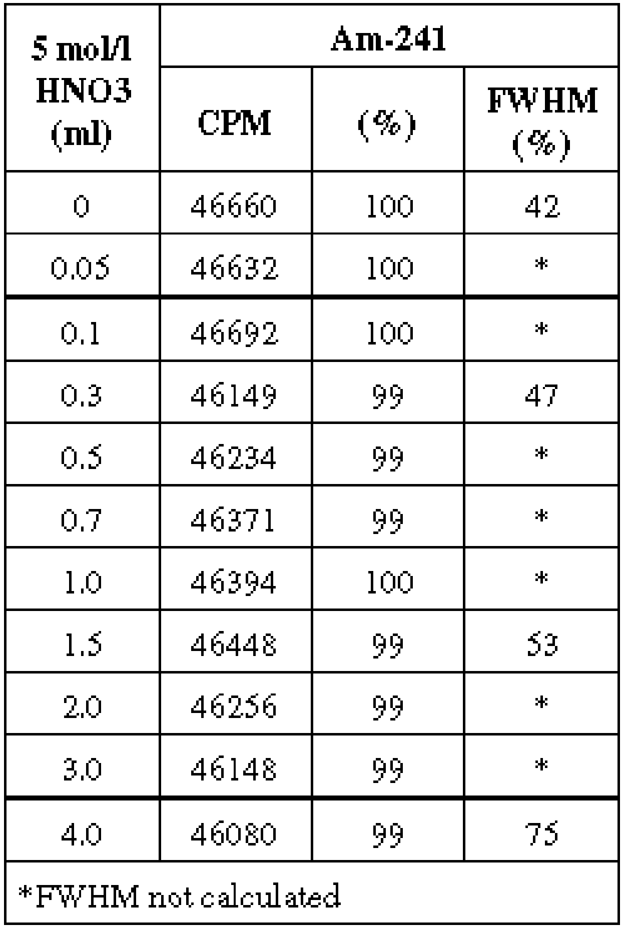


5 mol/l HNO4 (ml)	H-3	
	CPM	(%)
0	126287	100
0.05	115834	92
0.1	102218	81
0.3	61211	48
0.5	39846	32
0.7	25239	20
1.0	16091	13

Source: PerkinElmer, *The effect of quench on quantitating alpha radionuclides by liquid scintillation counting*, Application Note ABA-003

Effect of Quench on Spectrum



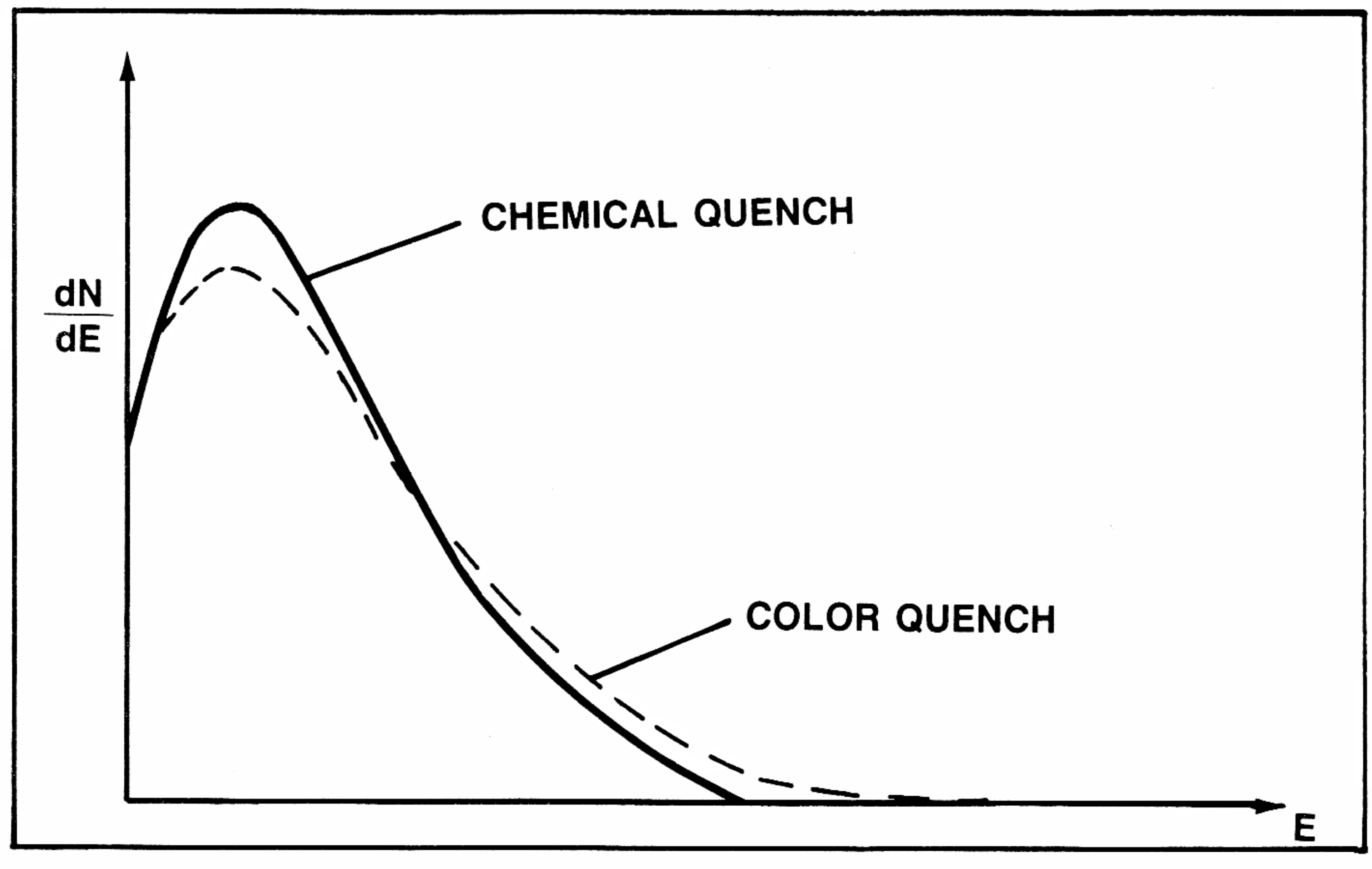


5 mol/l HNO3 (ml)	Am-241		
	CPM	(%)	FWHM (%)
0	46660	100	42
0.05	46632	100	*
0.1	46692	100	*
0.3	46149	99	47
0.5	46234	99	*
0.7	46371	99	*
1.0	46394	100	*
1.5	46448	99	53
2.0	46256	99	*
3.0	46148	99	*
4.0	46080	99	75

*FWHM not calculated

Source: PerkinElmer, *The effect of quench on quantitating alpha radionuclides by liquid scintillation counting*, Application Note ABA-003

Chemical Vs. Color Quench



Source: Packard, *Liquid scintillation analysis – Science and Technology*, Packard Instrument Company (1989)

Quenching

- As a result of quenching the overall number of photons produced is reduced.
- This consequently lowers the number of counts detected.
- The counting efficiency is affected by the degree of quenching in the sample.
- It is necessary to measure the level of quench of the samples to determine the absolute activity of a sample.

Quench Indicating Parameter (QIP)

- Sample Spectrum QIPs:
  - Spectral Index Sample (SIS)
  - Sample Channels Ratio (SCR)
  - Spectral Quench Parameter of Isotope (SQP(I))

Quench Indicating Parameter (QIP)

- External Standard Spectrum QIPs:
  - External Standard Counts (ESC)
  - External Standard Ratio (ESR)
  - Inflection Point Compton Edge ($H^{\#}$)
  - External Standard Pulse (ESP)
  - Spectral Index External Standard (SIE)
  - Spectral Quench Parameter of the External Standard (SQP(E))
  - Transformed Spectral Index of the External Standard (t-SIE)

Spectral Index Sample (SIS)

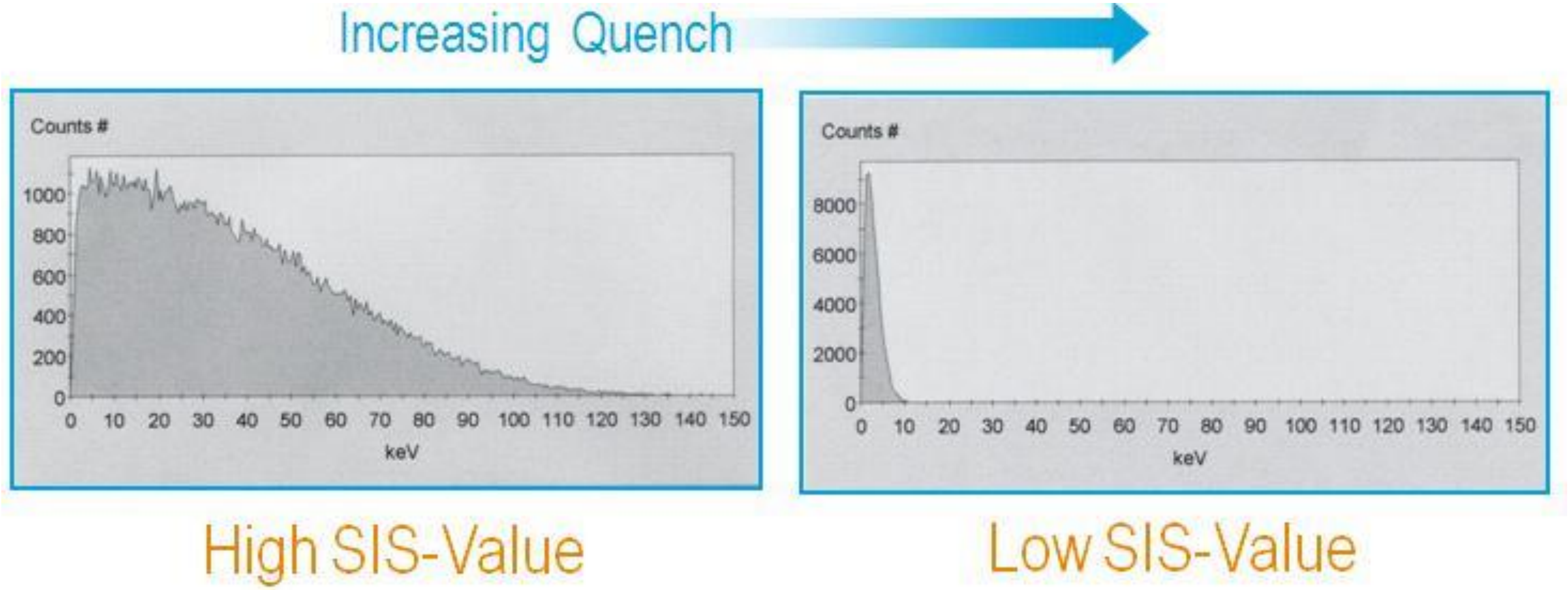
- This quench parameter is derived from the sample spectral endpoint.
- The beta-spectrum represents a probability distribution of beta-particles with a defined energy.
- From this distribution the average kinetic energy of all beta-particles can be calculated.

Spectral Index Sample (SIS)

- With increasing quench, the average kinetic energy of all beta-particles decreases.

- Consequently, the beta-spectrum is shifted to lower channel numbers.

Spectral Index Sample (SIS)



Source: PerkinElmer, http://www.perkinelmer.com/Resources/TechnicalResources/ApplicationSupportKnowledgebase/radiometric/quench.xhtml#Quenchcountingefficiencyandquenchcorrection-SIS, Retrieved May 20, 2014

Spectral Index Sample (SIS)

- For an accurate SIS, a good sample spectrum needs to be acquired.
- The SIS uses the sample isotope spectrum to track quench.
- It is most accurate with high-count rate samples.
- SIS cannot be used for low-activity samples since an accurate sample spectrum cannot be acquired.
  - At least 500 CPM activity in the sample

Transformed Spectral Index of the External Standard (t-SIE)

- The t-SIE value is derived from the external standard spectrum.
- Most counters include a built-in gamma source, ^{133}Ba or ^{152}Eu, external to the sample.
- The gamma radiation from the external source causes the ejection of an orbital electron.
  - Compton electron
- This electron will cause the same scintillation effects as a beta particle.

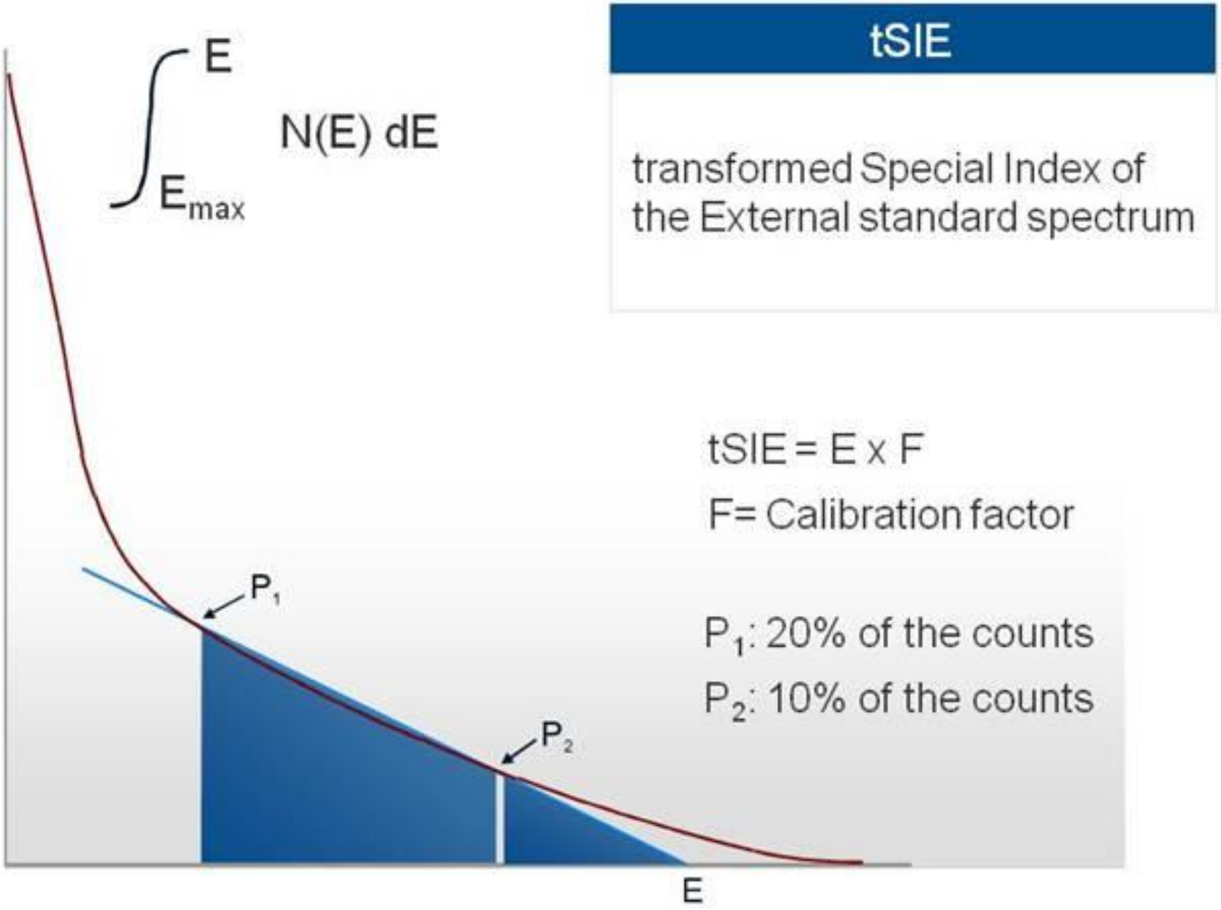
Transformed Spectral Index of the External Standard (t-SIE)

- The Reverse Spectral Transform (RST) technique is used to obtain the transformed spectrum of the external source.
- Two points in the spectrum are theoretically chosen.
- The first point corresponds to 20% of the counts and the second to 10% of the counts.
- A line is fitted between these points.

Transformed Spectral Index of the External Standard (t-SIE)

- The intersection of this line with the X-axis defines the t-SIE value.
- This process is also performed during instrument normalization.
  - Resets the t-SIE value of an unquenched sample to 1000.
- With increasing quench, the Compton-electron spectrum will be modified.
  - The t-SIE value decreases consequently.

Transformed Spectral Index of the External Standard (t-SIE)



$$\int_{E_{max}}^{E} N(E)\,dE$$

tSIE

transformed Special Index of the External standard spectrum

tSIE = E x F

F= Calibration factor

P_1: 20% of the counts

P_2: 10% of the counts

Source: PerkinElmer, http://www.perkinelmer.com/Resources/TechnicalResources/ApplicationSupportKnowledgebase/radiometric/quench.xhtml#Quenchcountingefficiencyandquenchcorrection-SIS, Retrieved May 20, 2014

Transformed Spectral Index of the External Standard (t-SIE)

- The t-SIE is independent of the sample isotope and of the activity in the vial.

- It also has a large dynamic range.

- This makes it a very reproducible means of tracking quench in the cocktail.

Quench Curves

- A quench curve is a graphical representation of the relationship between counting efficiency and the amount of quench.

- It is used to convert the measured counts into absolute activity.

- It is obtained by measuring a series of standards.
  - Absolute radioactivity per vial is constant
  - Amount of quench increases from vial to vial

Quench Curves

- The absolute activity of each standard is known.

- Each standard is assayed to:
  - Determine the relative number of counts
  - Measure the QIP for each standard

- The counting efficiency is given by:

$$\text{Counting Efficiency}(\%) = \frac{\text{CPM} * 100}{\text{DPM}}$$

Quench Curves

- A correlation is made between the QIP on one axis and the efficiency on the other axis.
- A mathematical function is fitted to the data points.
- The data and the fit are stored on the instrument.
  - This allows for automatic activity calculations.

Quench Curves

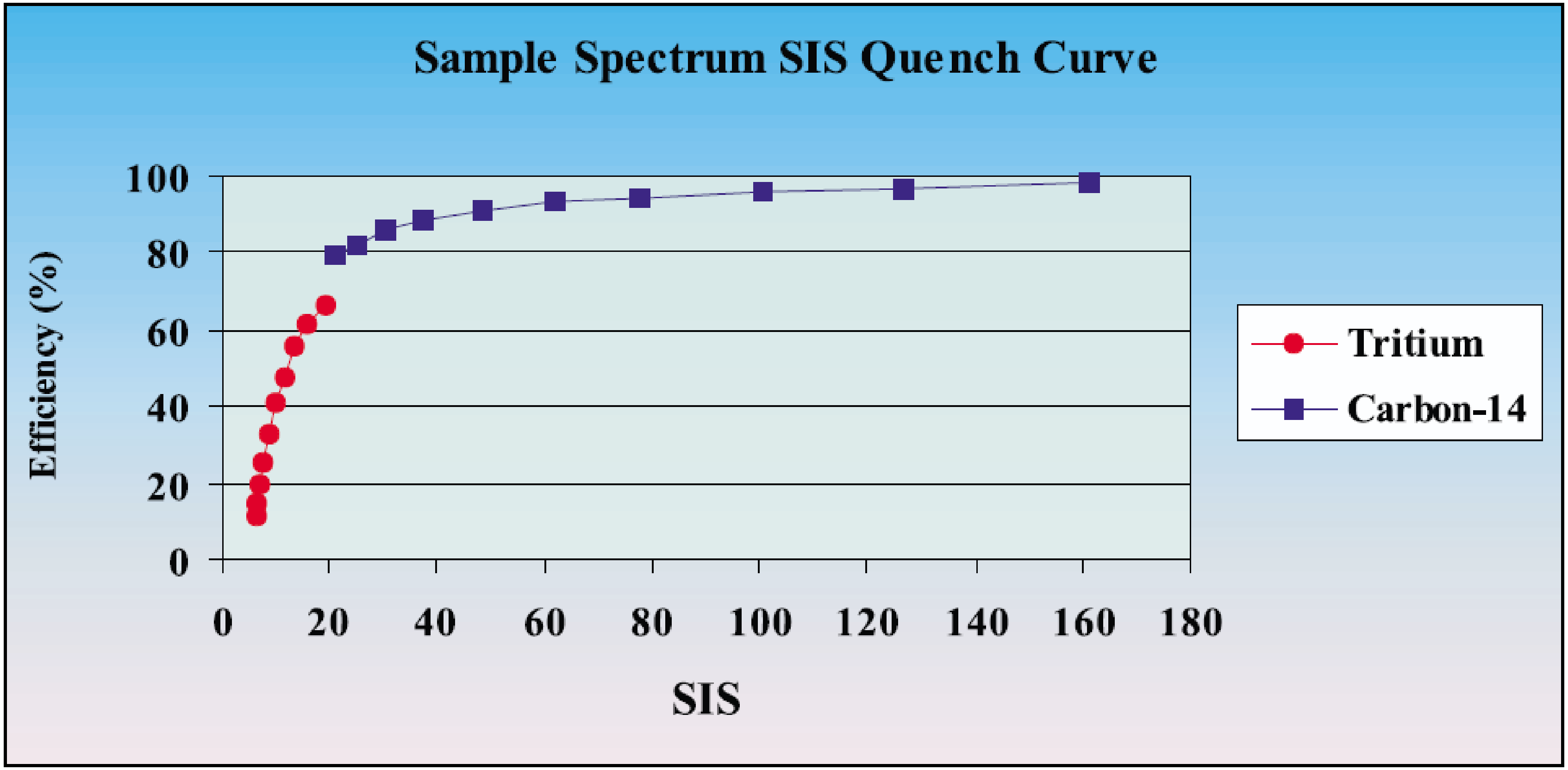


Figure 2. *Quench Curves for ^{3}H and ^{14}C Using SIS as the QIP*

Source: Thomson, J., *Use and preparation of quench curves*, Liquid Scintillation Counting Application Note P11399, PerkinElmer (2002)

Quench Curves

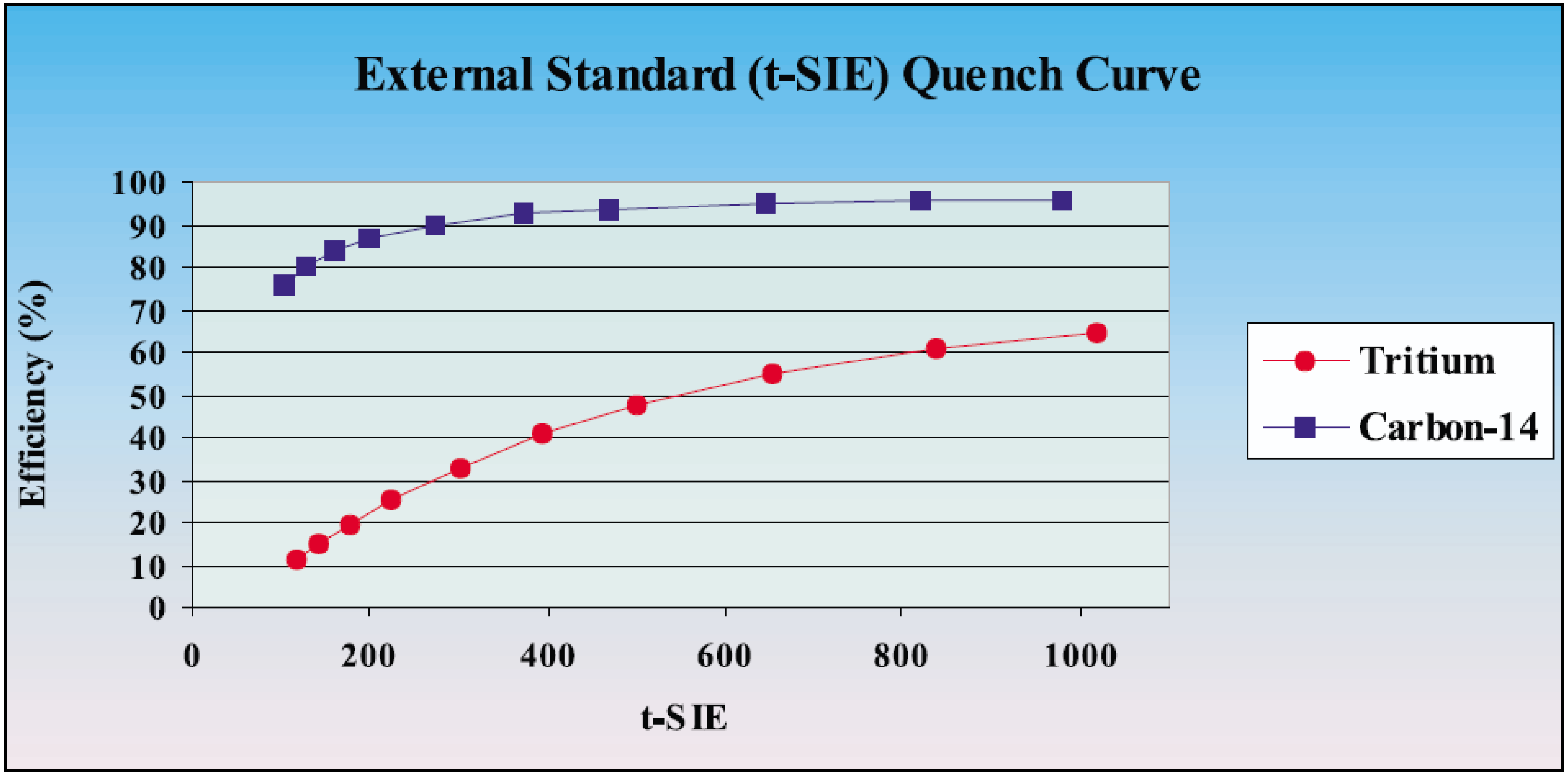


Figure 3. *Quench Curves for ^{3}H and ^{14}C Using t-SIE as the QIP*

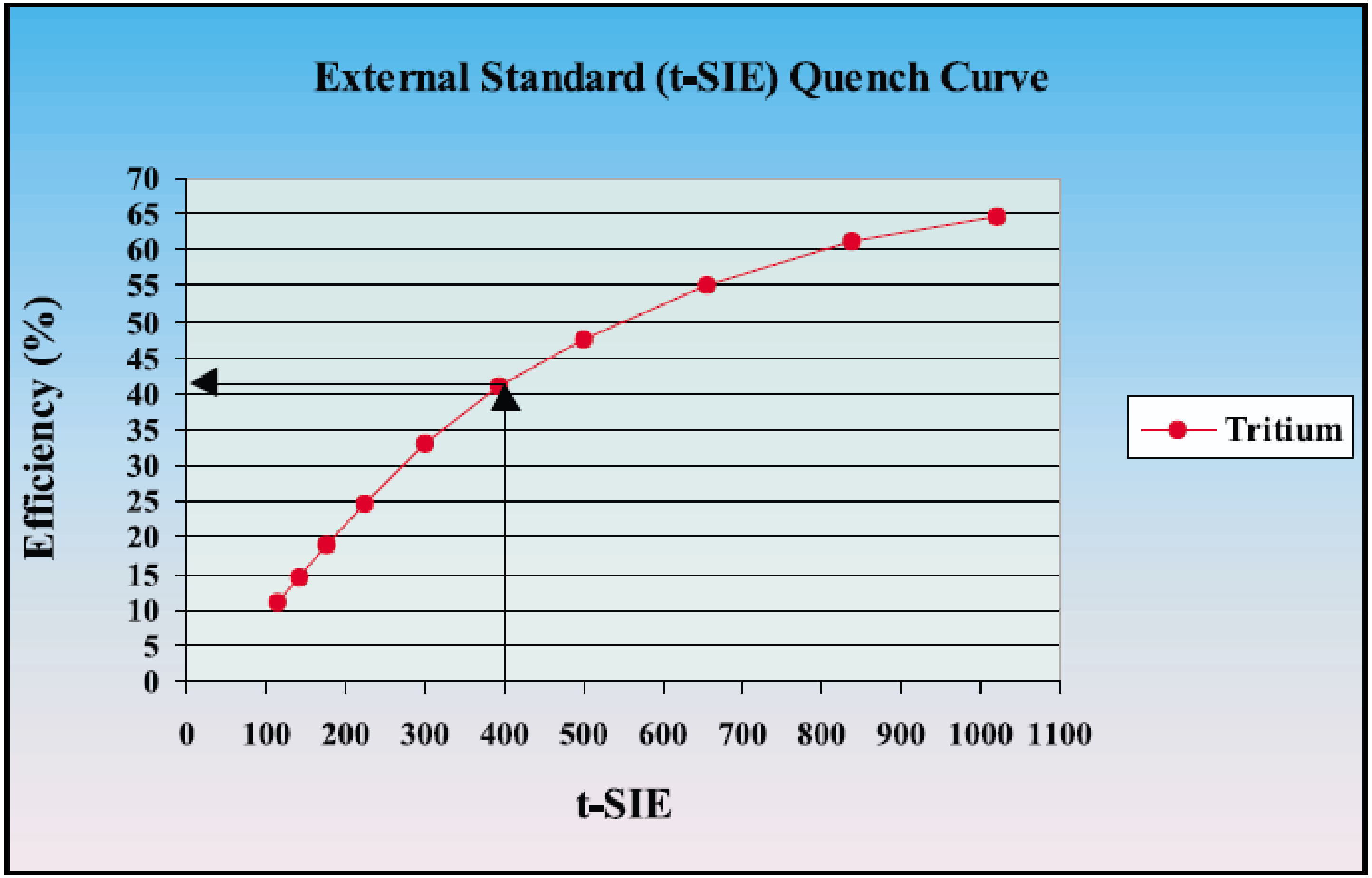
Source: Thomson, J., *Use and preparation of quench curves*, Liquid Scintillation Counting Application Note P11399, PerkinElmer (2002)

Quench Curves

- When a sample is counted, the relative counts are measured together with the QIP.
- The counting efficiency is determined from the quench curve based on the QIP.
- The absolute sample activity is then calculated by applying the appropriate efficiency to the counts.

$$\mathrm{DPM} = \frac{\mathrm{CPM}}{\mathrm{Counting\ Efficiency}}$$

Quench Curves



Source: Thomson, J., *Use and preparation of quench curves*, Liquid Scintillation Counting Application Note P11399, PerkinElmer (2002)

Quench Curves

- Standards and samples must be counted with the same energy regions.

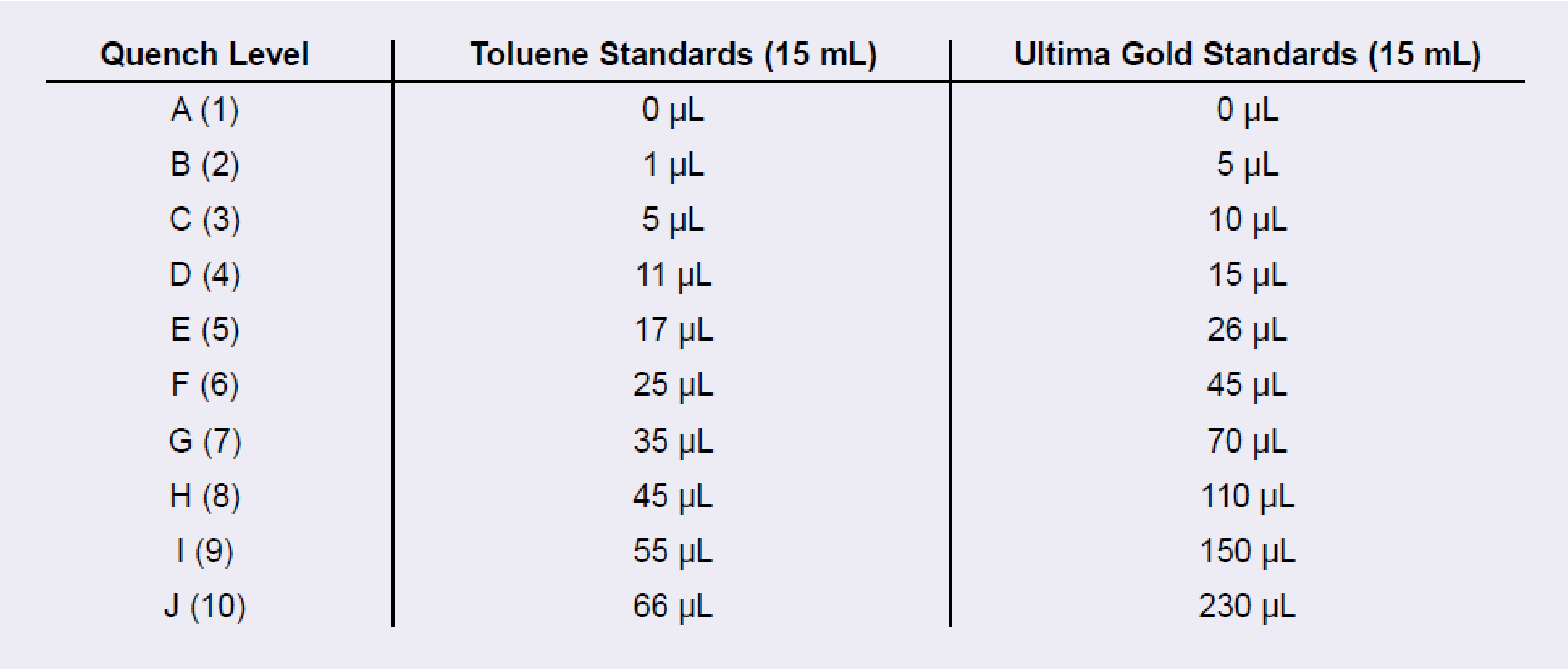
Preparation of Quench Standards

1. Dispense LSC cocktail into 10 high performance glass vials.
   - 10.0 mL or 15.0 mL
2. Add activity to each vial.
   - 200,000 DPM for ^{3}H or 100,000 DPM for ^{14}C
3. Count all 10 vials to ensure that the same amount of activity is in each vial.
   - A count time of about 5 minutes is recommended.

Preparation of Quench Standards

4. Number the vials 1 to 10 or A to J.
5. Add the suggested amounts of nitromethane.
6. Count the complete set under the conditions described in the instrument operation manual for storing a quench curve.
   - Recommended counting time is 30 minutes or until a pre-selected level of statistical accuracy is reached.

Preparation of Quench Standards



Quench Level	Toluene Standards (15 mL)	Ultima Gold Standards (15 mL)
A (1)	0 µL	0 µL
B (2)	1 µL	5 µL
C (3)	5 µL	10 µL
D (4)	11 µL	15 µL
E (5)	17 µL	26 µL
F (6)	25 µL	45 µL
G (7)	35 µL	70 µL
H (8)	45 µL	110 µL
I (9)	55 µL	150 µL
J (10)	66 µL	230 µL

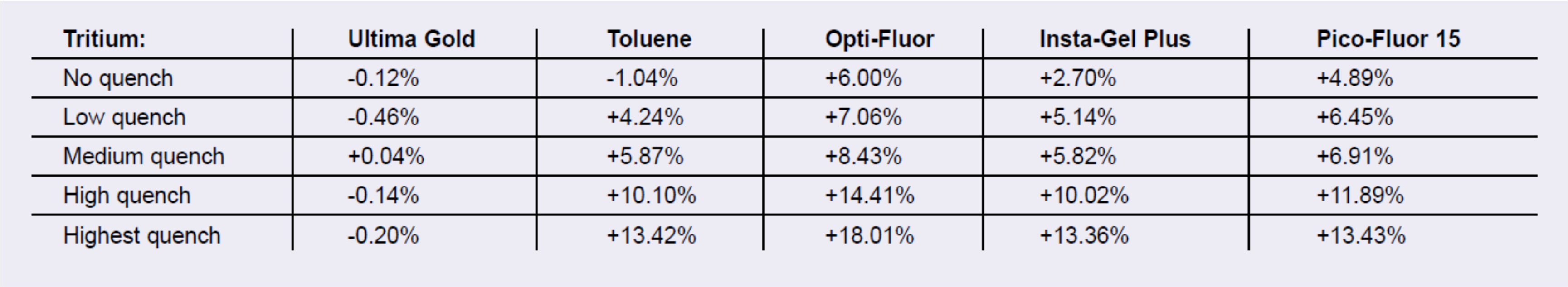
Table 1. *Volume of Nitromethane Needed for Quench Curve*

Source: Thomson, J., *Use and preparation of quench curves*, Liquid Scintillation Counting Application Note P11399, PerkinElmer (2002)

Preparation of Quench Standards

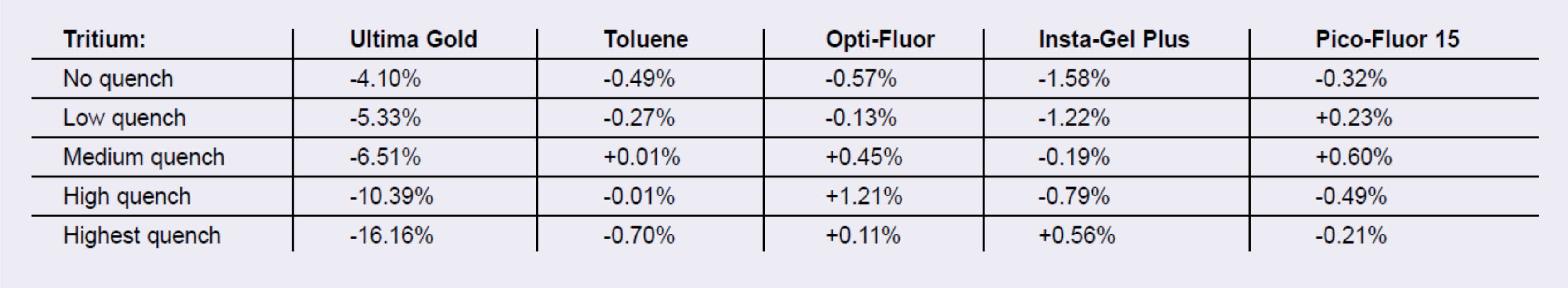
- Standards should be stored in the dark, at 5°C to 10°C for best stability.
- The quench curve should cover a wide QIP range in order to provide accurate results.
  - tSIE range 800-300

Quench Curve & Various Cocktails



Tritium:	Ultima Gold	Toluene	Opti-Fluor	Insta-Gel Plus	Pico-Fluor 15
No quench	-0.12%	-1.04%	+6.00%	+2.70%	+4.89%
Low quench	-0.46%	+4.24%	+7.06%	+5.14%	+6.45%
Medium quench	+0.04%	+5.87%	+8.43%	+5.82%	+6.91%
High quench	-0.14%	+10.10%	+14.41%	+10.02%	+11.89%
Highest quench	-0.20%	+13.42%	+18.01%	+13.36%	+13.43%

Table 3. *Various Cocktails vs. Ultima Gold Quench Curve (Tritium)*

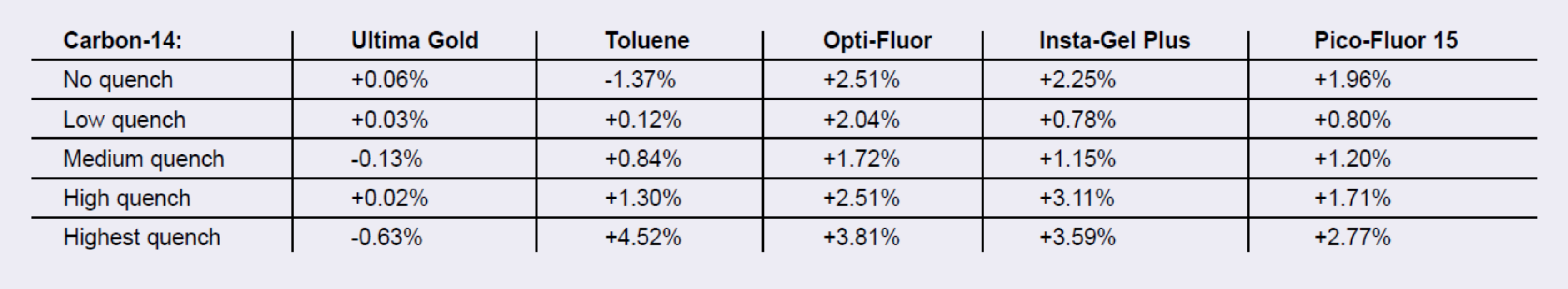


Tritium:	Ultima Gold	Toluene	Opti-Fluor	Insta-Gel Plus	Pico-Fluor 15
No quench	-4.10%	-0.49%	-0.57%	-1.58%	-0.32%
Low quench	-5.33%	-0.27%	-0.13%	-1.22%	+0.23%
Medium quench	-6.51%	+0.01%	+0.45%	-0.19%	+0.60%
High quench	-10.39%	-0.01%	+1.21%	-0.79%	-0.49%
Highest quench	-16.16%	-0.70%	+0.11%	+0.56%	-0.21%

Table 4. *Various Cocktails vs. Toluene Quench Curve (Tritium)*

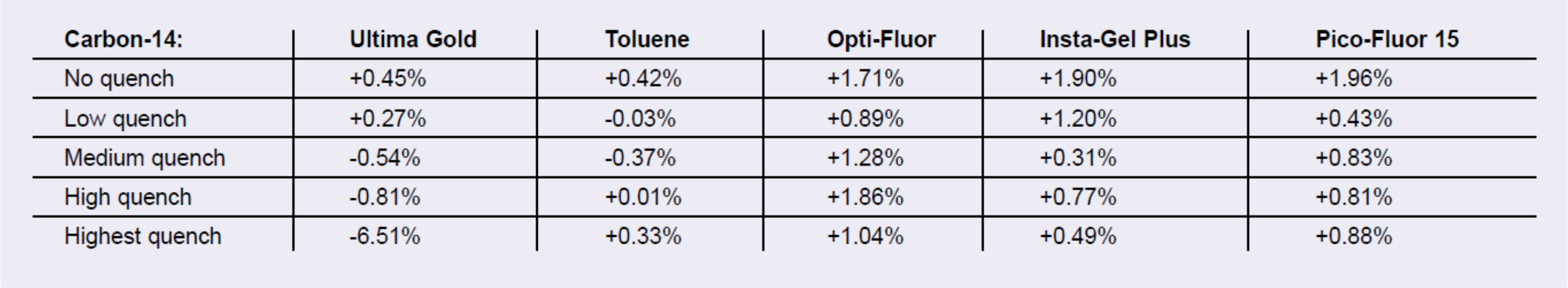
Source: Thomson, J., *Use and preparation of quench curves*, Liquid Scintillation Counting Application Note P11399, PerkinElmer (2002)

Quench Curve & Various Cocktails



Carbon-14:	Ultima Gold	Toluene	Opti-Fluor	Insta-Gel Plus	Pico-Fluor 15
No quench	+0.06%	-1.37%	+2.51%	+2.25%	+1.96%
Low quench	+0.03%	+0.12%	+2.04%	+0.78%	+0.80%
Medium quench	-0.13%	+0.84%	+1.72%	+1.15%	+1.20%
High quench	+0.02%	+1.30%	+2.51%	+3.11%	+1.71%
Highest quench	-0.63%	+4.52%	+3.81%	+3.59%	+2.77%

Table 5. *Various Cocktails vs. Ultima Gold Quench Curve (Carbon-14)*

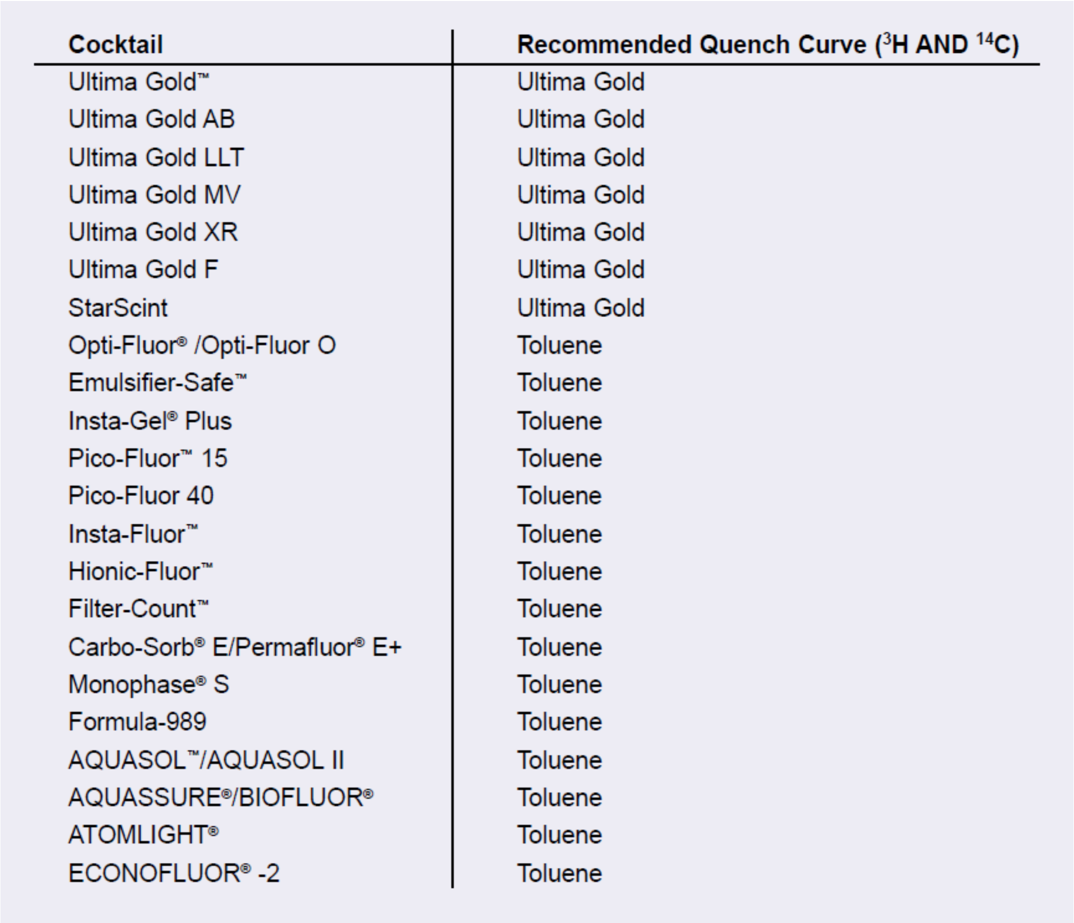


Carbon-14:	Ultima Gold	Toluene	Opti-Fluor	Insta-Gel Plus	Pico-Fluor 15
No quench	+0.45%	+0.42%	+1.71%	+1.90%	+1.96%
Low quench	+0.27%	-0.03%	+0.89%	+1.20%	+0.43%
Medium quench	-0.54%	-0.37%	+1.28%	+0.31%	+0.83%
High quench	-0.81%	+0.01%	+1.86%	+0.77%	+0.81%
Highest quench	-6.51%	+0.33%	+1.04%	+0.49%	+0.88%

Table 6. *Various Cocktails vs. Toluene Quench Curve (Carbon-14)*

Source: Thomson, J., *Use and preparation of quench curves*, Liquid Scintillation Counting Application Note P11399, PerkinElmer (2002)

Quench Curve & Various Cocktails



Cocktail	Recommended Quench Curve (^{3}H AND ^{14}C)
Ultima Gold™	Ultima Gold
Ultima Gold AB	Ultima Gold
Ultima Gold LLT	Ultima Gold
Ultima Gold MV	Ultima Gold
Ultima Gold XR	Ultima Gold
Ultima Gold F	Ultima Gold
StarScint	Ultima Gold
Opti-Fluor® /Opti-Fluor O	Toluene
Emulsifier-Safe™	Toluene
Insta-Gel® Plus	Toluene
Pico-Fluor™ 15	Toluene
Pico-Fluor 40	Toluene
Insta-Fluor™	Toluene
Hionic-Fluor™	Toluene
Filter-Count™	Toluene
Carbo-Sorb® E/Permafluor® E+	Toluene
Monophase® S	Toluene
Formula-989	Toluene
AQUASOL™/AQUASOL II	Toluene
AQUASSURE®/BIOFLUOR®	Toluene
ATOMLIGHT®	Toluene
ECONOFLUOR® -2	Toluene

Source: Thomson, J., *Use and preparation of quench curves*, Liquid Scintillation Counting Application Note P11399, PerkinElmer (2002)

Color Quench Curves

- There is no difference between chemical and color quenching if only a small amount of color is present in a sample.

- Standard chemical quench curves can be used.
  - Applies to samples with tSIE = 100 - 400

- However, if the tSIE value is smaller than 100, then a color quench curve should be prepared.

Color Quench Curves

- Aqueous soluble food dyes are a good quench agent for preparing a color quench curve.
  - Provide a stable color
  - Available in a wide range of colors
- The color of the sample must match the color used in the quench curve.
- pH indicators should not be used because some cocktails contain acidic components.
  - Can lead to color changes

Color Quench Curves

- The preparation of a color quench curve is similar to the method used for chemical quench.
  - Only difference is the quench agent
- If considerable color is present in the sample it may be better to modify the sample preparation method.
  - Adjust to remove or reduce the level of color

How to Reduce Sample Color?

- Decrease the sample size.
- Increase the volume of cocktail.
- Consider H_2O_2 treatment to bleach out the color.
  - If the color is the result of sample solubilization
- Sample oxidation.
  - For plant samples
- Change to alternate colorless anion.
  - If the color stems from the inorganic matrix

Sources of Background

- Instrument Background
  - Results from the dark noise of the photomultiplier tubes
    - Low energetic
- Crosstalk
  - A random scintillation event in the photocathode of the first PMT gives rises to photons that are seen by the second PMT.
    - Low energetic

Sources of Background

- Vial glass and PMT face
  - Background scintillation in vial wall and PMT face due to cosmic and environmental radiation
    - Glass contains K-40
    - Evenly distributed over a broad energy range
- Scintillator background
  - Background in the scintillator due to cosmic and environmental radiation
    - Evenly distributed over a broad energy range

Sources of Background

Source	Contribution
Instrument	10 %
Crosstalk	22 %
Vial glass & PMT Face	37 %
Scintillator (14 mL)	31 %

Background Spectrum

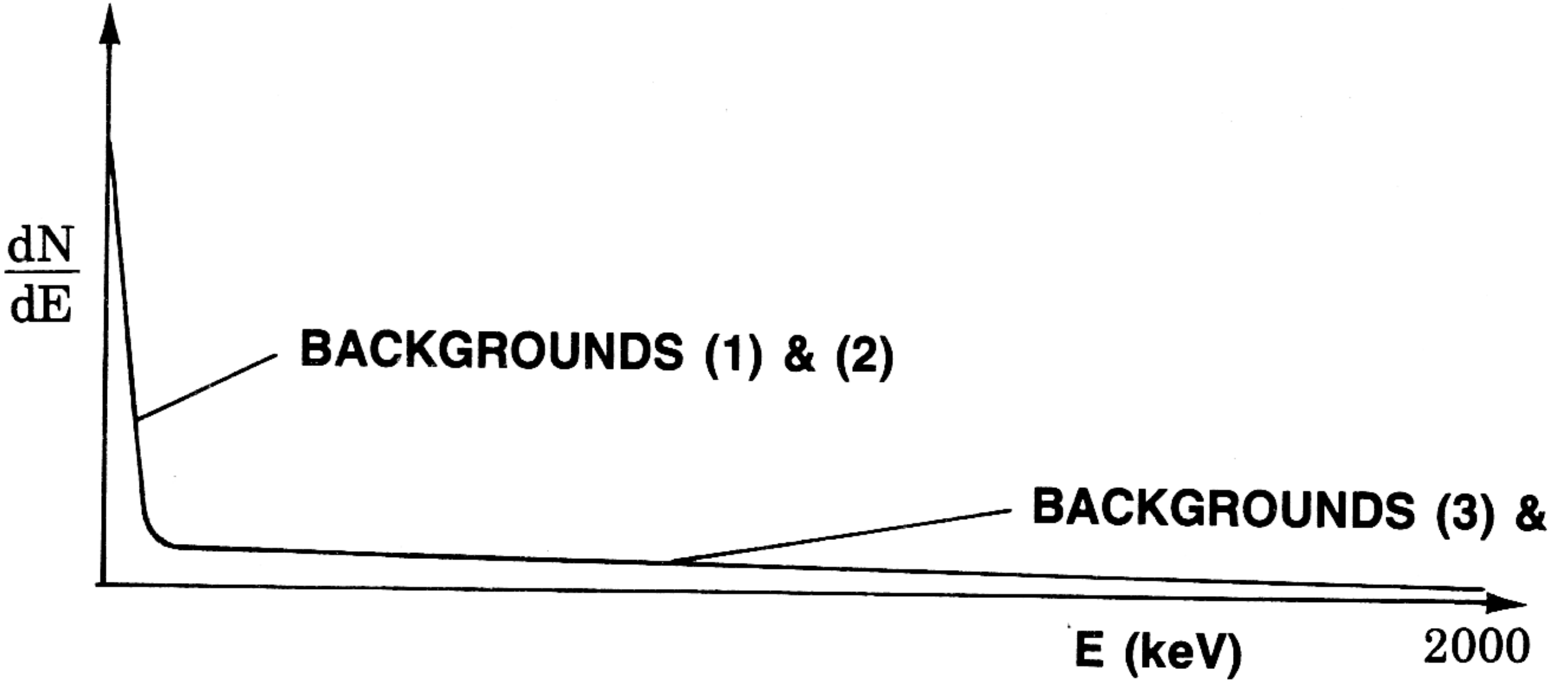


Figure 2-31. Backgrounds.

Source: Packard, *Liquid scintillation analysis – Science and Technology*, Packard Instrument Company (1989)

Effect of Vial Size & Type

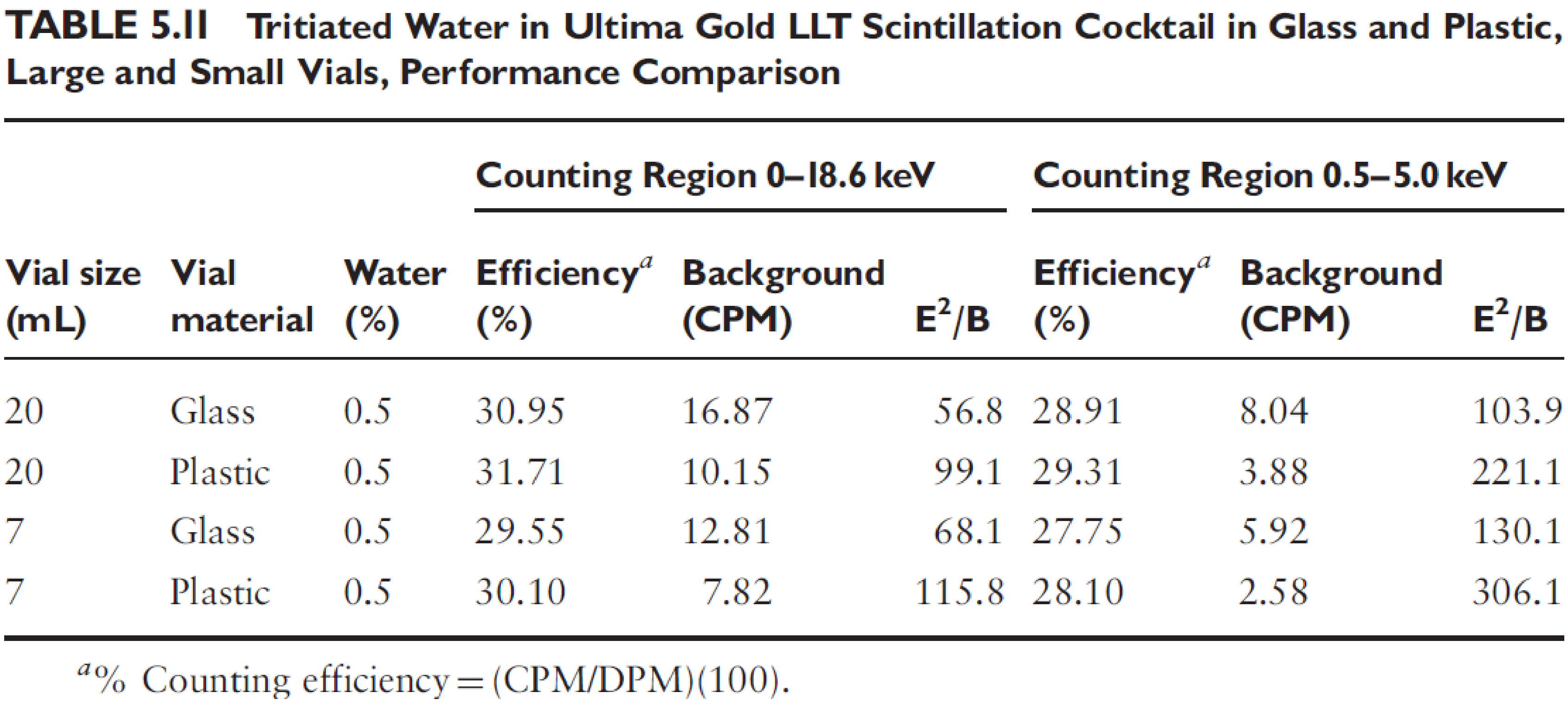


TABLE 5.11 Tritiated Water in Ultima Gold LLT Scintillation Cocktail in Glass and Plastic, Large and Small Vials, Performance Comparison

			Counting Region 0–18.6 keV			Counting Region 0.5–5.0 keV		
Vial size (mL)	Vial material	Water (%)	Efficiency[a] (%)	Background (CPM)	E^2/B	Efficiency[a] (%)	Background (CPM)	E^2/B
20	Glass	0.5	30.95	16.87	56.8	28.91	8.04	103.9
20	Plastic	0.5	31.71	10.15	99.1	29.31	3.88	221.1
7	Glass	0.5	29.55	12.81	68.1	27.75	5.92	130.1
7	Plastic	0.5	30.10	7.82	115.8	28.10	2.58	306.1

[a] % Counting efficiency = (CPM/DPM)(100).

Source: L'Annunziata, M.F., *Handbook of Radioactivity Analysis*, 2nd Edition, Academic Press (2003)

References

1. L'Annunziata, M.F., Handbook of Radioactivity Analysis, 3rd Edition, Academic Press (2012)
2. Packard Instrument Company, *Liquid Scintillation Analysis – Science and Technology* (1989)
3. MARLAP, *Multi-Agency Radiological Laboratory Analytical Protocols Manual*, NUREG-1576 (2004)

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- Introduction to the Fuel Cycle – June 26, 2014
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Visit the NAMP website at www.wipp.energy.gov/namp

Instrument Sensitivity

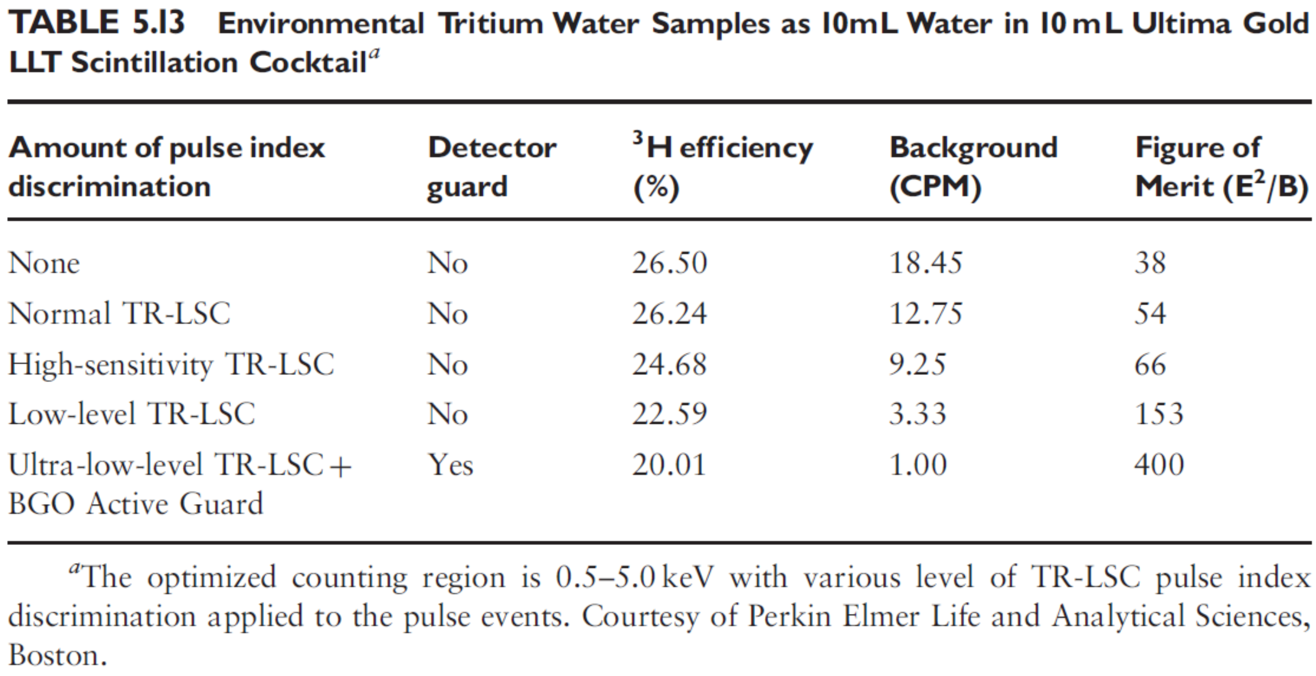


TABLE 5.13 **Environmental Tritium Water Samples as 10mL Water in 10 mL Ultima Gold LLT Scintillation Cocktail**[a]

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

[a] The optimized counting region is 0.5–5.0 keV with various level of TR-LSC pulse index discrimination applied to the pulse events. Courtesy of Perkin Elmer Life and Analytical Sciences, Boston.

Source: L'Annunziata, M.F., *Handbook of Radioactivity Analysis*, 2nd Edition, Academic Press (2003)

Selection of Cocktail

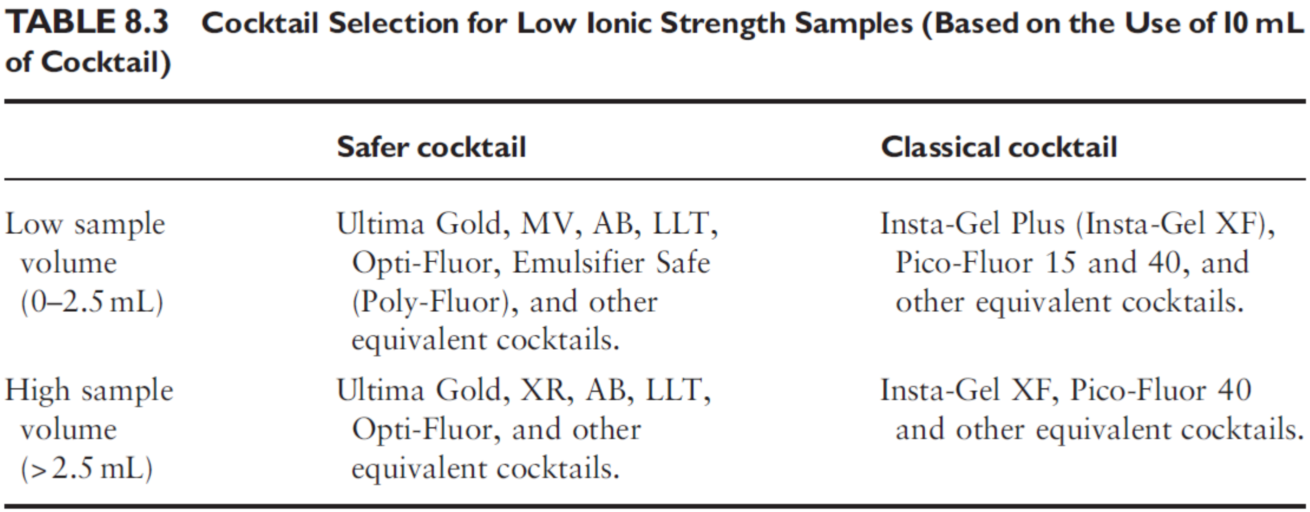


TABLE 8.3 **Cocktail Selection for Low Ionic Strength Samples (Based on the Use of 10 mL of Cocktail)**

	Safer cocktail	Classical cocktail
Low sample volume (0–2.5 mL)	Ultima Gold, MV, AB, LLT, Opti-Fluor, Emulsifier Safe (Poly-Fluor), and other equivalent cocktails.	Insta-Gel Plus (Insta-Gel XF), Pico-Fluor 15 and 40, and other equivalent cocktails.
High sample volume (>2.5 mL)	Ultima Gold, XR, AB, LLT, Opti-Fluor, and other equivalent cocktails.	Insta-Gel XF, Pico-Fluor 40 and other equivalent cocktails.

Source: L'Annunziata, M.F., *Handbook of Radioactivity Analysis*, 2nd Edition, Academic Press (2003)

Selection of Cocktail

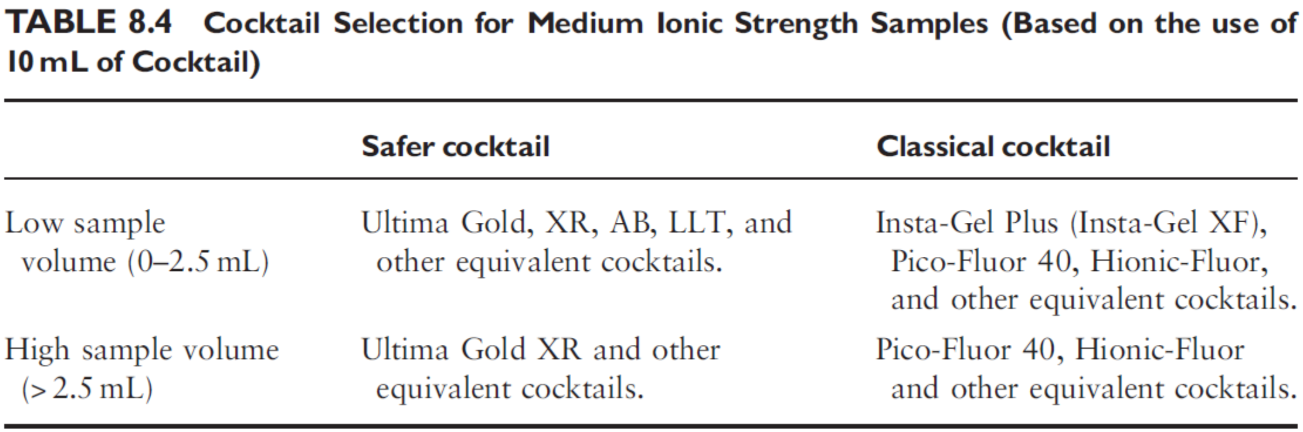


TABLE 8.4 **Cocktail Selection for Medium Ionic Strength Samples (Based on the use of 10 mL of Cocktail)**

	Safer cocktail	Classical cocktail
Low sample volume (0–2.5 mL)	Ultima Gold, XR, AB, LLT, and other equivalent cocktails.	Insta-Gel Plus (Insta-Gel XF), Pico-Fluor 40, Hionic-Fluor, and other equivalent cocktails.
High sample volume (> 2.5 mL)	Ultima Gold XR and other equivalent cocktails.	Pico-Fluor 40, Hionic-Fluor and other equivalent cocktails.

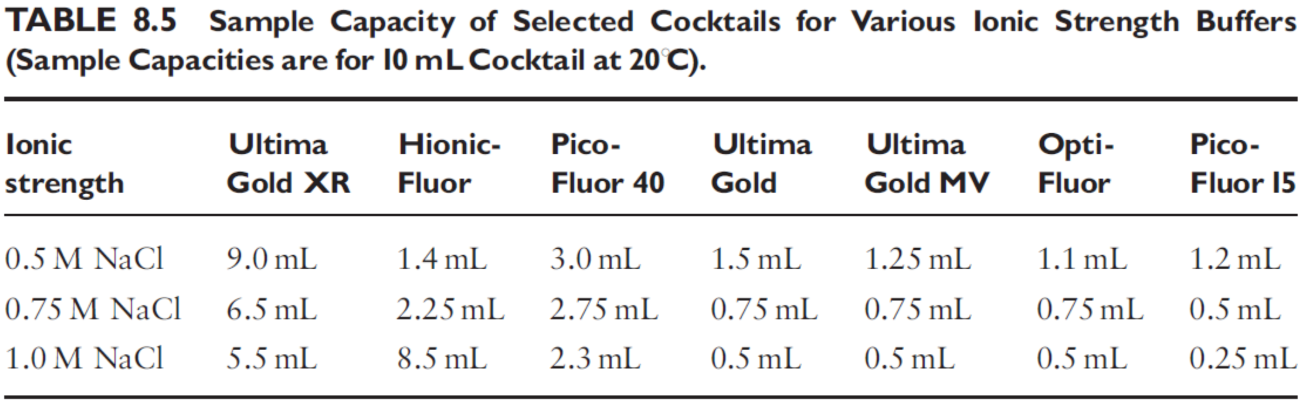


TABLE 8.5 **Sample Capacity of Selected Cocktails for Various Ionic Strength Buffers (Sample Capacities are for 10 mL Cocktail at 20°C).**

Ionic strength	Ultima Gold XR	Hionic-Fluor	Pico-Fluor 40	Ultima Gold	Ultima Gold MV	Opti-Fluor	Pico-Fluor 15
0.5 M NaCl	9.0 mL	1.4 mL	3.0 mL	1.5 mL	1.25 mL	1.1 mL	1.2 mL
0.75 M NaCl	6.5 mL	2.25 mL	2.75 mL	0.75 mL	0.75 mL	0.75 mL	0.5 mL
1.0 M NaCl	5.5 mL	8.5 mL	2.3 mL	0.5 mL	0.5 mL	0.5 mL	0.25 mL

Source: L'Annunziata, M.F., *Handbook of Radioactivity Analysis*, 2nd Edition, Academic Press (2003)

Selection of Cocktail

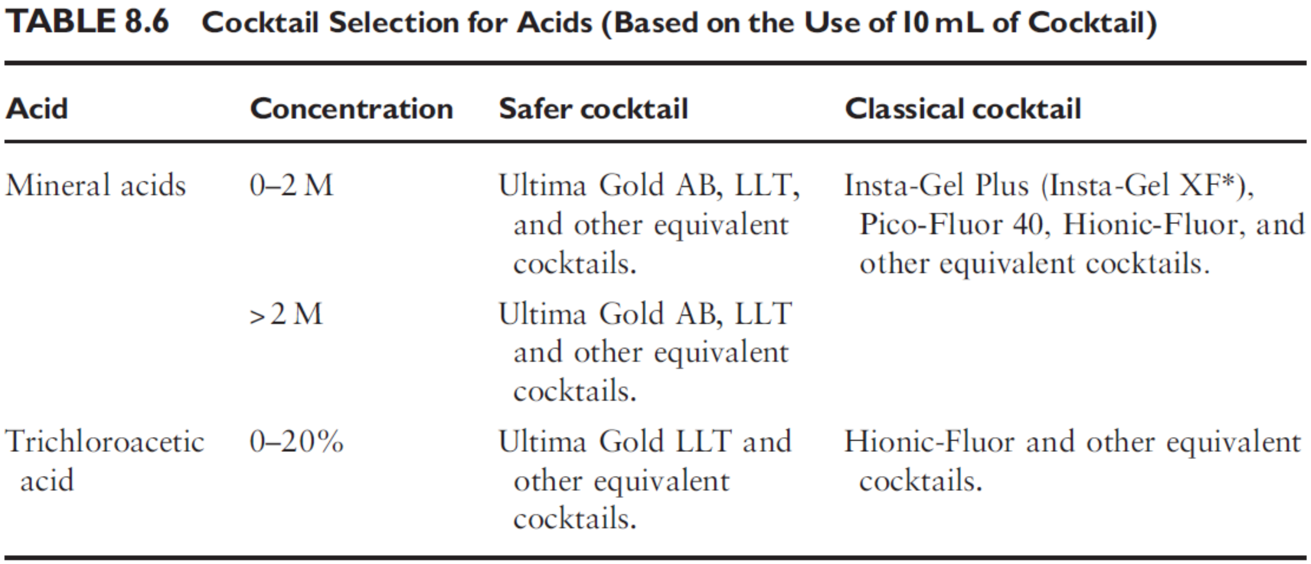


TABLE 8.6 Cocktail Selection for Acids (Based on the Use of 10 mL of Cocktail)

Acid	Concentration	Safer cocktail	Classical cocktail
Mineral acids	0–2 M	Ultima Gold AB, LLT, and other equivalent cocktails.	Insta-Gel Plus (Insta-Gel XF*), Pico-Fluor 40, Hionic-Fluor, and other equivalent cocktails.
	>2 M	Ultima Gold AB, LLT and other equivalent cocktails.	
Trichloroacetic acid	0–20%	Ultima Gold LLT and other equivalent cocktails.	Hionic-Fluor and other equivalent cocktails.

Source: L'Annunziata, M.F., *Handbook of Radioactivity Analysis*, 2nd Edition, Academic Press (2003)

Sample Capacity - Acid

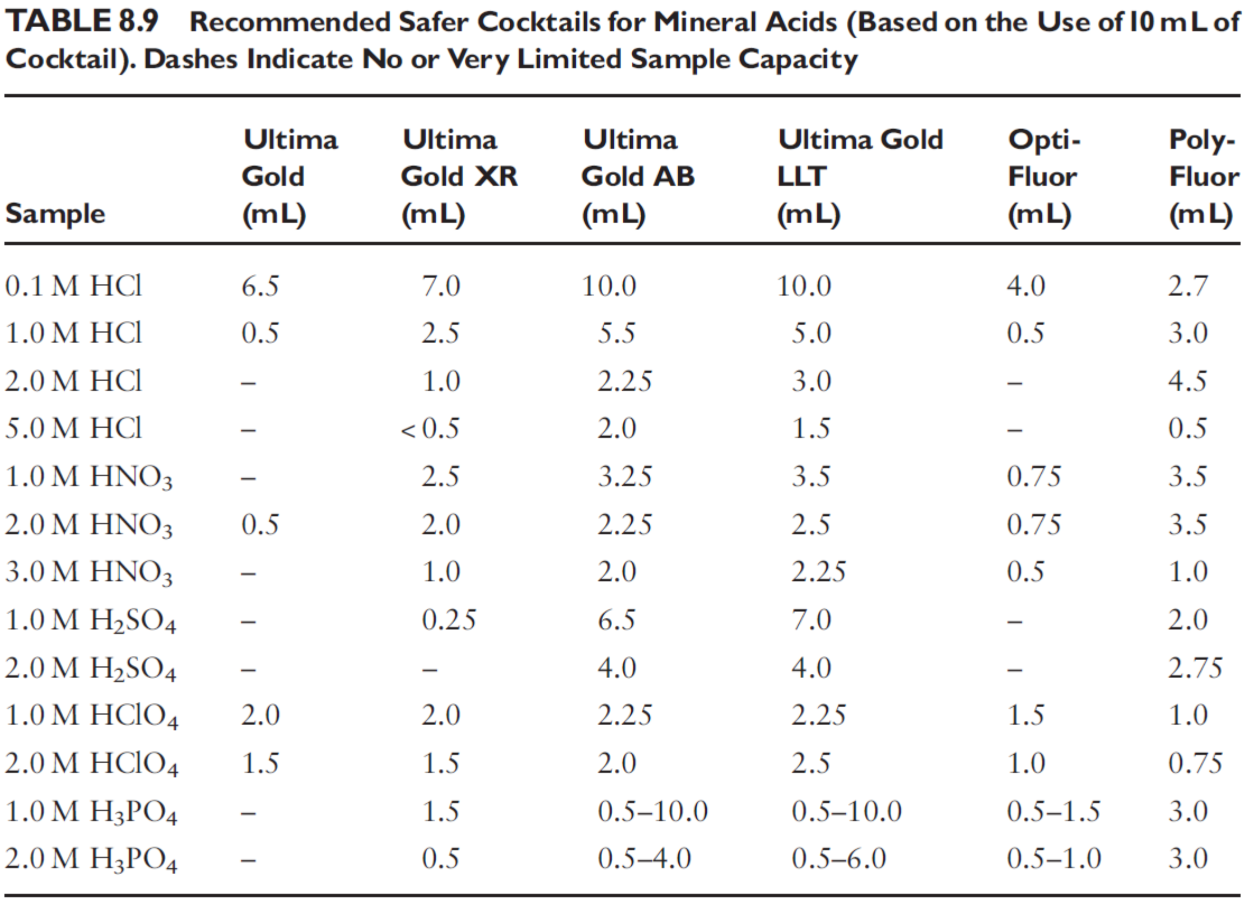
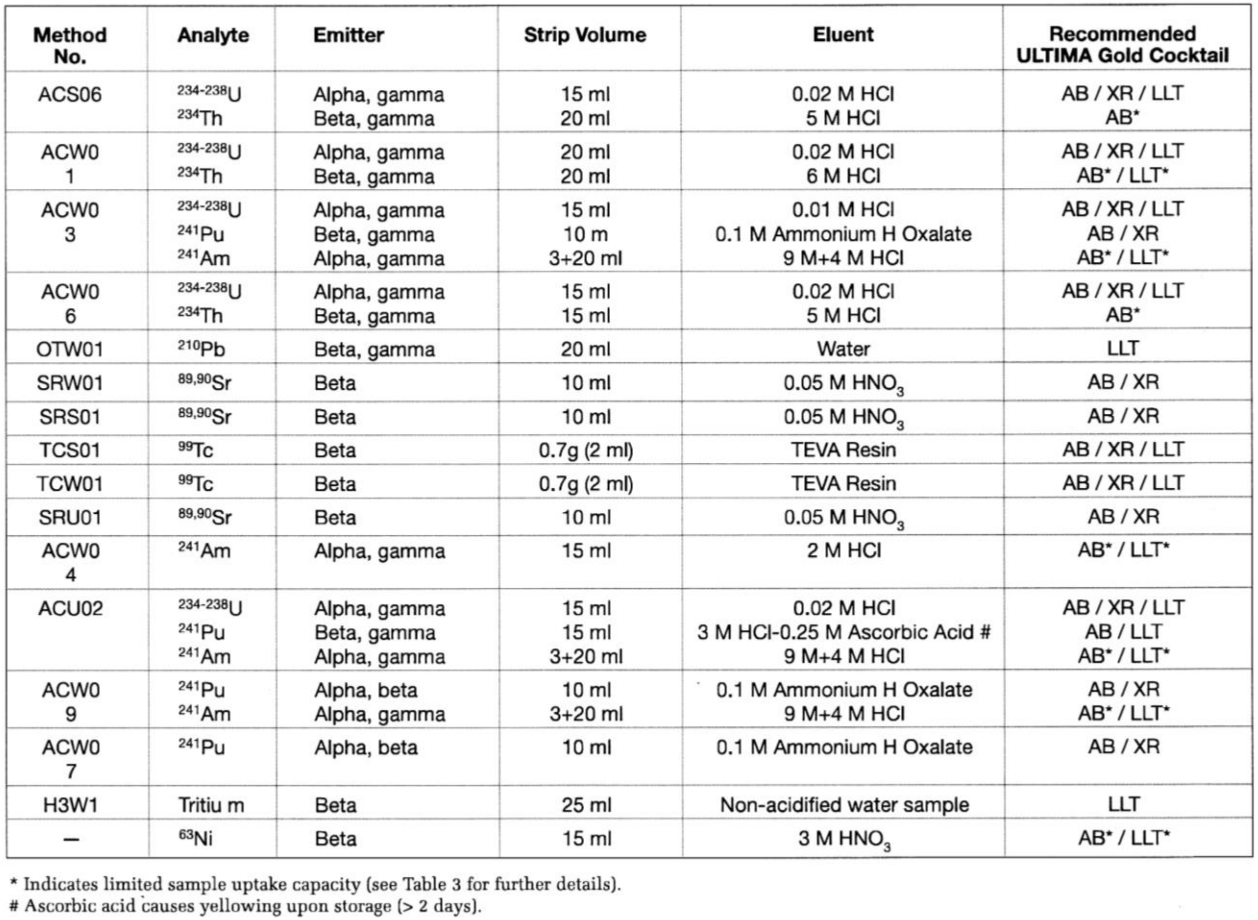


TABLE 8.9 **Recommended Safer Cocktails for Mineral Acids (Based on the Use of 10 mL of Cocktail). Dashes Indicate No or Very Limited Sample Capacity**

Sample	Ultima Gold (mL)	Ultima Gold XR (mL)	Ultima Gold AB (mL)	Ultima Gold LLT (mL)	Opti-Fluor (mL)	Poly-Fluor (mL)
0.1 M HCl	6.5	7.0	10.0	10.0	4.0	2.7
1.0 M HCl	0.5	2.5	5.5	5.0	0.5	3.0
2.0 M HCl	–	1.0	2.25	3.0	–	4.5
5.0 M HCl	–	< 0.5	2.0	1.5	–	0.5
1.0 M HNO_3	–	2.5	3.25	3.5	0.75	3.5
2.0 M HNO_3	0.5	2.0	2.25	2.5	0.75	3.5
3.0 M HNO_3	–	1.0	2.0	2.25	0.5	1.0
1.0 M H_2SO_4	–	0.25	6.5	7.0	–	2.0
2.0 M H_2SO_4	–	–	4.0	4.0	–	2.75
1.0 M $HClO_4$	2.0	2.0	2.25	2.25	1.5	1.0
2.0 M $HClO_4$	1.5	1.5	2.0	2.5	1.0	0.75
1.0 M H_3PO_4	–	1.5	0.5–10.0	0.5–10.0	0.5–1.5	3.0
2.0 M H_3PO_4	–	0.5	0.5–4.0	0.5–6.0	0.5–1.0	3.0

Source: L'Annunziata, M.F., *Handbook of Radioactivity Analysis*, 2nd Edition, Academic Press (2003)

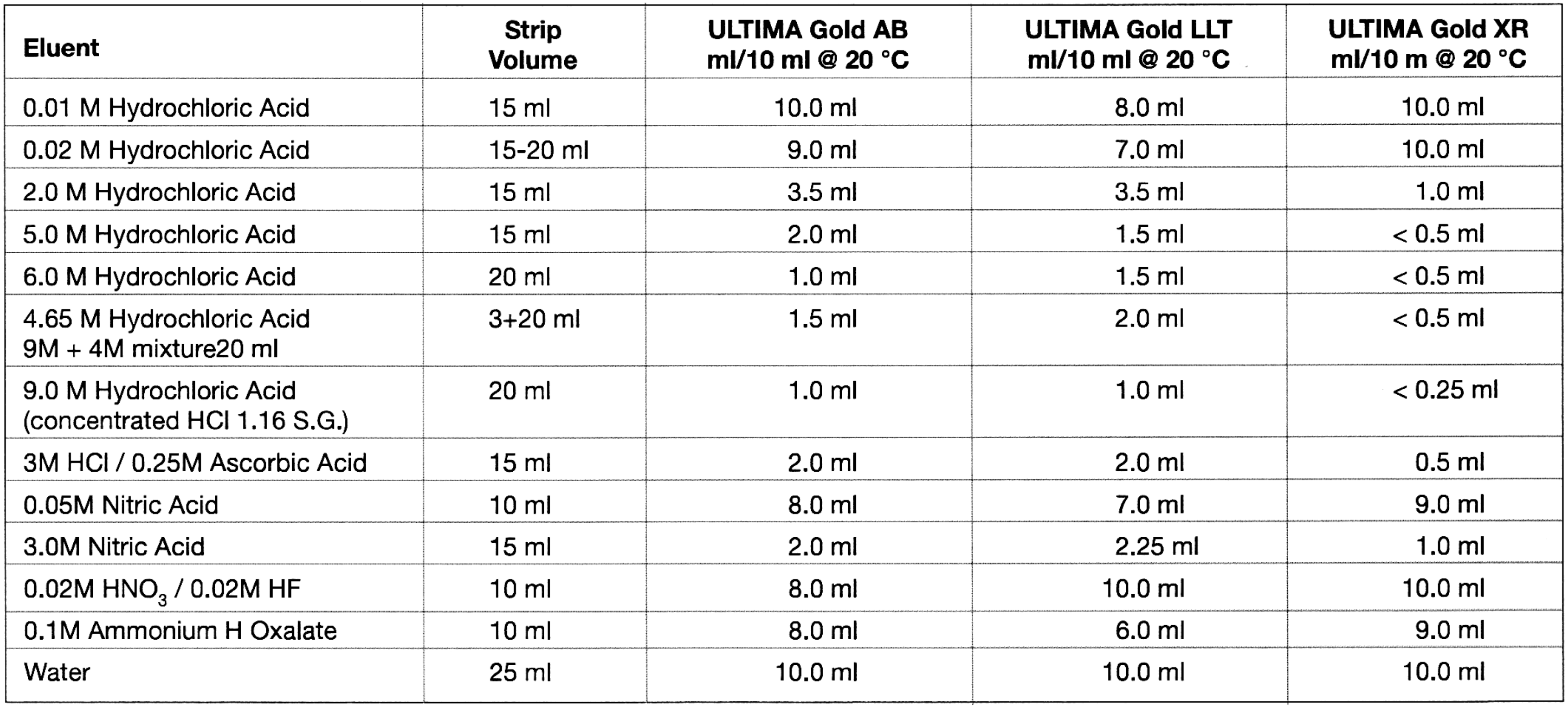
Selection of Cocktail



Method No.	Analyte	Emitter	Strip Volume	Eluent	Recommended ULTIMA Gold Cocktail
ACS06	$^{234-238}$U ^{234}Th	Alpha, gamma Beta, gamma	15 ml 20 ml	0.02 M HCl 5 M HCl	AB / XR / LLT AB*
ACW01	$^{234-238}$U ^{234}Th	Alpha, gamma Beta, gamma	20 ml 20 ml	0.02 M HCl 6 M HCl	AB / XR / LLT AB* / LLT*
ACW03	$^{234-238}$U ^{241}Pu ^{241}Am	Alpha, gamma Beta, gamma Alpha, gamma	15 ml 10 m 3+20 ml	0.01 M HCl 0.1 M Ammonium H Oxalate 9 M+4 M HCl	AB / XR / LLT AB / XR AB* / LLT*
ACW06	$^{234-238}$U ^{234}Th	Alpha, gamma Beta, gamma	15 ml 15 ml	0.02 M HCl 5 M HCl	AB / XR / LLT AB*
OTW01	^{210}Pb	Beta, gamma	20 ml	Water	LLT
SRW01	^{89,90}Sr	Beta	10 ml	0.05 M HNO$_3$	AB / XR
SRS01	^{89,90}Sr	Beta	10 ml	0.05 M HNO$_3$	AB / XR
TCS01	^{99}Tc	Beta	0.7g (2 ml)	TEVA Resin	AB / XR / LLT
TCW01	^{99}Tc	Beta	0.7g (2 ml)	TEVA Resin	AB / XR / LLT
SRU01	^{89,90}Sr	Beta	10 ml	0.05 M HNO$_3$	AB / XR
ACW04	^{241}Am	Alpha, gamma	15 ml	2 M HCl	AB* / LLT*
ACU02	$^{234-238}$U ^{241}Pu ^{241}Am	Alpha, gamma Beta, gamma Alpha, gamma	15 ml 15 ml 3+20 ml	0.02 M HCl 3 M HCl-0.25 M Ascorbic Acid # 9 M+4 M HCl	AB / XR / LLT AB / LLT AB* / LLT*
ACW09	^{241}Pu ^{241}Am	Alpha, beta Alpha, gamma	10 ml 3+20 ml	0.1 M Ammonium H Oxalate 9 M+4 M HCl	AB / XR AB* / LLT*
ACW07	^{241}Pu	Alpha, beta	10 ml	0.1 M Ammonium H Oxalate	AB / XR
H3W1	Tritium	Beta	25 ml	Non-acidified water sample	LLT
—	^{63}Ni	Beta	15 ml	3 M HNO$_3$	AB* / LLT*

* Indicates limited sample uptake capacity (see Table 3 for further details).
# Ascorbic acid causes yellowing upon storage (> 2 days).

Sample Capacity - Eluents



Eluent	**Strip Volume**	**ULTIMA Gold AB ml/10 ml @ 20 °C**	**ULTIMA Gold LLT ml/10 ml @ 20 °C**	**ULTIMA Gold XR ml/10 m @ 20 °C**
0.01 M Hydrochloric Acid	15 ml	10.0 ml	8.0 ml	10.0 ml
0.02 M Hydrochloric Acid	15-20 ml	9.0 ml	7.0 ml	10.0 ml
2.0 M Hydrochloric Acid	15 ml	3.5 ml	3.5 ml	1.0 ml
5.0 M Hydrochloric Acid	15 ml	2.0 ml	1.5 ml	< 0.5 ml
6.0 M Hydrochloric Acid	20 ml	1.0 ml	1.5 ml	< 0.5 ml
4.65 M Hydrochloric Acid 9M + 4M mixture20 ml	3+20 ml	1.5 ml	2.0 ml	< 0.5 ml
9.0 M Hydrochloric Acid (concentrated HCl 1.16 S.G.)	20 ml	1.0 ml	1.0 ml	< 0.25 ml
3M HCl / 0.25M Ascorbic Acid	15 ml	2.0 ml	2.0 ml	0.5 ml
0.05M Nitric Acid	10 ml	8.0 ml	7.0 ml	9.0 ml
3.0M Nitric Acid	15 ml	2.0 ml	2.25 ml	1.0 ml
0.02M HNO_3 / 0.02M HF	10 ml	8.0 ml	10.0 ml	10.0 ml
0.1M Ammonium H Oxalate	10 ml	8.0 ml	6.0 ml	9.0 ml
Water	25 ml	10.0 ml	10.0 ml	10.0 ml