

IAEA virtual training on measurement techniques for natural and artificial radionuclides and radiochemical methods for their determination in marine environment

11 October 2021 - 12 November 2021

TN-MAL7007-
2102662

MALAYSIA



IAEA

International Atomic Energy Agency
Atoms for Peace and Development

21 October 2021

Session 27. **Basic principles of LSC – Liquid scintillation Counting**

Ines KRAJCAR BRONIĆ (Ruđer Bošković Institute, Zagreb, Croatia)

MYA7008-2104243

MYANMAR

Content

History

Steps in LS counting process

LS counting - introduction

Scintillation and scintillation detection

Mechanism of LS counting

Components - scintillation cocktail, vials

Sample preparation

Quench

LS counters/spectrometers

Spectra

Background

Counting efficiency

Application areas of LS counting

Literature

History

- 1930s – development of photomultiplier tubes
- „modern” LSC invented in 1947 – successful detection of scintillation produced by alpha and beta radiation by phototubes, scintillation of organic and inorganic (NaI) crystals discovered
- Tested for measurement of natural ^{14}C in 1953
- LSC for ^{14}C could compete with gas counting after the invention of two tube coincidence technique, and practical benzene synthesis in early 1960s
- 1970s and 1980s – specially constructed systems developed, with heavy shielding and guard counters
- 1984 – first successful really low-level LSC Quantulus, by Wallac
- Currently - Liquid scintillation counting (LSC) is the standard laboratory method to quantify the radioactivity of low energy radioisotopes, mostly beta-emitting and alpha-emitting isotopes. A well-established technique is applied in numerous practical applications.

Steps in the LS counting process

Sampling

Sample preparation

Mixing with a scintillation cocktail in a vial

Measurement

Sample quality control (quench)

Data acquisition

Data evaluation

Activity calculation

Quality assurance
and quality control
– in each step

Liquid scintillation counting theory - introduction

- **Liquid scintillation counting** is the measurement of activity of a radioisotope in a sample material
- the active material is mixed with a liquid scintillator, a material that emits photons upon interaction with a particle emitted by a radioactive decay
- Instruments count the resultant photon emissions.

The main advantages of LSC methods in measurements of low-energy beta activities („low-level counting”) such as tritium's are its rapidity, sensitivity and simplicity, low detection limits that can be achieved, convenient even for natural tritium concentration determination. - **caution!**

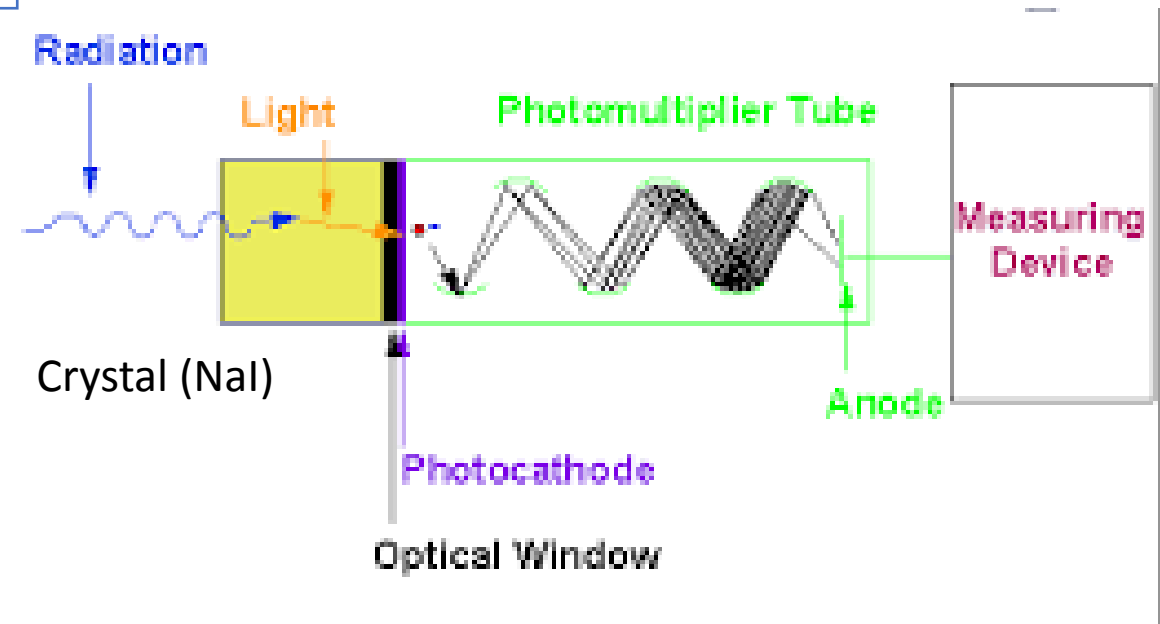
One main problem of liquid scintillation spectroscopy in general is **quench** presence in samples which can alter detection efficiency and thus affect obtained activity concentrations. However, reliable results can be assured if corrections of possible quench occurrence are established for each method, instrument and additional equipment (LS cocktail and vial used, for example), and laboratory conditions in which sample preparation and their counting take place.

Scintillation

Interaction of ionizing particles (beta or alpha particles) with matter (atoms and/or molecules) results in ionization, excitations and elastic collisions.

Some irradiated atoms are not fully ionized by collision with emitted particles, but instead have electrons promoted to an excited state. **Excited atoms can return to ground state by releasing energy**, in some cases as a photon of light. Such scintillation phenomena form the basis of a set of very sensitive radiation detection systems.

Scintillation Detection



In **solid scintillation systems**, a crystal of inorganic or organic material, the scintillator, is irradiated by the sample. The light emitted in response to this irradiation is taken as a measure of the amount of radioactivity in the sample. Solid scintillation is excellent **for γ radiation** which is highly penetrating and can cause scintillation throughout a large crystal. An advantage of these techniques is that the same crystal is used for each sample, which enhances reproducibility. As opposed to the gas counting where the ionization events are counted, a gas phase sample is not required.

Scintillation Detection

solid scintillation for α or β counting has severe limitations – these particles are easily stopped by a barrier

The crystal must be protected from contamination by the sample, meaning that the α and β particles must traverse a barrier prior to reaching the scintillator.

α -particles in particular are severely attenuated by even 0.05 mm of aluminum or copper, and so cannot be expected to reach a scintillator crystal through even the thinnest shielding.

Question: How to detect scintillations caused by α and β particles?

Mechanism of Liquid Scintillation Counting

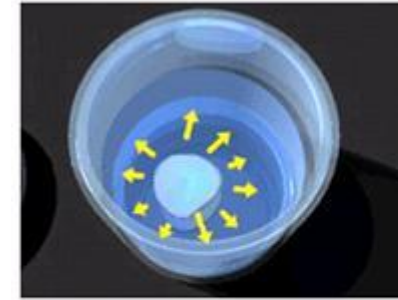
LSC detects radioactivity via the same type of light emission events which are used in solid scintillation. The key difference is that in LSC the scintillation takes place in a solution of scintillator, rather than in a solid crystal. This allows close contact between the isotope atoms and the scintillator (with no material barriers). With LSC the short path length of soft β emissions is not an obstacle to detection.

Liquid scintillation cocktails absorb the energy emitted by radioisotopes and re-emit it as flashes of light. To accomplish these two actions, absorption and re-emission, cocktails contain **two basic components**, the solvent and the scintillator. The solvent carries out the bulk of the energy absorption. Dissolved in the solvent, molecules of scintillator convert the absorbed energy into light.

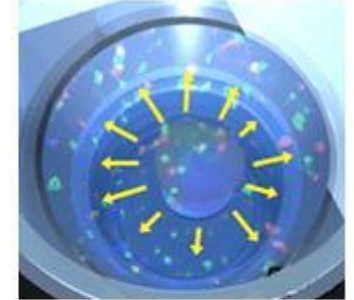
Many cocktails contain additional materials to extend their range of use to different sample compositions.

Mechanism of Liquid Scintillation Counting

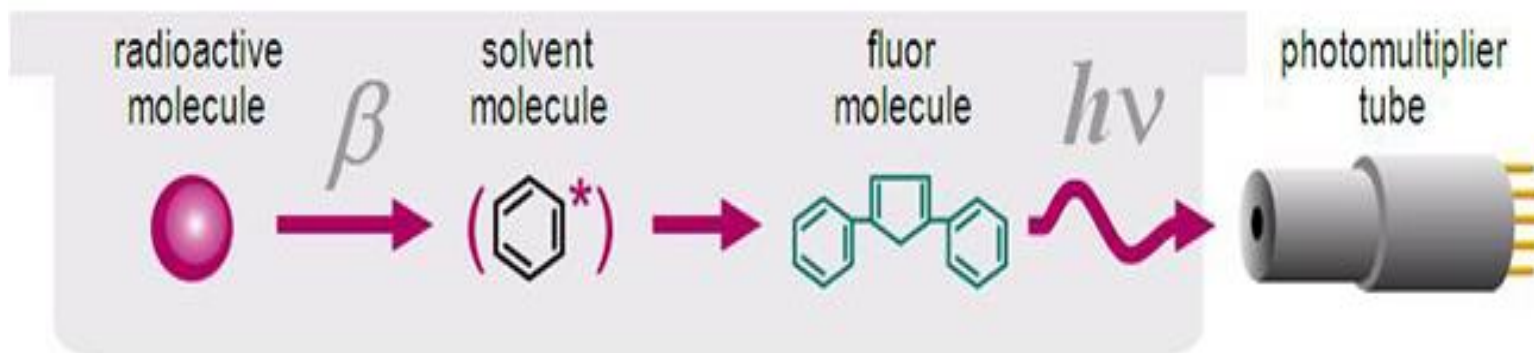
1. Excitation of the aromatic solvent molecules through the energy released from a radioactive decay
2. The energy is next transferred to the scintillator (also sometimes referred to as the "phosphor" or "fluor").
3. The energy absorbed through the scintillators produces excited states of the electrons, which decay to the ground state and produce a light pulse characteristic for the scintillator.
4. The light is detected by the photomultiplier tube (PMT) of the liquid scintillation counter.



Beta particles are emitted, which cause solvent molecules to become excited



The energy of the solvent molecules is transferred to the fluor molecules, which in turn emit light



Liquid scintillation counting principle

Scintillation cocktails

The LSC detection method requires specific „scintillation cocktails” to absorb the energy of the decay and transform it into detectable light pulses.

All liquid scintillation cocktails contain at least an organic solvent and one or more scintillators.

The major part of the LSC cocktails, the so-called emulsifying cocktails, contain a combination of surfactants (detergents) to be able to hold aqueous samples.

The basic component of the LSC cocktail is **solvent**, which comprises 60 - 99% of the total solution.

Classical solvents

Safer solvents

The **scintillator(s)**

Primary scintillators

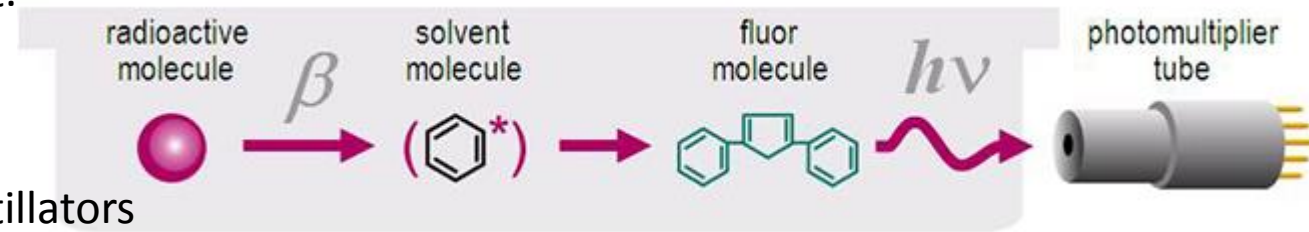
Secondary scintillators

For the aqueous-based samples, a cocktails must contain also a **surfactant**.

Solvent

When a radioisotope dissolved in the cocktail undergoes an emission event, it is highly probable that the particle or ray will encounter only solvent molecules before its energy is spent.

- the solvent must absorb the energy efficiently
- there must be an efficient energy transfer to the scintillators
- the solvent must not quench
- scintillators (fluors) should have a good solubility in the solvent

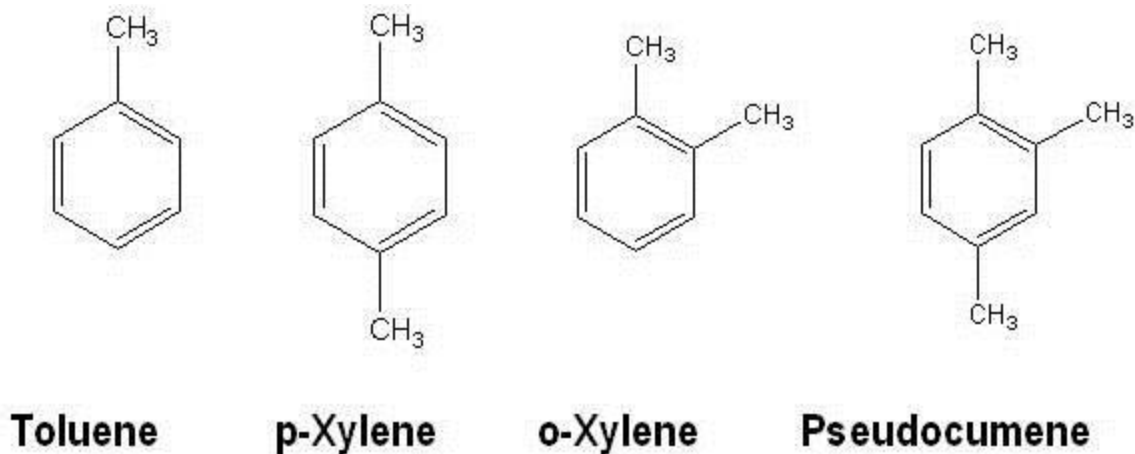


Aromatic organics have proven to be the best solvents for LSC (toluen). The π cloud of the toluene ring (or any aromatic ring) provides a target for β -interaction, which captures the energy of the incident particle. This captured energy is generally lost through transfer to an- other solvent molecule, as toluene has little tendency to emit light or undergo other alternate decay modes. The energized solvent molecules typically transfer the captured energy back and forth with other solvent molecules until the energy is finally transferred to a primary scintillator. Thus, a β -particle passing through a toluene solution leaves in its wake a number of energized toluene molecules. The energy from these molecules passes back and forth among the solvent ring systems, allowing efficient capture by dissolved scintillator.

Classical solvents

Aromatic organic solvents have proven to be the best solvents for liquid scintillation counting due to the high electron density, which provides a target for β -interaction, capturing the energy of the nuclear decay.

The structures of the four main traditional solvents (Toluene, Xylene (mixture of isomers) and Pseudocumene) are shown below. Other benzene derivatives can be used as well.

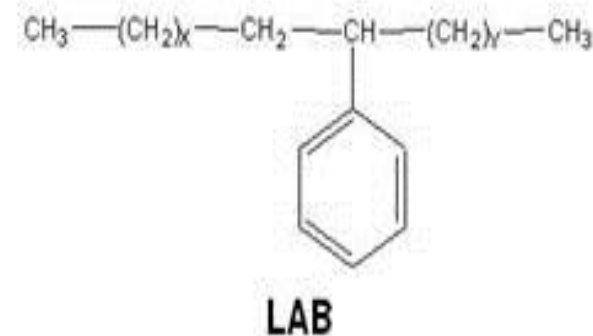
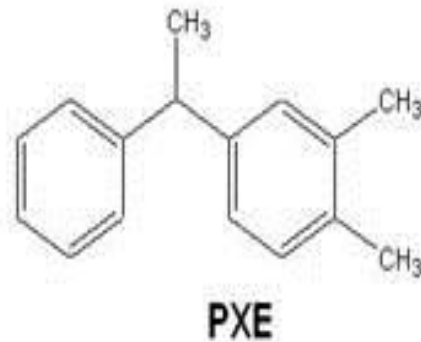
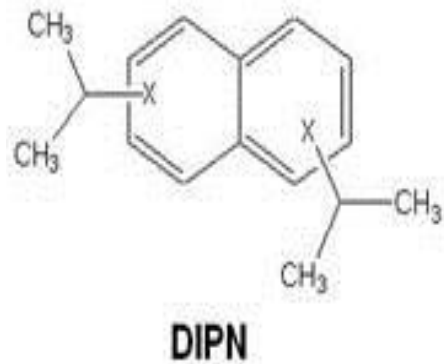


These solvents are hazardous by inhalation (and skin absorption), and can be irritating to skin and eyes. They have a high vapor pressure, a low flash point [from 5 - 50°C (flammable)], and storage in laboratories is restricted and should be used in fume hoods. Nowadays in practice Pseudocumene is used exclusively in classical cocktails.

Safer solvents

Why safer, not just “safe”? Although these solvents are much safer in practical use, we must bear in mind that we are dealing with chemicals. All the safety aspects are favourable compared to the classical solvents.

The main "safer" solvents used in the composition of scintillation cocktails (DIPN, PXE, LAB) have low toxicity and are classified as harmless for transport and storage. They have a low vapour pressure and a high flash point [above 140°C (non-flammable)].



Scintillator

The molecules of the scintillator dissolved in the solvent absorb the energy released by the solvent and re-emit this energy (at a higher wavelength) as visible light of a wavelength around 420 nm. The scintillators preferably have a fast decay time and a high Fluorescence Quantum Yield.

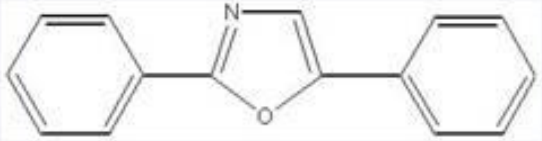
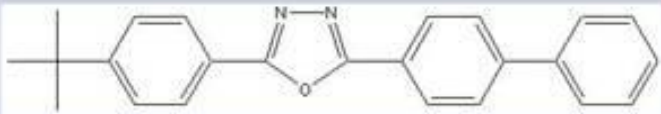

two classes of scintillators: the **primary** and the **secondary** scintillators

The emission wavelength of primary scintillators does not fully match the optimum sensitivity of the PMT's (i.e., does not allow efficient detection), thus in LSC cocktails a secondary scintillator is present with the purpose to absorb the fluorescence energy of the primary phosphor and re-emit at a longer wavelength .

Primary scintillators

Primary scintillators allow direct transfer of energy between excited solvent molecules and the scintillator. The most common primary scintillator is PPO (2,5-diphenyloxazole). The next common primary scintillator is butyl PBD [2(4-Biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole].

Note emission wavelength below 400 nm

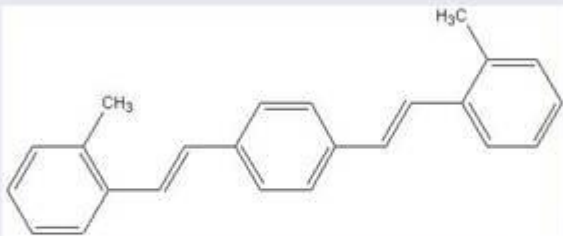
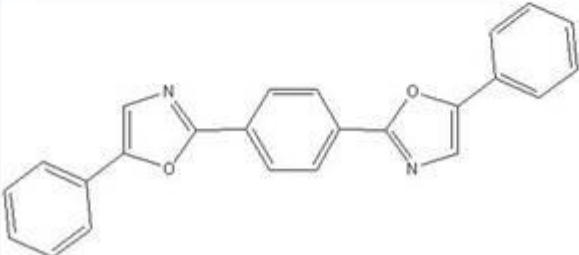
Primary Scintillators		
Scintillator	Molecular structure	Emission wavelength
PPO		357 nm
Butyl-PBD		363 nm
<i>p</i> -Terphenyl		340 nm

Secondary scintillators

The secondary scintillators were used originally as a **wavelength shifter** to increase the sensitivity of the light for the photomultiplier tube (PMT) to 415-425 nm.

The most common secondary scintillator is Bis-MSB [*p*-bis-(*o*-MethylStyryl)-Benzene]. POPOP [1-4,bis-2-(5-Phenyloxazolyl)-benzene] is still applied in LSC cocktails and plastic scintillators.

Note. Modern phototubes are generally capable of counting the light pulses from the primary scintillator. Secondary scintillators have been found to improve efficiency in many cases and are still included in the major part of LSC cocktails.

Secondary Scintillators		
Scintillator	Molecular structure	Emission wavelength
Bis-MSB		477 nm
POPOP		410 nm

Surfactant

The majority of radioactive species are present in an aqueous format, and as such are not miscible with aromatic organic solvents. The presence of emulsifiers (also called detergents or surfactants) in a cocktail enables an aqueous sample to come into intimate contact with the aromatic solvent by forming a stable, clear microemulsion, necessary for stable conditions over the counting period.

Upon addition of water to a LSC cocktail, large aggregates are formed in which the water molecule is in the middle. The aggregate is surrounded by the hydrophilic parts of the surfactant. The non-polar head of the surfactant is directed outside into the direction of the solvent/scintillator molecules; a stable microemulsion is obtained, also called micelle formation.

The result is that the water is mixed with an organic solvent with the help of surfactants and the radioactive species present is now still in close contact with the organic solvent.

Vials

The radioactive samples and cocktail are placed in small transparent or translucent (often glass or plastic) vials that are loaded into as a liquid scintillation counter.

Glass Vials

Glass provides unparalleled optical clarity (good visibility) and is chemically inert, making it suitable for use with aggressive reagents and solvents. However, glass vials can break when falling on the ground, increasing the risk of contamination.

Borosilicate (Pyrex) glass is preferred due to its lower content of potassium, as compared with soda-glass. Potassium-40 is the largest contributor to background in glass vials. A maximum volume of 20 mL is fixed due to the dimensions of current photomultiplier tubes.

Note: Glass is always contaminated with K/Th/U, low-potassium glass vials; difference in „contamination” between types, even between batches of the same type



Pico Glass Vial



Glass Vial



Oximate vial

Plastic Vials

Plastic exhibits lower background levels than glass, but be aware of static electricity. For this reason, anti-static vials are available.

Plastic is combustible and therefore easier for waste disposal. In addition, it is shatterproof. Plastic (polyethylene) is produced from fossil petrochemicals and therefore is preferred because these raw materials contain minimal measurable background.



Pico Pro Vial



Pony Vial



Pico Hang-In vial



Hinge Cap Vial



Midi Vial



Maxi Vial



Super Polyethylene Vial glass vial thread



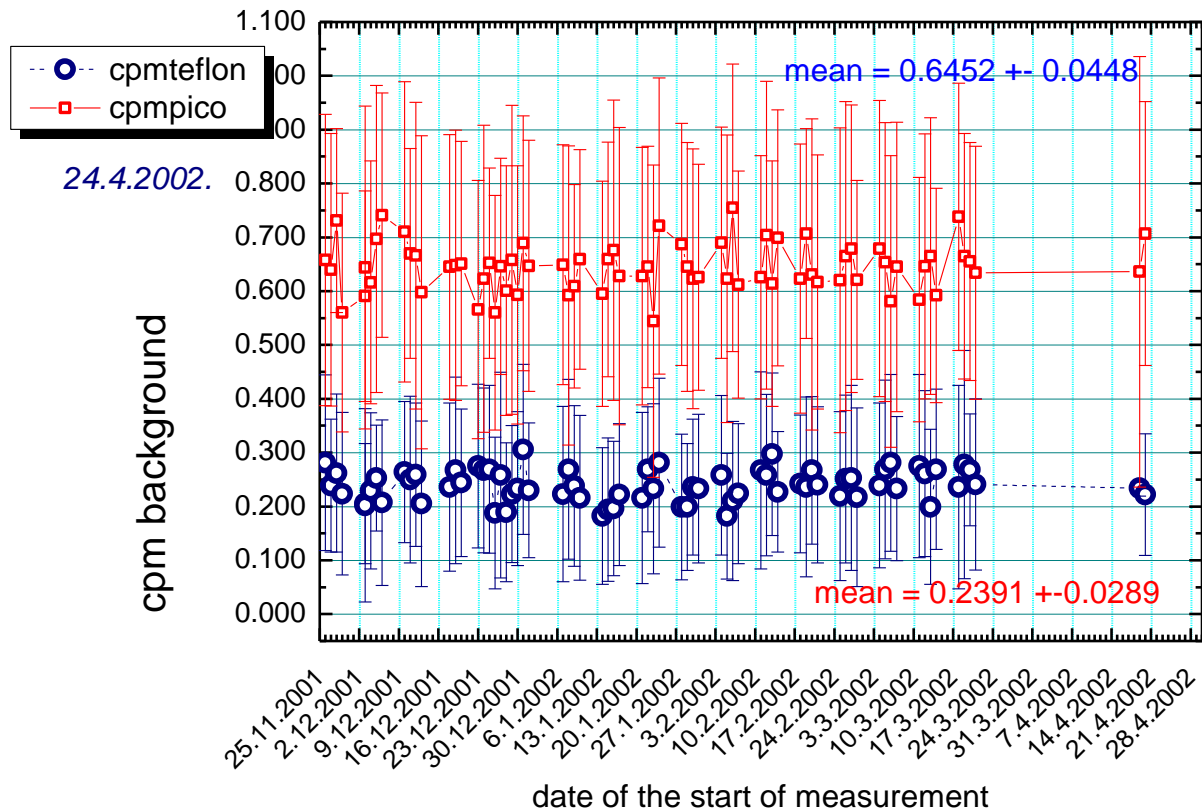
Super Polyethylene Vial quick closure



Low Diffusion Vial

In addition, teflon-copper vials (7 mL) and Teflon black vials (3 mL) are available

Supposed to be cleaned and re-used, possible cross-contamination, careful cleaning needed, occasional tests



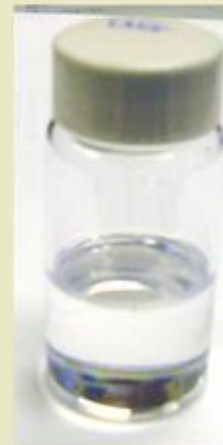
Sample preparation

Preparation will **vary by sample type**. Depending on the procedure, specific liquid scintillation cocktails may need to be used, and the choice of cocktail will impact the efficiency and the results. The goal is to obtain a liquid sample prior to counting in order to get a better mixture with the scintillation cocktail, and to assure that maximum radiation will reach the scintillator molecules.

- A variety of sample types of different origin require a selection of LSC cocktails to finally obtain the best counting results.
- Homogeneity of sample and cocktail is essential to assure the optimum result for radioisotope detection by LSC.
- A poorly-prepared sample can only produce bad or unreliable results, regardless how good the Scintillation Counter is.

GOOD

Clear microemulsion



BAD

'Milky' appearance



2-phase separation



On standing

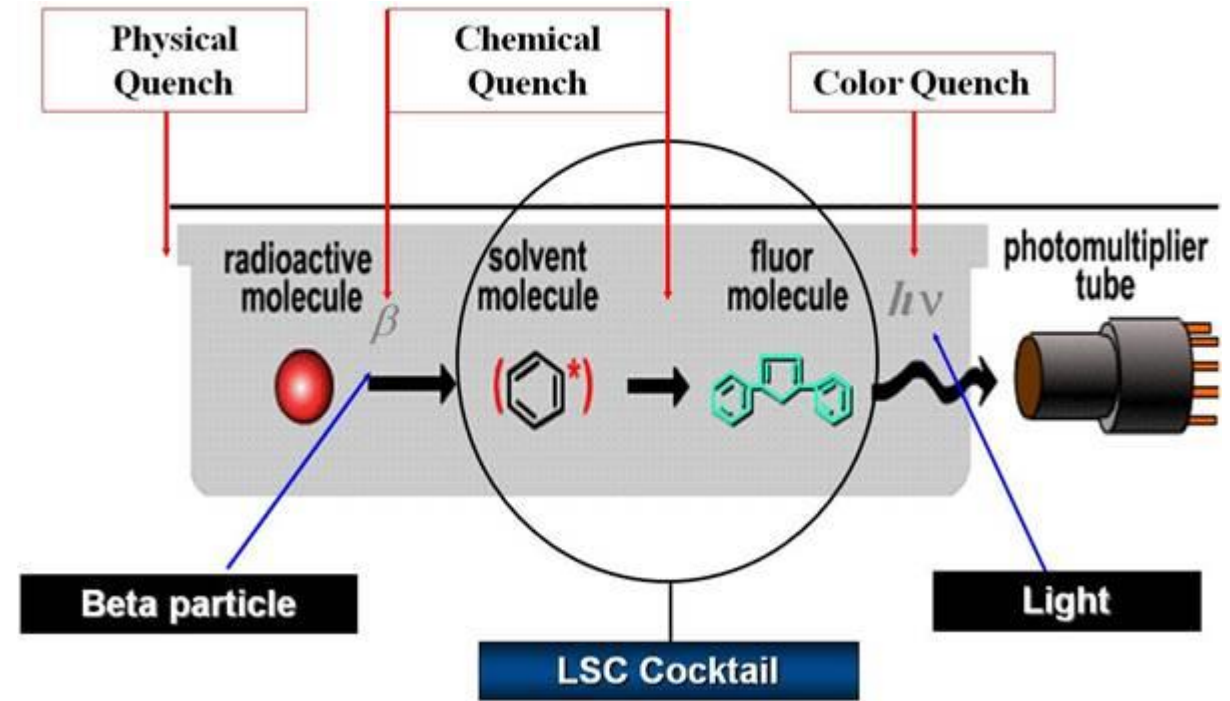
Quench

Quenching occurs when the energy emitted by a radioisotope is not transferred completely into light and therefore is not detected by the PMT of the counting instrument.

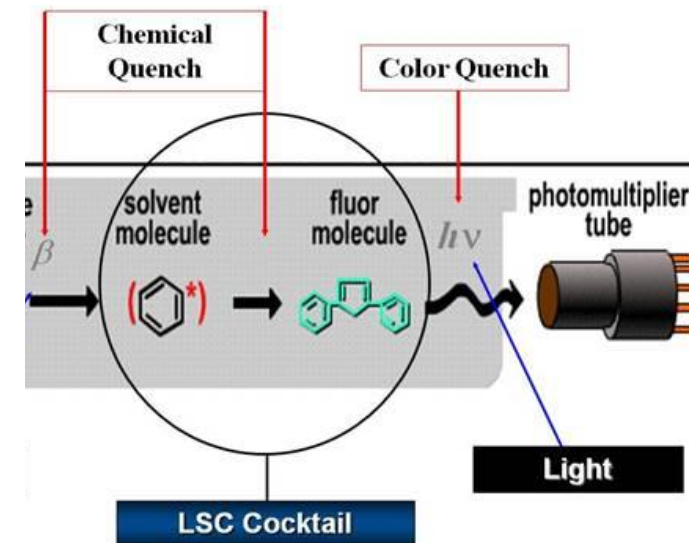
The decrease in final signal, as a result of quenching, can occur at various steps of the energy transfer process:

1. The radioisotope can be physically separated from the solution in which the scintillator is dissolved. Properly homogenizing the solution will avoid **physical quench**.

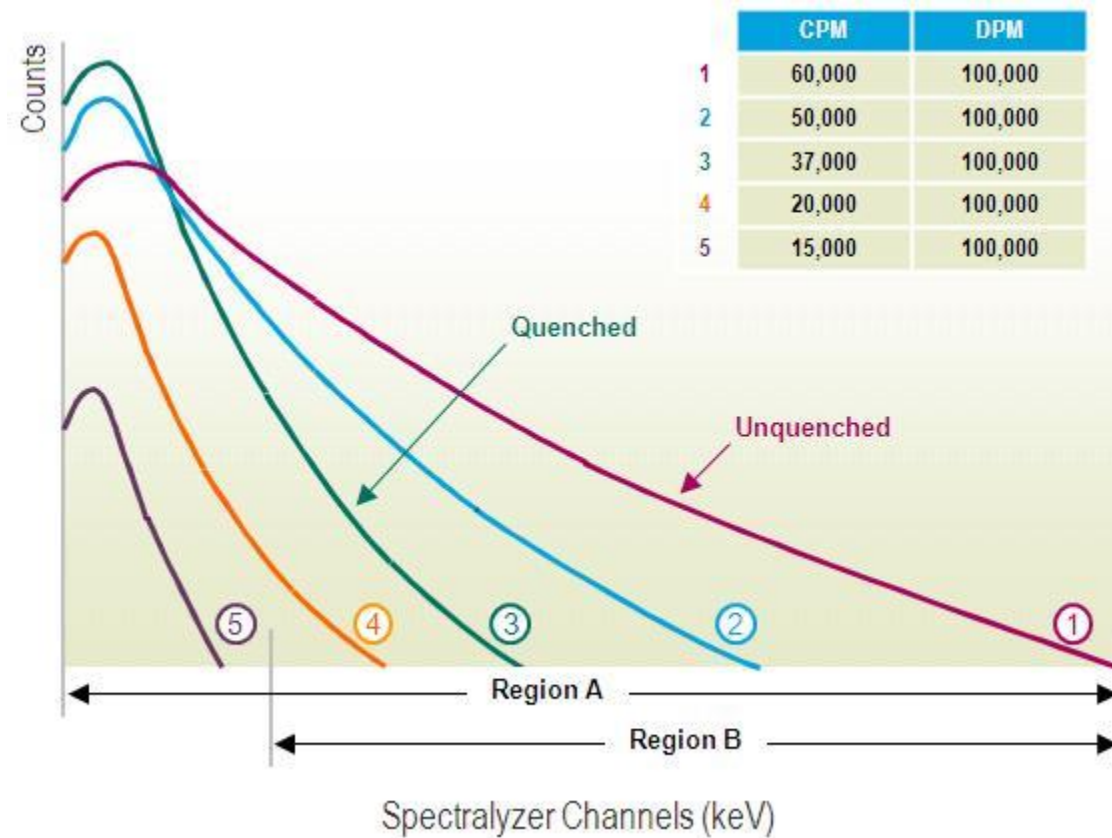
Physical Quench occurs when the radioisotope is physically separated from the solution in which the scintillator is dissolved. Another example is when a barrier is present, such as activity on solid supports. Properly homogenizing the solution will avoid physical quench.



- Chemical Quench** occurs when the energy of the beta particle is absorbed by compounds („quenching agents”) that will not (or with too low efficiency) re-emit the energy during the transfer to the solvent molecules. The energy of the beta particle will not reach the scintillator and consequently, no light will reach the detector. Many chemicals are able to intercept the energy from a radioactive emission event before it can be converted to light. The effect: lower counts, and proportionally more low energy counts.
 Water can be a chemical quencher - to ensure consistent efficiency, all samples should have the same amount of water added. Molecular Oxygen is another quenching agent, it can be removed by warming the sample to degas it. Organic compounds containing oxygen (i.e. aldehydes and alcohols), or halogens (e.g. chloroform) are generally strong chemical quenchers. Such samples should be counted in as dilute a solution as possible, to minimize the quenching effect
- Color Quench** occurs when the emitted light is absorbed by color in the sample. The energy transmission can occur correctly, but once the light is emitted by the scintillator it is absorbed by color in the sample. As a consequence, the signal detected at the photomultiplier tube will not represent the total quantity of light truly emitted. In general, samples which appear yellow or brown will be quenched to some extent. Quenching shifts counts from high to low energy- a shift in the ratio of high and low channels

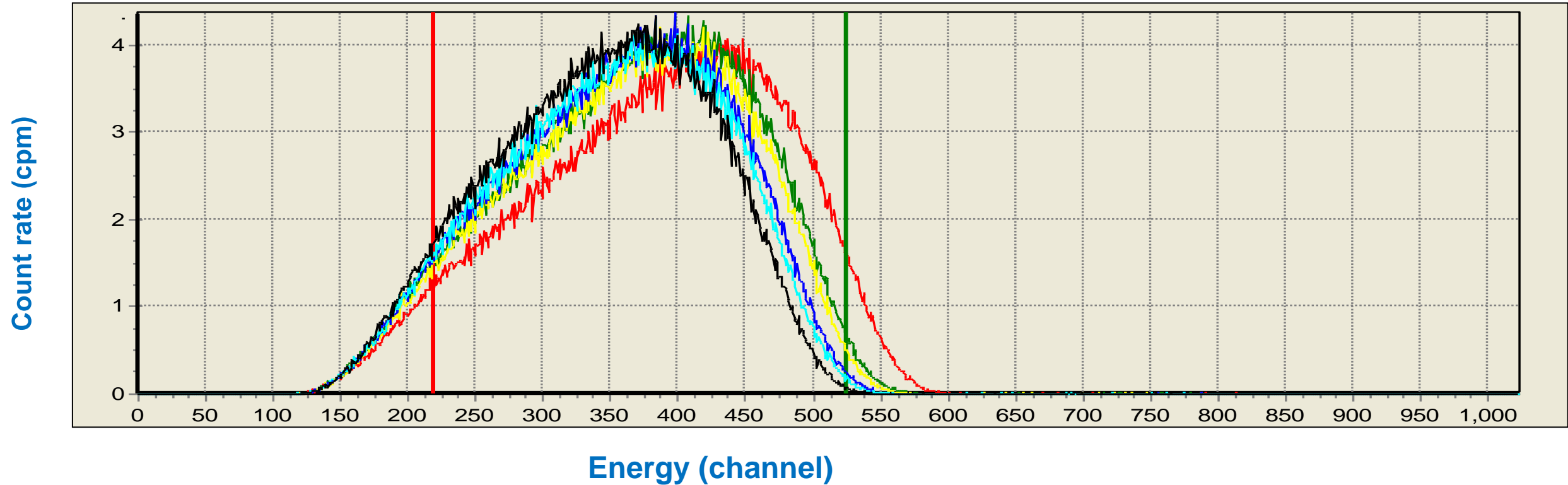


An increase in quench will reduce the counting efficiency: fewer photons will hit the detector, and the quantity of counts will be lower for a quantity of radioactive events.



Quench effects can be minimized by optimizing sample preparation and choosing the correct instrument settings (i.e., choosing the correct energy windows and optimizing the counting windows). Quench corrections will be given in more details in next lessons.

Quenching in ^{14}C spectra



Quenched spectra are moved towards lower energies due to impurities (benzene samples)

Quench curves

A standard quench curve is a series of standards in which the absolute radioactivity (DPM) per vial is constant and the amount of quench increases from vial to vial.

Each standard is counted and the CPM is measured.

At the same time, the quench indicating parameter (QIP) is also measured for each vial.

Quench sets usually contain 10 vials of known activity with increasing quantity of a quenching agent.

A correlation is made using the QIP on one axis (X) and the % efficiency on the other axis (Y).

A curve is fitted to the standard points.

When unknowns are counted, CPM and the QIP of the sample are measured.

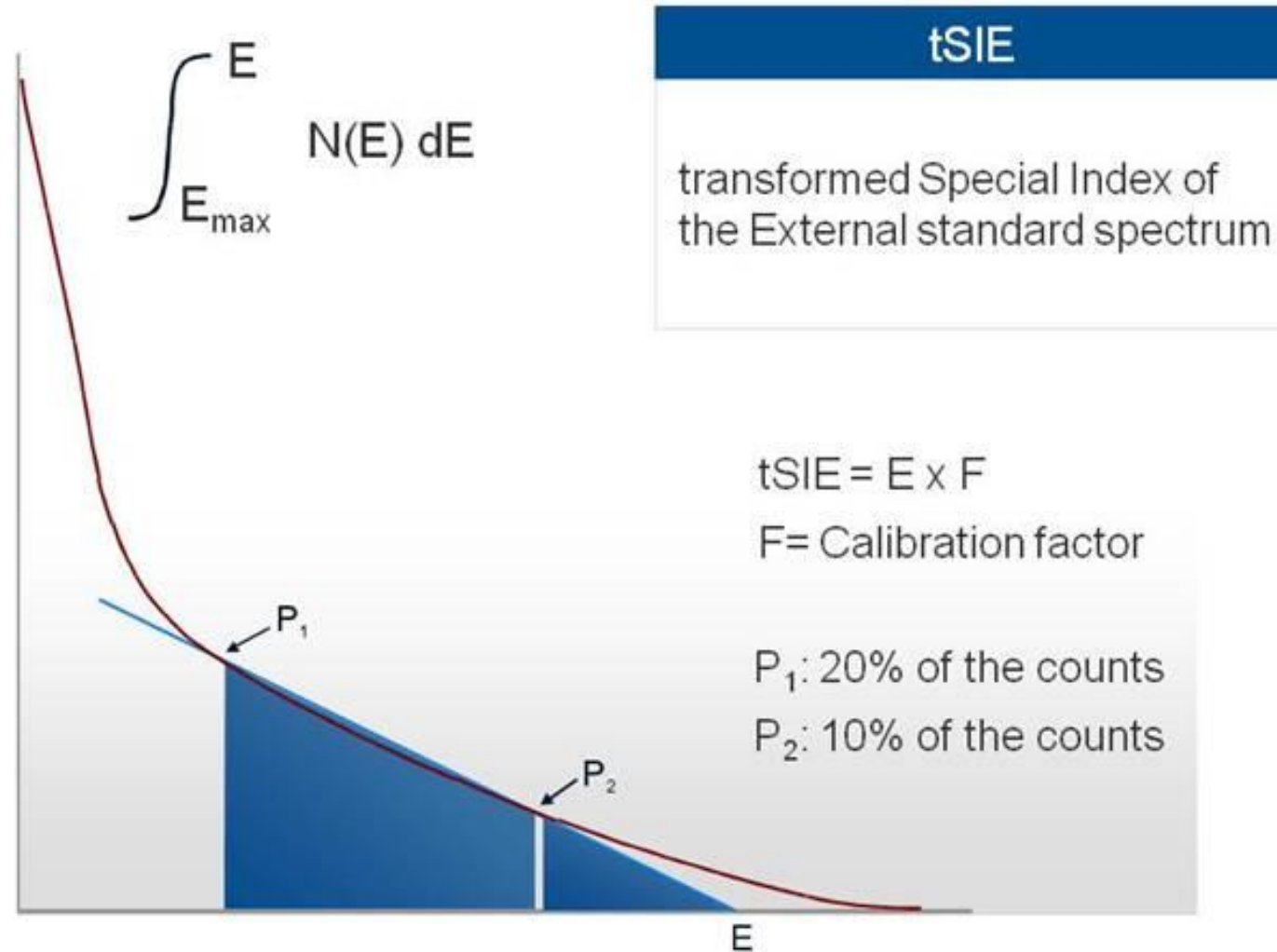
Using the QIP, the counting efficiency is determined from the quench curve, and the sample DPM are calculated by applying the appropriate efficiency to the CPM of the sample.

quench indicating parameter (QIP)

t-SIE

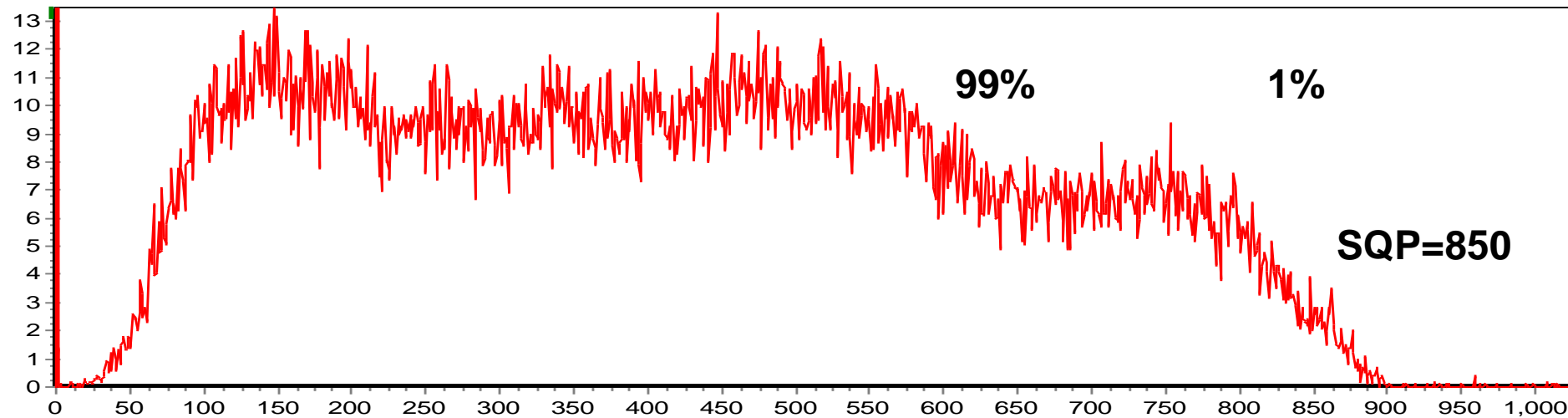
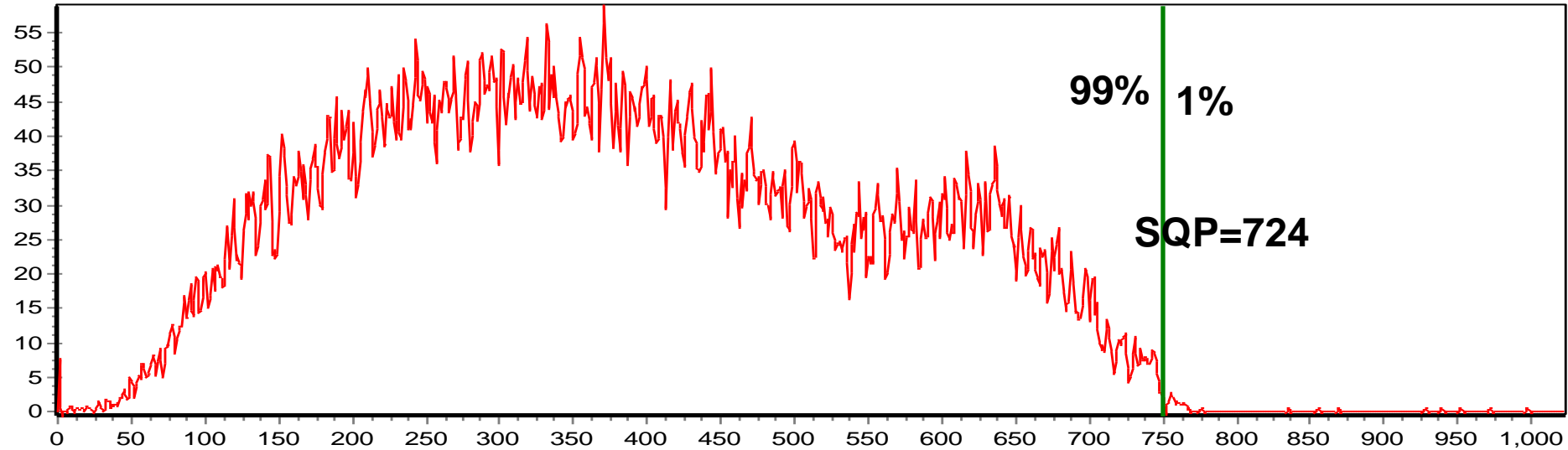
SQP(E)

t-SIE



Two points are theoretically chosen by the software, the first at 20% of the counts and the second at 10% of the counts. Between these points a line is drawn, whose intersection with the X-axis defines the tSIE value.

SQP – Standard Quench Parameter, measured for each sample, each cycle



Important notes

- Sample preparation depends on the sample type and the radioisotope to be determined - the preferred method of sample preparation depends primarily on the nature of the sample and the number of samples that need to be processed (and the required precision)
- Choose the appropriate scintillation cocktail
- Choose the appropriate vial
- Choose the proper „Geometry” – ratio sample:scintillation cocktail, total volume/mass,
- Be consistent in the scintillation cocktail and vial type
- Include referent material/standards, background samples

Detectors

General properties of detectors

The signal is derived from the ionization and excitations of atoms/molecules, produced by charged (ionizing) particles travelling through the detecting medium

The original signal can be a consequence of

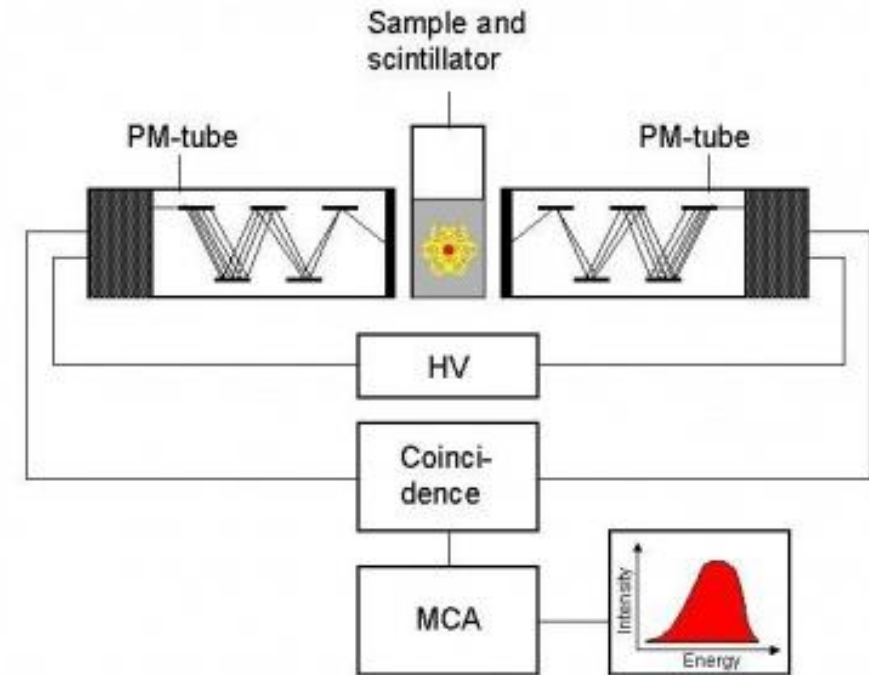
- The primary ionization (gas counting)
- Or the scintillation photons as a consequence of interaction of the particle with the medium

The detected electrical signal is usually nearly proportional to the energy deposited in the detecting medium

Scintillation counters - spectrometers

Components of the counter

Sample tray – sample exchange system –
high voltage supply – photomultiplier(s) –
coincidence circuit - guard detectors in
anticoincidence for background count rate
suppression, MCA, data acquisition



Counters have usually plates/trays for many samples (60 - 96) that can be (quazy)simultaneously measured.

Many counters have two photo multiplier tubes connected in a coincidence circuit. The coincidence circuit assures that genuine light pulses, which reach both photomultiplier tubes, are counted, while spurious pulses (due to line noise, for example), which would only affect one of the tubes, are ignored.

Scintillation counters - spectrometers

Tri-Carb® Series

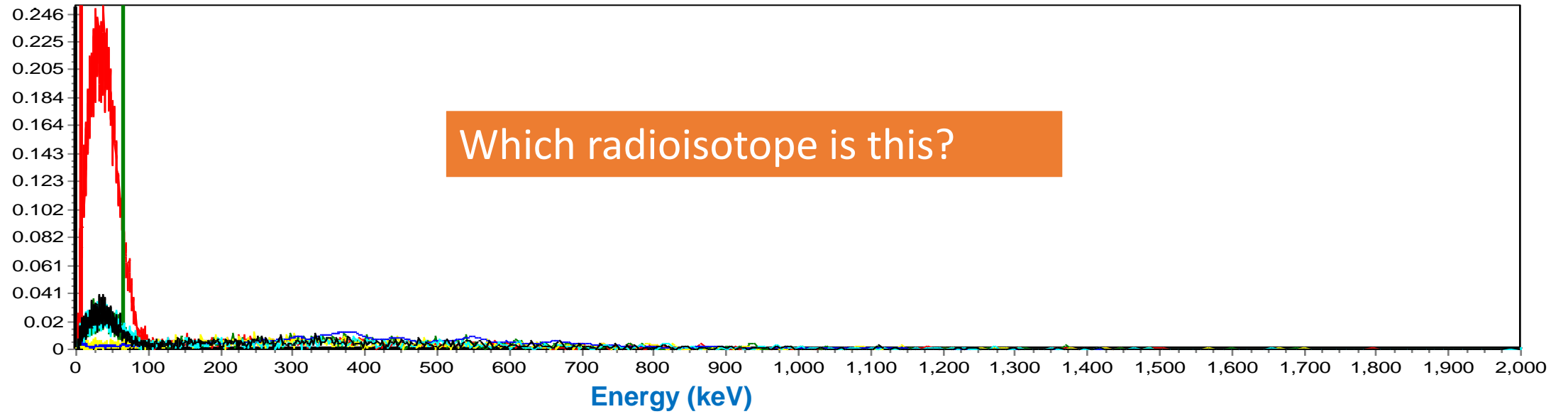
Tri-Carb Liquid Scintillation Counters are beta counters, and count sample vials with volumes from 4 mL up to 20 mL. They can discriminate between alpha- and beta-radiations, and also allow luminescence measurements.

QUANTULUS®

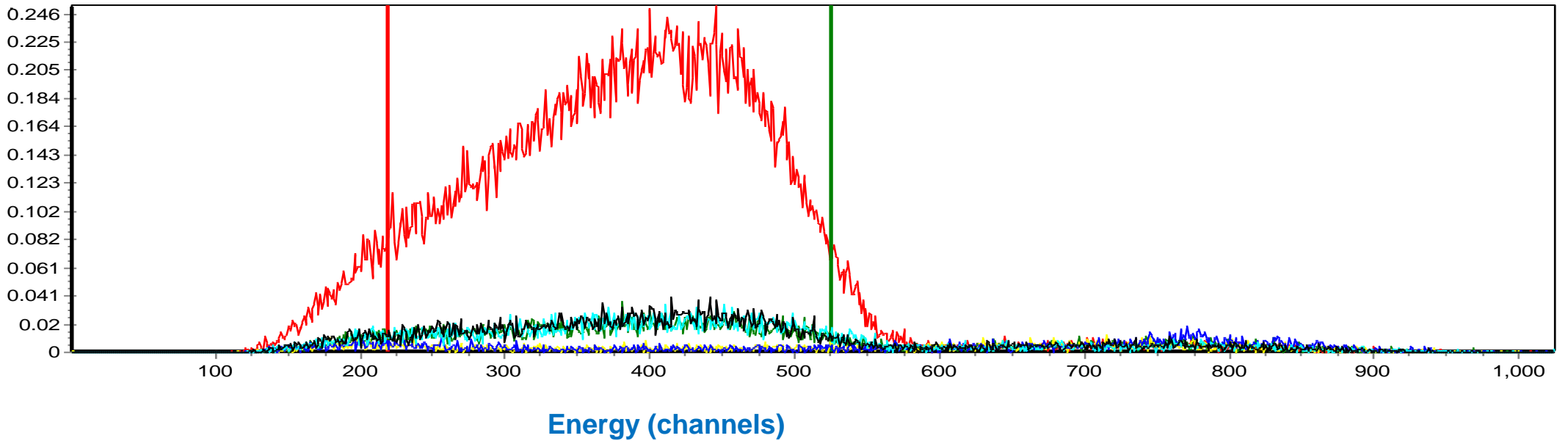
The QUANTULUS Liquid Scintillation Spectrometer is a beta counter dedicated to ultra low level counting: the thicker shield eliminates effects of cosmic radiations and consequently reduces background. This makes the QUANTULUS Liquid Scintillation Spectrometer a good choice for Carbon-14-dating.



Counts per minute (cpm)



Counts per minute (cpm)



Spectra on energy scale and on logarithmic channel scale

Background

- **Count rate of the detector in absence of a radioactive sample**

Or

- **Count rate obtained with the same kind of sample as to be measured, but one that is free of radioactivity**

Background is more important in low-level counting (when the count rate of a sample is comparable to that of the background sample) than for high-activity samples

Background depends on the cosmic ray contribution, sample type, vials, counter ...

Various measures can be taken to reduce the background

- Underground laboratories (higher overburden) or basements
- Radiocontamination-free materials

Detector walls (GPC)

Low-potassium glass vials

LSC: vials and scintillation cocktails should be free of radiocontamination

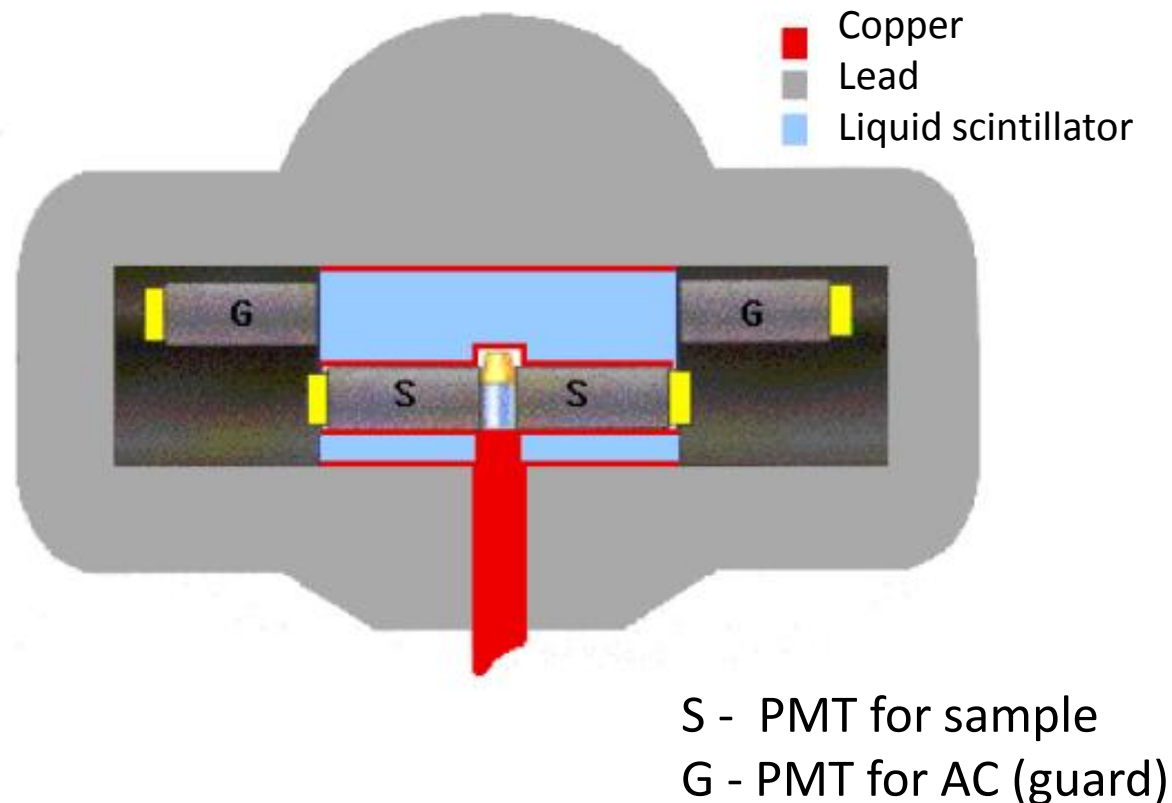
Passive shielding –

- Lead (but care should be taken – new lead is contaminated with ^{210}Pb , and „old“ lead should be used)
- Iron (also „old“ iron preferable)
- Boron-parafine (against neutrons)

Active shielding –

- Anticoincidence circuits, guard counters
- Background reduction through pulse shape analysis
- Computer/software background reduction

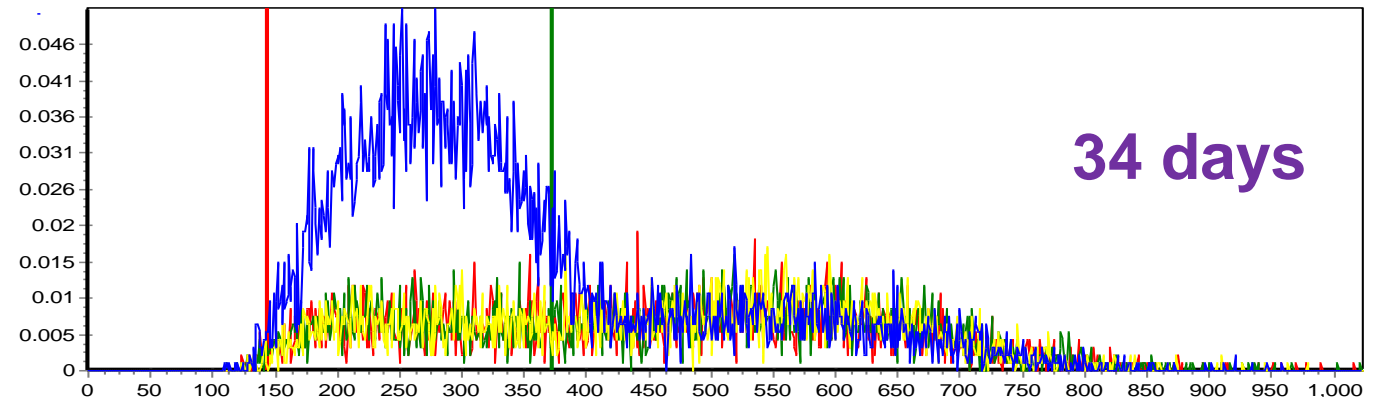
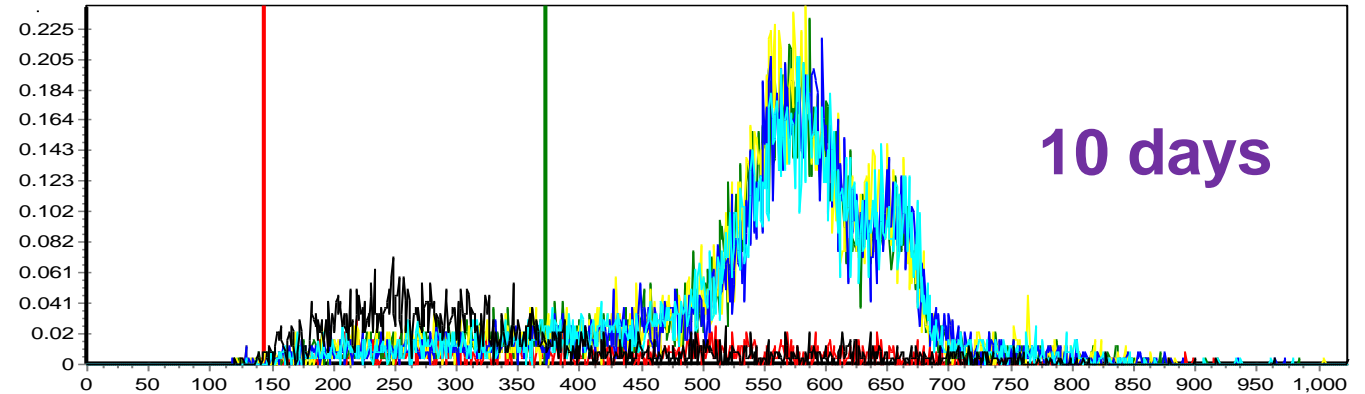
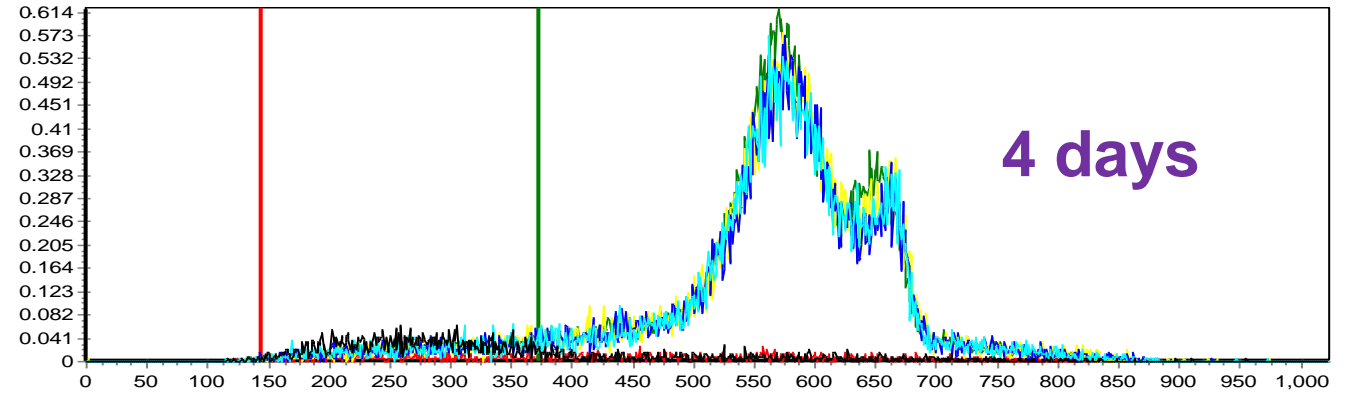
....



Stability of the counting instrument – important for long-time measurements, weak radioactivity

Radon contributing to background

- Radon in air
- Radon in samples
- Radon in chemicals



Counting efficiency

dpm – disintegration per minute, the (real) number of decay events in a sample

(note that not volume or mass is defined!)

The SI unit for radiation, the Becquerel (Bq) describes one disintegration per second, s^{-1}

→ $1 \text{ Bq} = 60 \text{ dpm}$

Counting dpm is not possible in most real situations → counting efficiency

$$\text{counting efficiency} = (\text{cpm}_{\text{sample}} - \text{cpm}_{\text{B}}) / \text{dpm}$$

→

$$\text{dpm} = \frac{(\text{cpm}_{\text{sample}} - \text{cpm}_{\text{B}})}{\text{counting efficiency}}$$

Counting efficiencies under ideal conditions range from about 30% for tritium (a low-energy beta emitter) to nearly 100% for phosphorus-32, a high-energy beta emitter.

Application areas for LSC in environmental studies:

1. Measurement of **natural series** radionuclides
 - Routine measurements in a range of sample matrixes (water, soil, air)
 - Radon, Radium, Uranium, Thorium, etc.
2. Monitoring the environment around nuclear facilities, including fall out
 - Beta emitters without significant gamma emissions (^3H , ^{14}C , ^{89}Sr , ^{90}Sr , ^{99}Tc , ^{241}Pu)
 - These isotopes are monitored not only around nuclear installations, but also in the other end of the chain (^3H in water and ^{14}C in food)
3. Studying the environmental processes
 - Radiocarbon dating
 - Carbon cycle (^{14}C)
 - Hydrological cycle (^3H): precipitation, groundwater, surface waters)
 - Marine applications

Cherenkov counting

Cherenkov radiation are electromagnetic rays (light) emitted by charged particle passing through a dielectric medium with **a velocity greater than the speed of light in that medium**

Cherenkov light emission is being detected directly by the photomultiplier tubes.

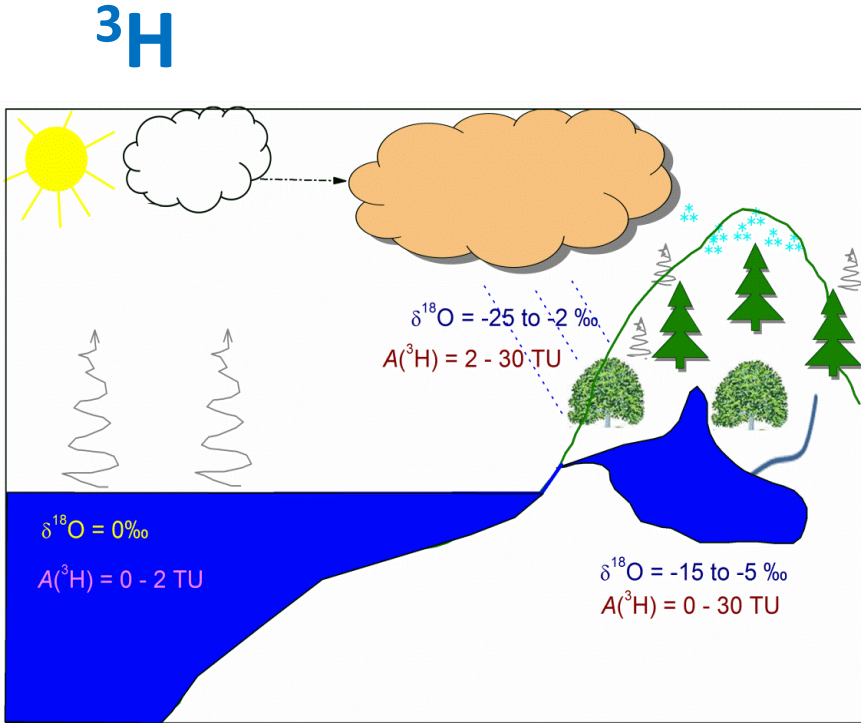
- widely used for the measurement of high energy beta-emitting radionuclides ([phosphorus-32](#), [yttrium-90](#))
- rapid screening of high energy beta-emitting radionuclides in metrological and environmental applications
- alpha-emitting nuclides and low-energy would not produce Cherenkov light;
- no addition of scintillation cocktail is needed (the sample remains unchanged for further analysis);
- no sample preparation;
- chemical quenching would not interfere with Cherenkov counting;
- Cherenkov counting efficiency can be strongly affected by color quenching;

Alpha/beta discrimination

- the method of choice when screening for gross alpha/gross beta activity
- simultaneous quantitation of alpha and beta particles in the same sample
- interesting features of LSC: near 100% counting efficiency for alphas, the reduced sample preparation for most samples (especially liquids), and low background.

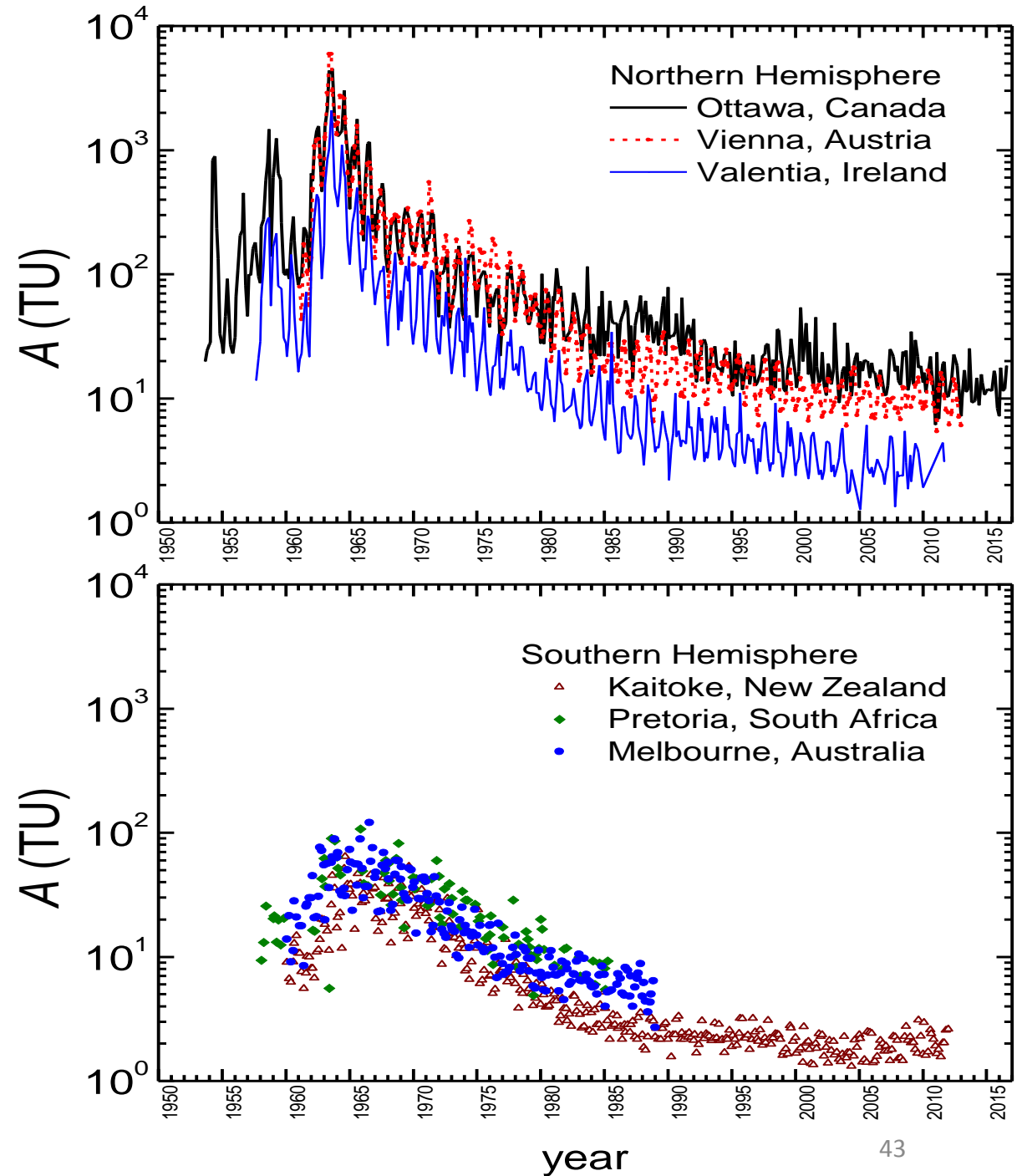
The method requires a liquid scintillation counter employing a Pulse Decay Analysis (PDA) technique to discriminate alpha events from beta events in samples.

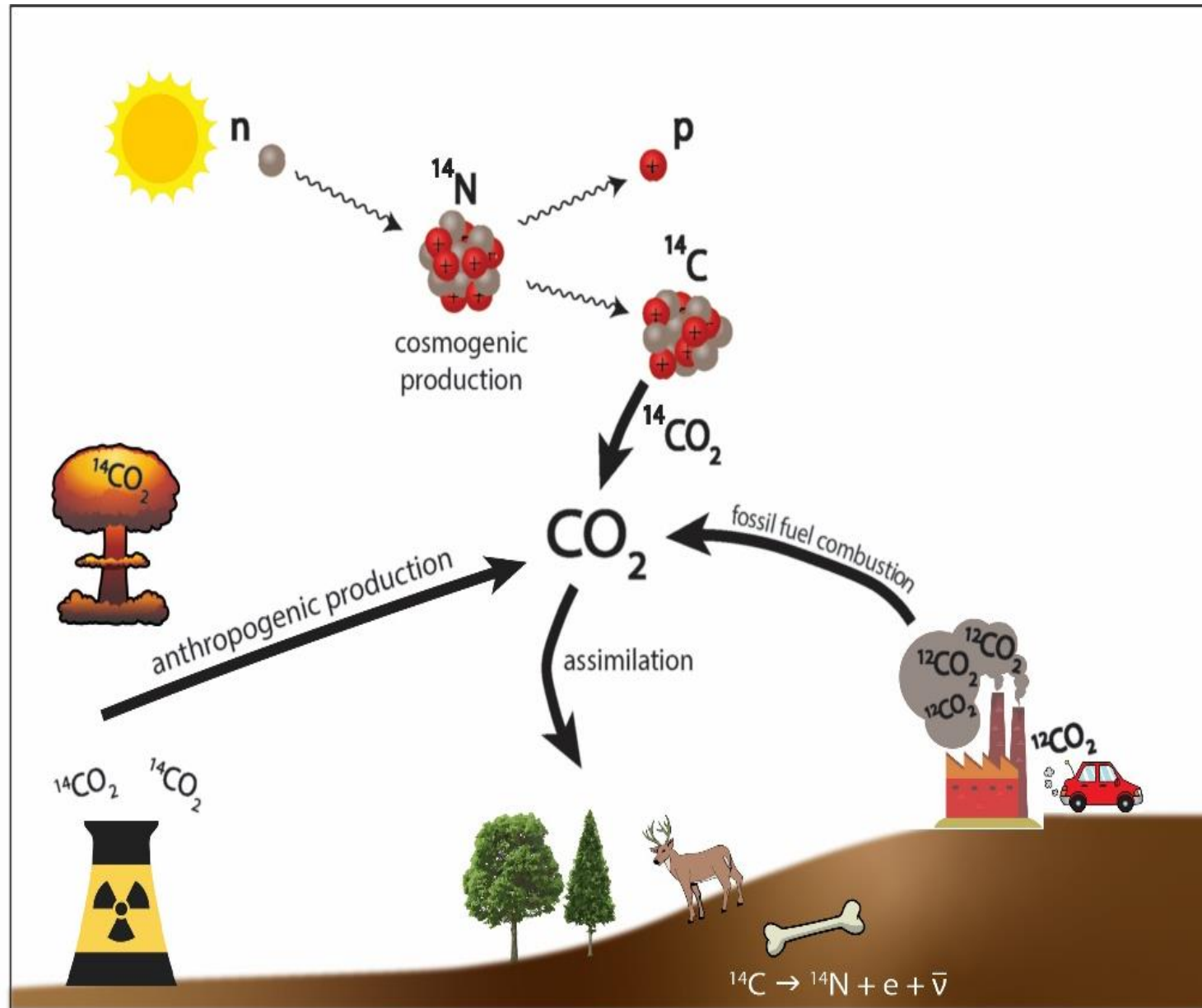
Discrimination is based on the duration of the light pulses they produce in a liquid scintillator. The pulse duration for alpha particles is typically longer than for betas.



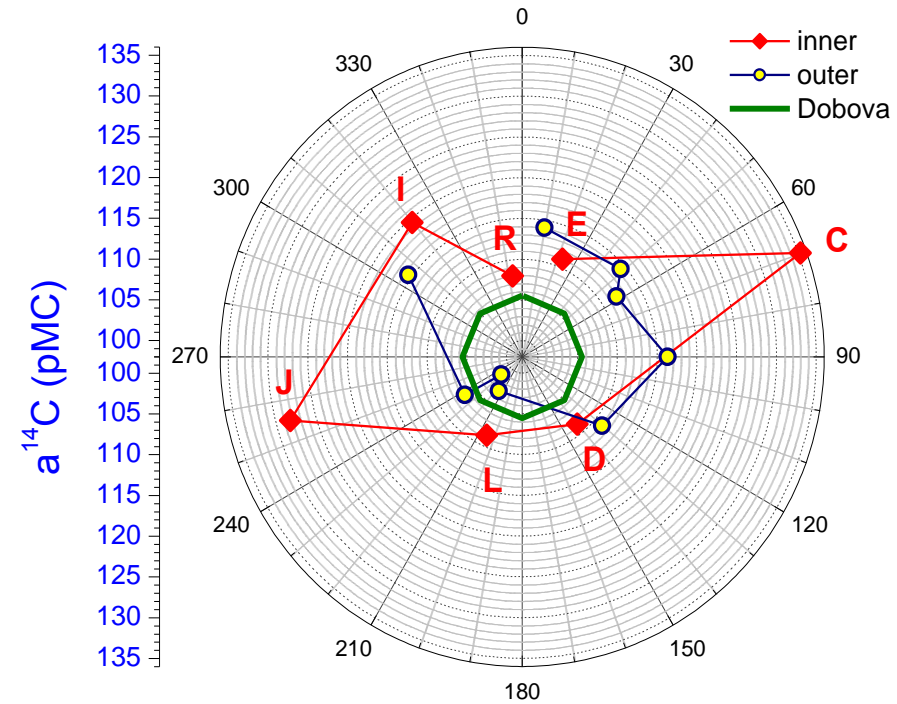
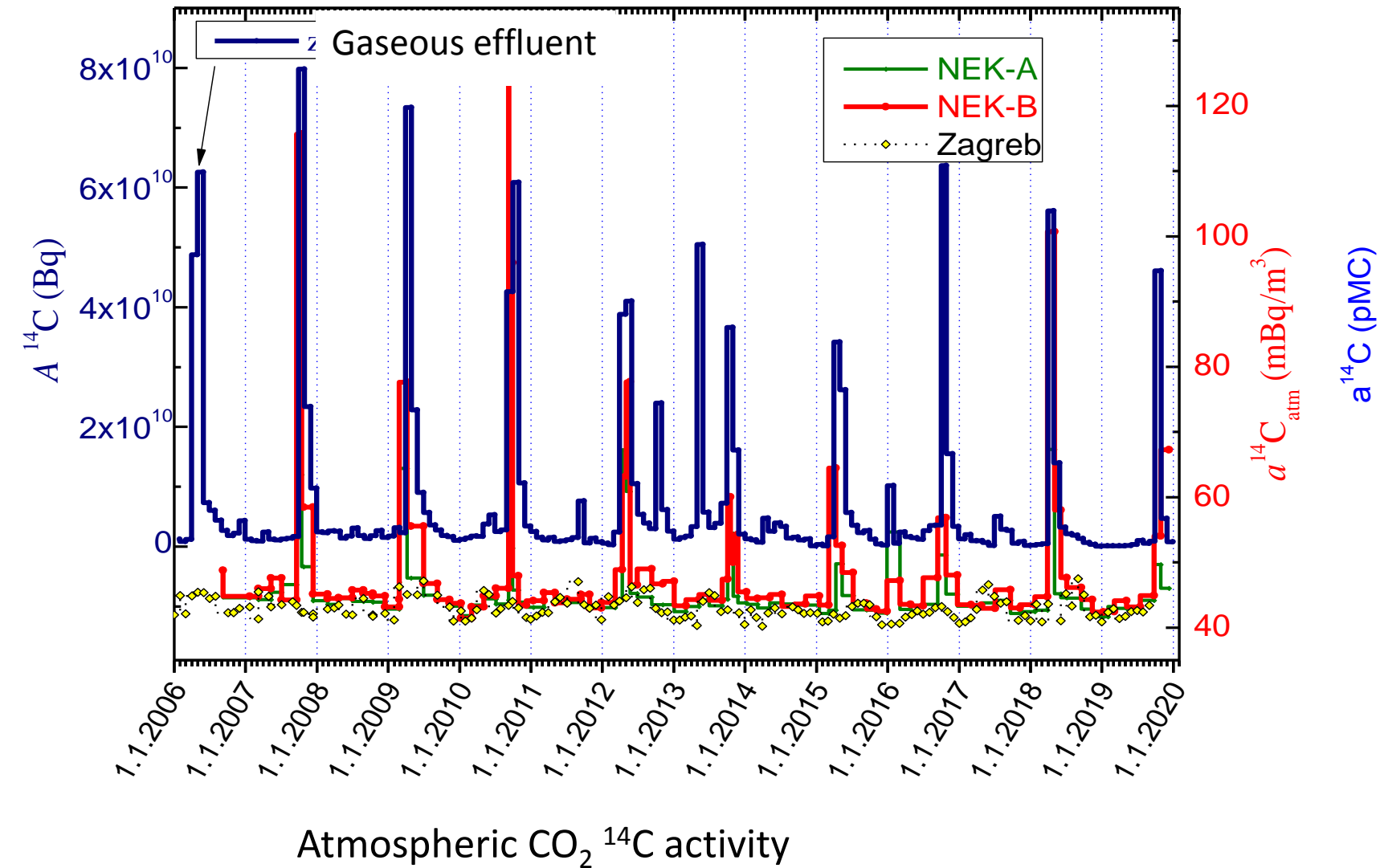
Schematic simplified representation of the hydrological cycle. Characteristic “isotopic fingerprints,” i.e., $\delta^{18}\text{O}$ and tritium activity concentration A , are shown for sea water, precipitation and surface waters

Tritium activity concentration A in monthly precipitation period 1950 – 2016.





Monitoring ^{14}C around nuclear power plant



Literature

- Principles and Applications of Liquid Scintillation Counting, https://ehs.psu.edu/sites/ehs/files/lsc_theory_of_operation_part_1.pdf
- L'Annunziata. M.F. 2012. *Handbook of Radioactivity Analysis*. Volume I: NUCLEAR RADIATION, ITS INTERACTION WITH MATTER AND RADIOISOTOPE DECAY. Academic Press, 3rd edition
- L'Annunziata. M.F. (editor) *Handbook of Radioactivity Analysis*, Volume 2: Radioanalytical Applications, ISBN: 978-0-12-814395-7, Academic Press 2020 (4th Edition)
- Theodorsson, P. *Measurement of weak radioactivity*. World Scientific 1996. ISBN 9810223153.