



Principles of liquid scintillation counting: theories and applications

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R&D projects of the PSI radioanalytical laboratory

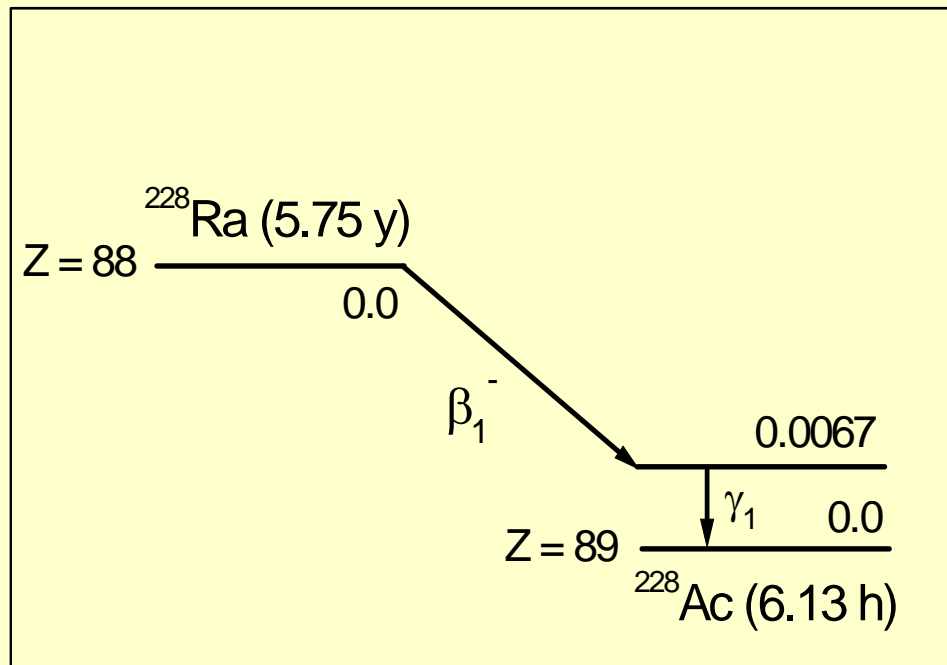
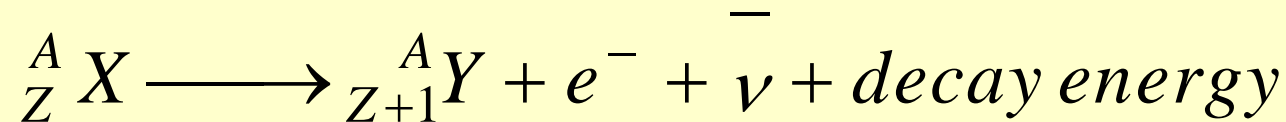
- Development and implementation of radiochemical separation techniques for emission and immission measurements such as actinides in soil samples Ra isotopes in groundwater etc.
- Research projects with universities: dating of Pleistocene samples with applications in volcanology, paleoearth quake dating , ice core samples (global warming)

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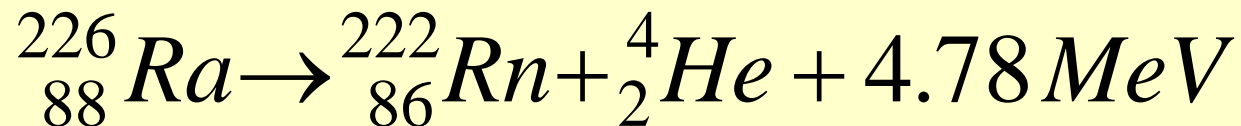
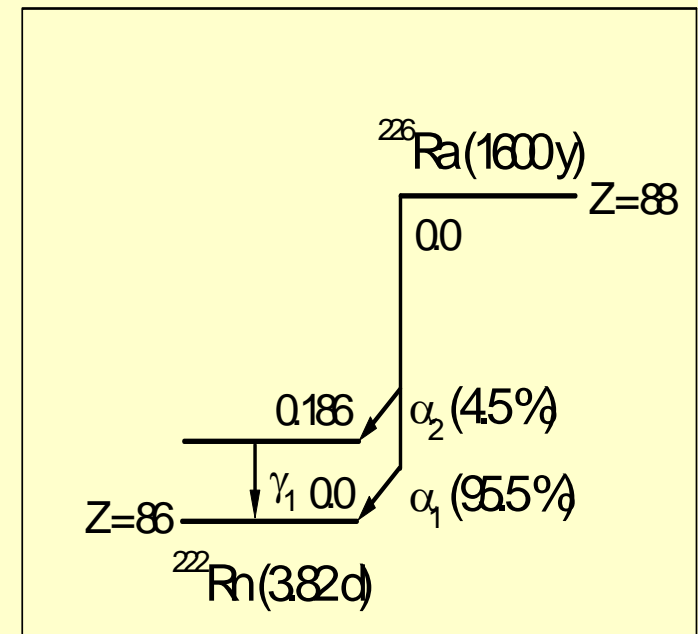
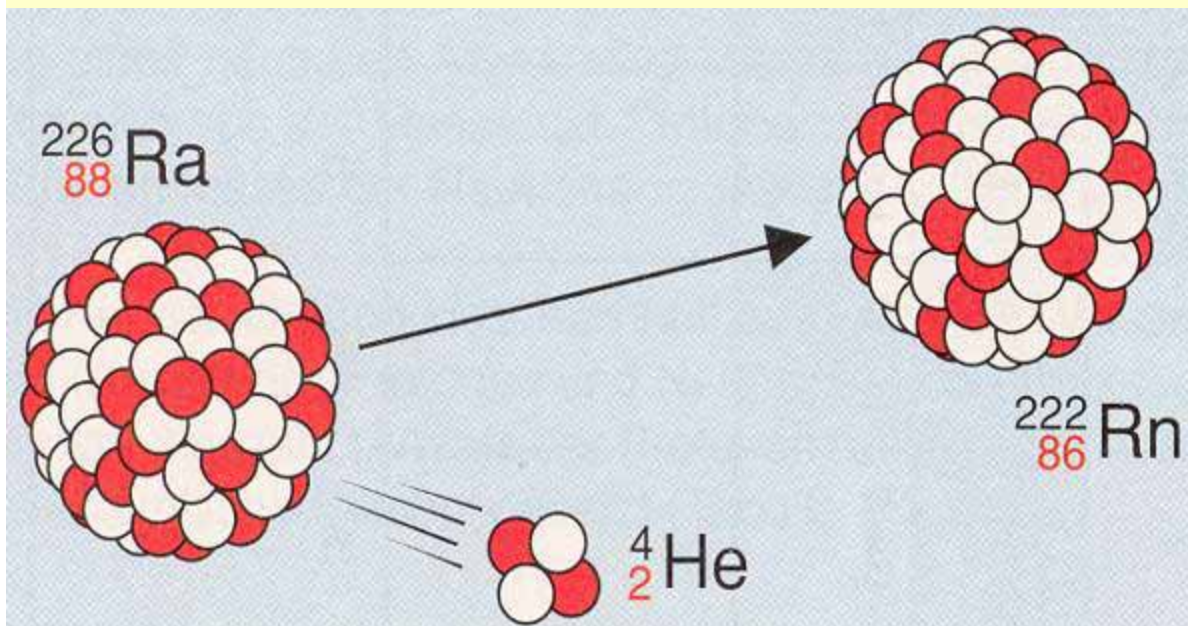
1. Introduction to the LSC counting technique
2. Quenching effects and correction procedures
3. Alpha/Beta separation via pulse shape analysis
4. Introduction to the triple to double coincidence ratio measurement technique (TDCR)
5. Example of a simultaneous alpha/beta analysis using Radium isotopes in drinking water

Particle radiation, pure β -emitting isotopes

Example: decay scheme of β -emitting ^{228}Ra



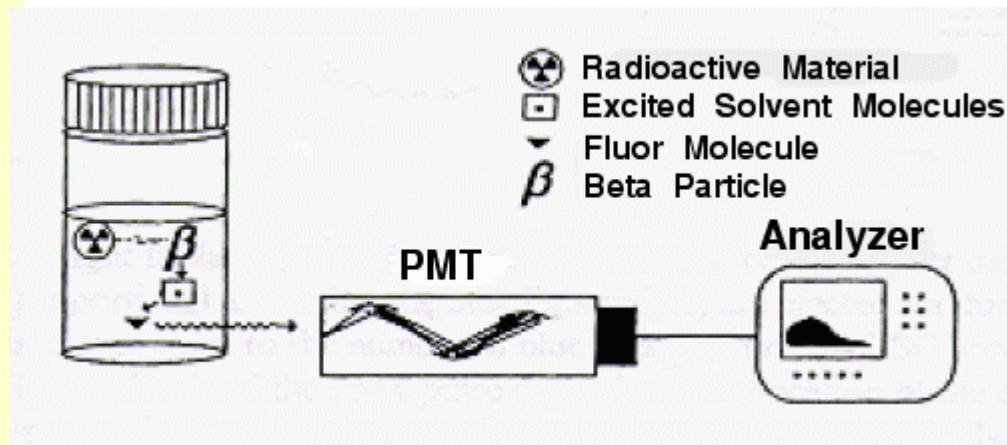
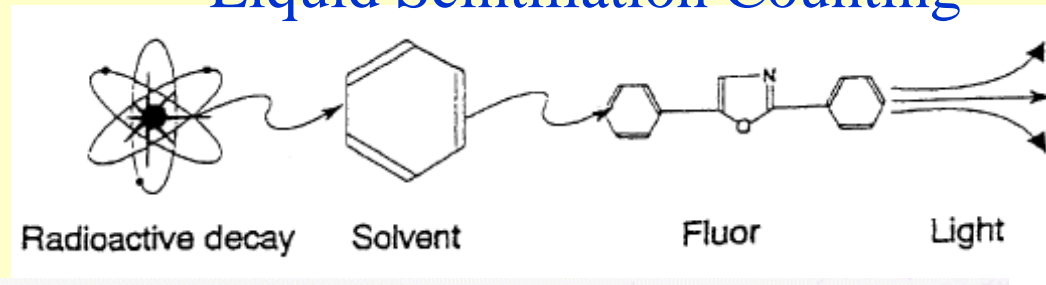
Schematic view of radioactive transformation



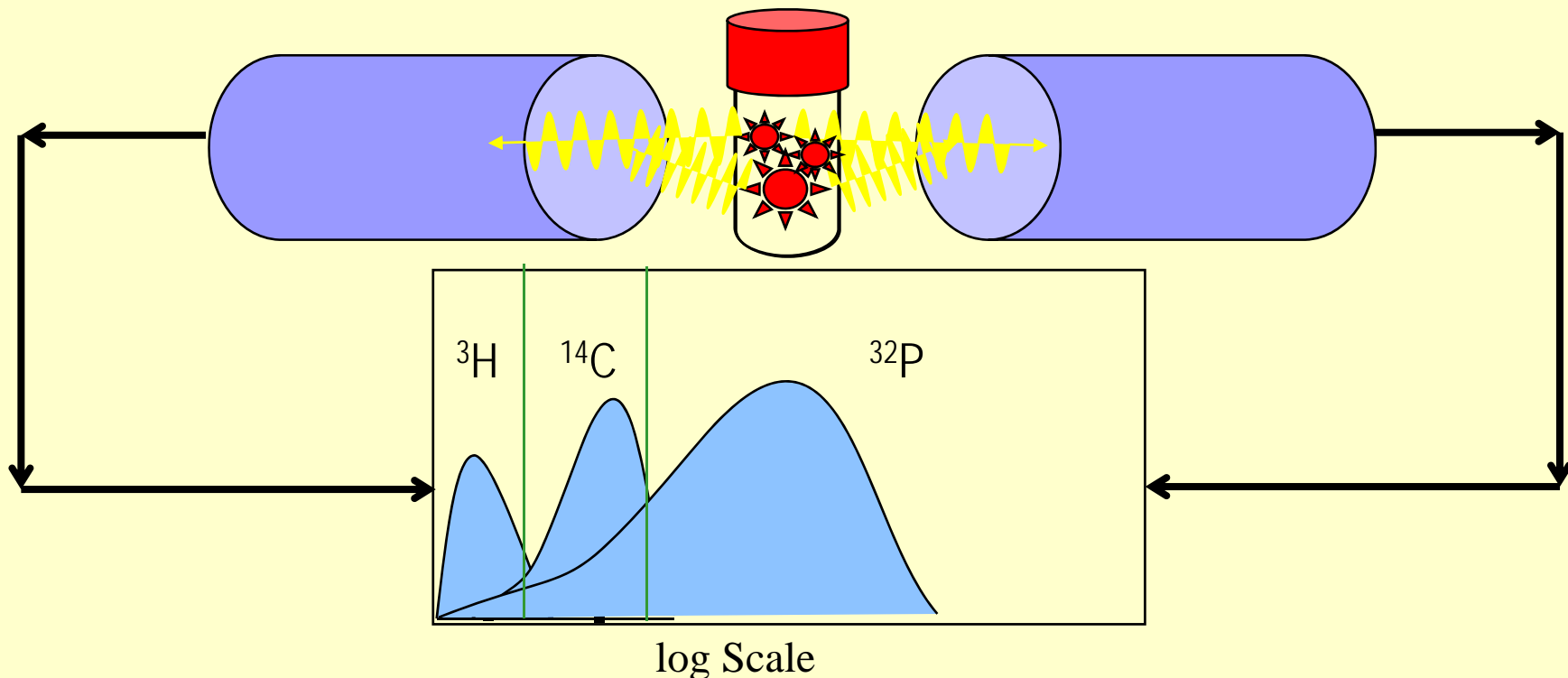
principle of liquid scintillation spectrometry (LSC)

- **Sample is in a cocktail with a organic scintillator and homogenously mixed**
- **Particle radiation (α or β) disturbs the electron configuration (orbital) of the scintillation liquid**
- **During recombination of the electron structure light ($h\nu$) is emitted which is measured in photomultiplier tubes**

Liquid Scintillation Counting



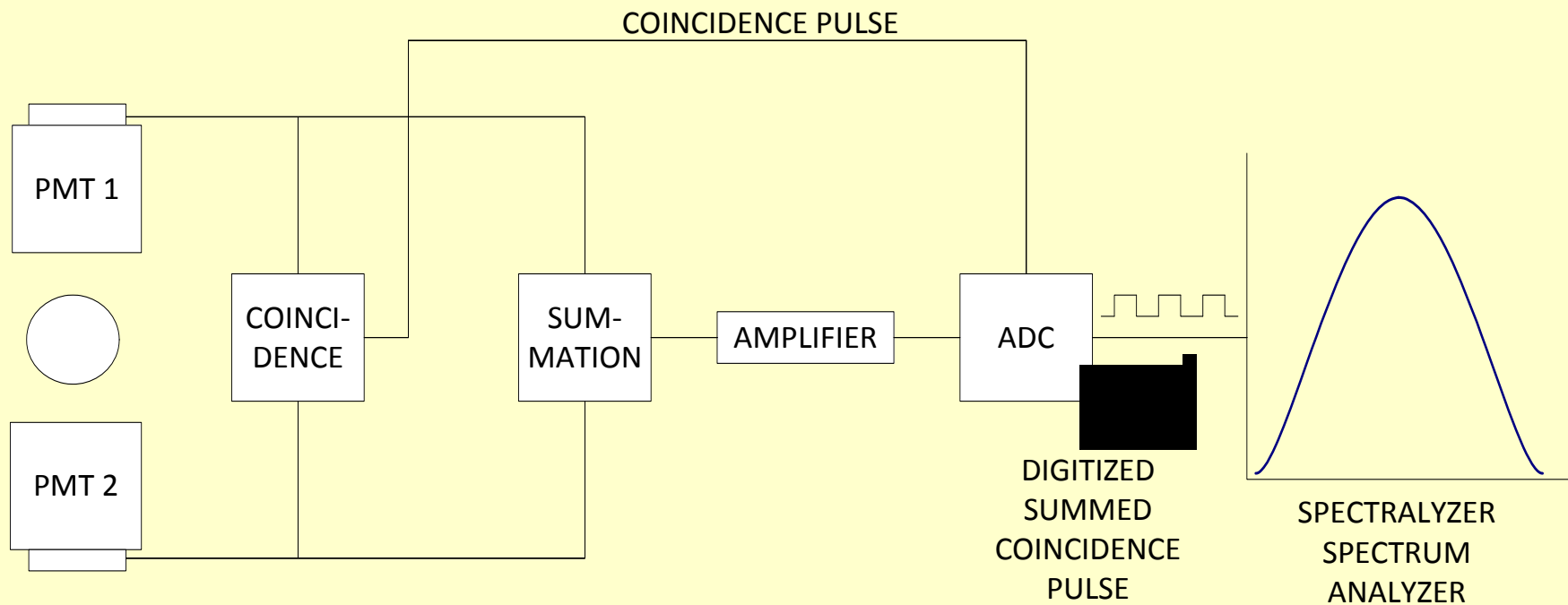
- Samples are dissolved or suspended in a "cocktail" containing an aromatic solvent and small amounts of other additives known as fluors
- Beta particles emitted from the sample transfer energy to the solvent molecules, which in turn transfer their energy to the fluors; the excited fluor molecules dissipate the energy by emitting light
- In this way, each beta emission results in a pulse of light



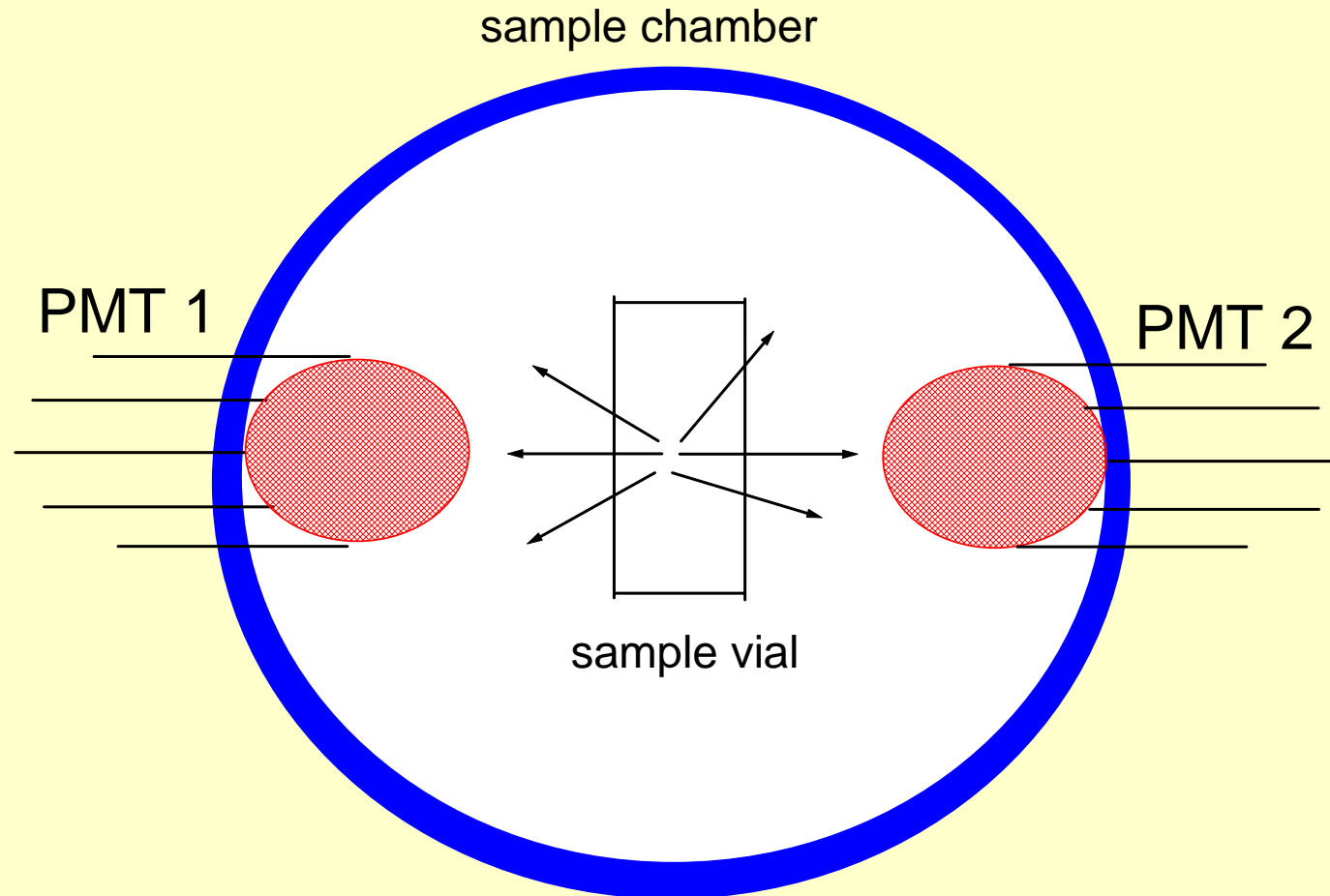
Principle of LS Coincidence/Anticoincidence Counting

- The counter has two photomultiplier tubes connected in a coincidence circuit. The coincidence circuit assures that genuine light pulses, which reach both photomultiplier tubes, are counted, while other pulses (due to noise, for example), which would only affect one of the tubes, are ignored.

Classical two photomultiplier LS electronic set-up



principle of LSC coincidence/anticoincidence counting



LSC, Perkin Elmer Model TriCarb 3100 TR/SL

LSC with BGO detector guard



HIDEX Model SL 300 with guard detector

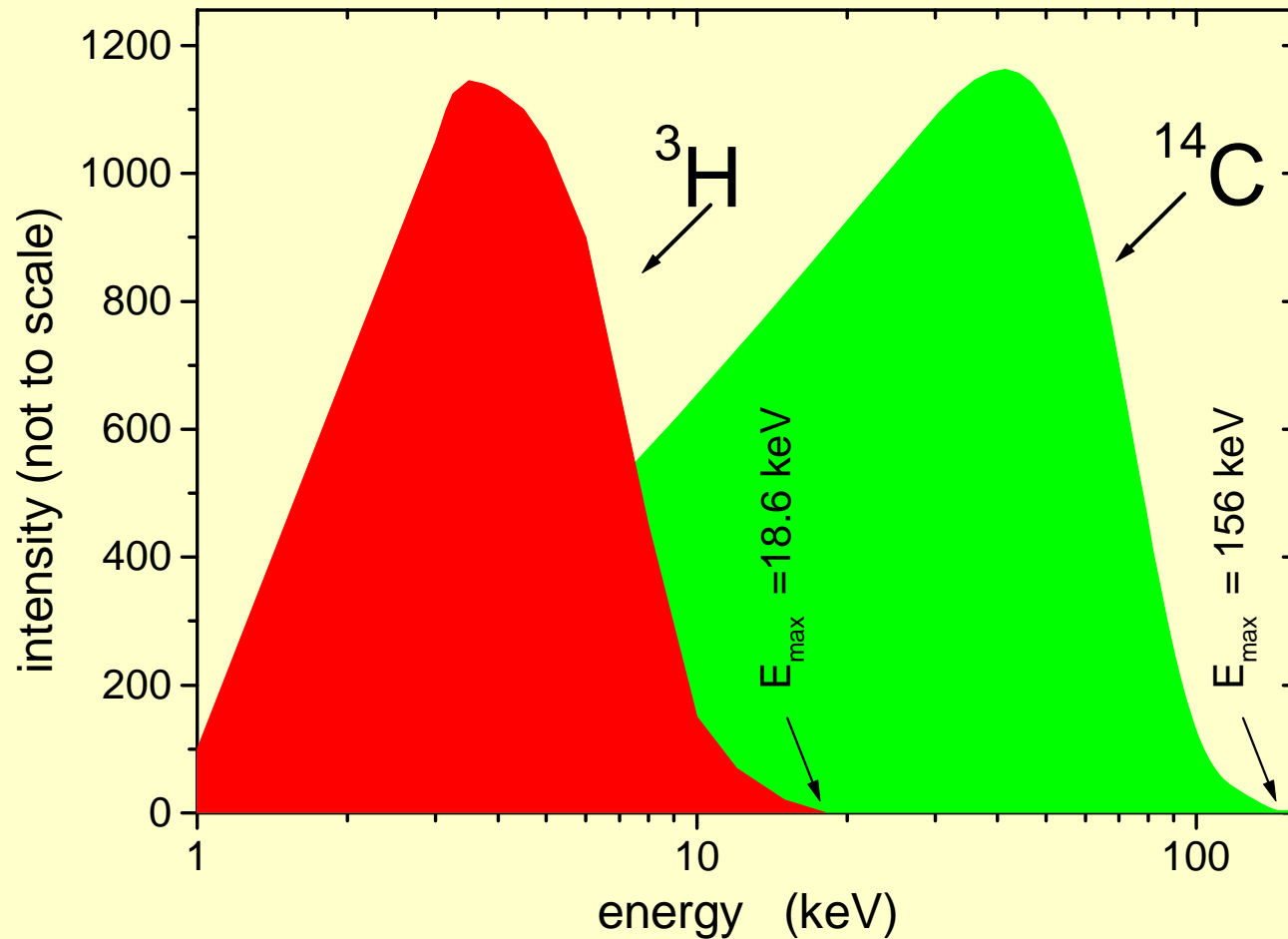


LSC: relevant isotopes in the nuclear fuel cycle, radiopharmaceutical application and environmental analysis

- Pure β - or ec-emitters Tritium (H-3) and Radiocarbon (C-14) others, : Cl-36, Fe-55, Ni-63, Sr-90, Biological application: P-32, P-33, etc.
- Alpha-emitters, actinides : Th, U, Pu, Am, Cm
- Alpha- and Beta-emitters from the U and Th decay series: Ra-228, Ra-226, Pb-210, Po-210

β -continuum-spectra: ${}^3\text{H}$, ${}^{14}\text{C}$

LSC: spectrum of ${}^{14}\text{C}$ und ${}^3\text{H}$



Calculation of activity concentrations via classical and TDCR measurements

- Direct counting (standardization) and two window counting (e.g. ^3H , ^{14}C)
- Use of quench curves
- Efficiency tracing methods (CIEMAT/NIST, needs modeling)
- Triple to double coincidence ratio measurements (TDCR)

general relationship between activity and counting rate

$$A = \frac{I}{t \cdot \varepsilon} = \frac{N}{\varepsilon}$$

**Example H-3, C-14, two window counting
window A: H-3 + C-14, window B: C-14**

$$cpm_A(H-3) = cpm_{A,net} - \left(\frac{cpm_A}{cmp_B}\right)_{C-14} \cdot cpm_B(C-14)$$

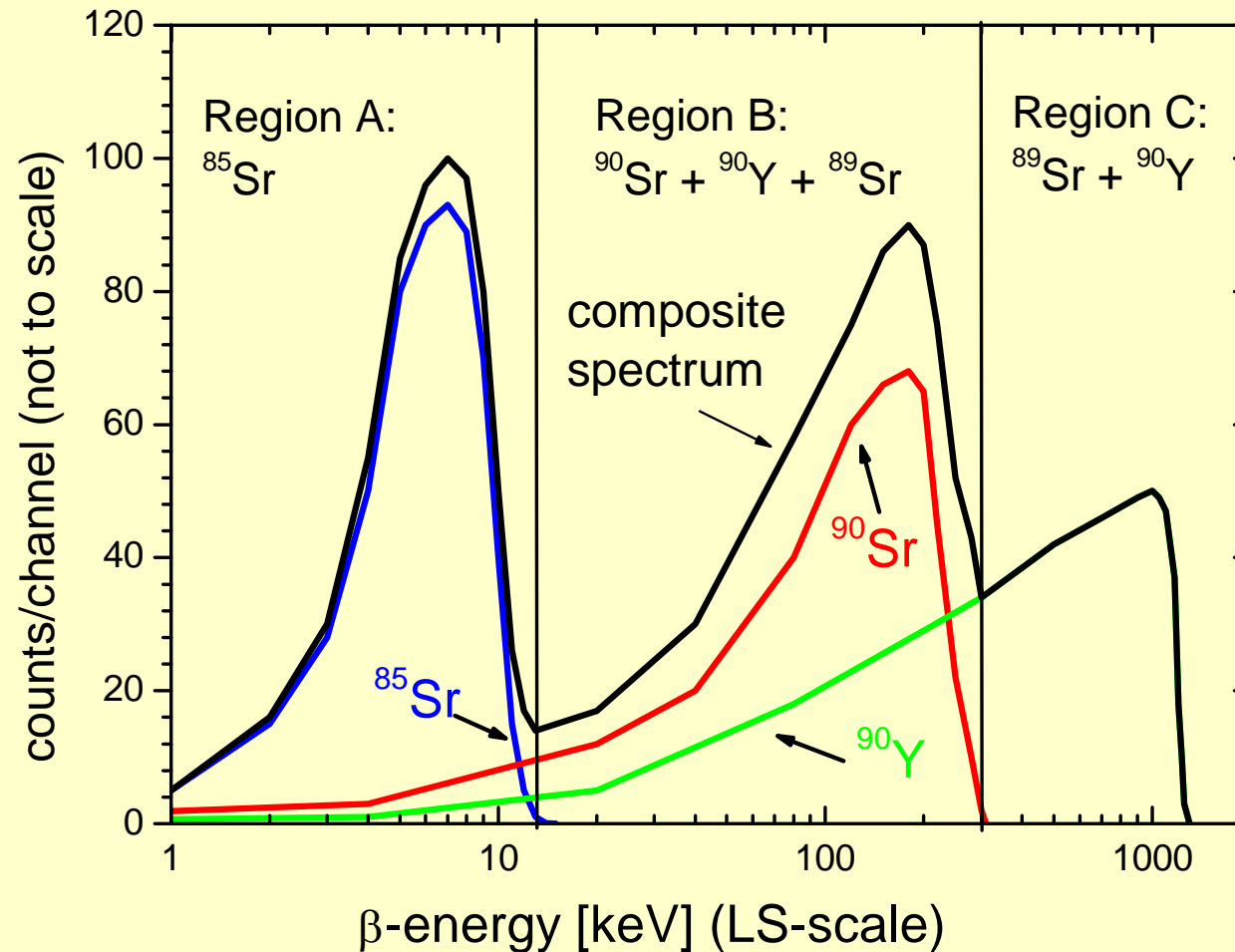
Determination of the counting efficiency (a) by adding spike of the same isotope

$$\varepsilon = \frac{N}{A}$$

$$\varepsilon_i = \frac{N_{i,afteraddition} - N_{i,beforeaddition}}{A_{i,added}}$$

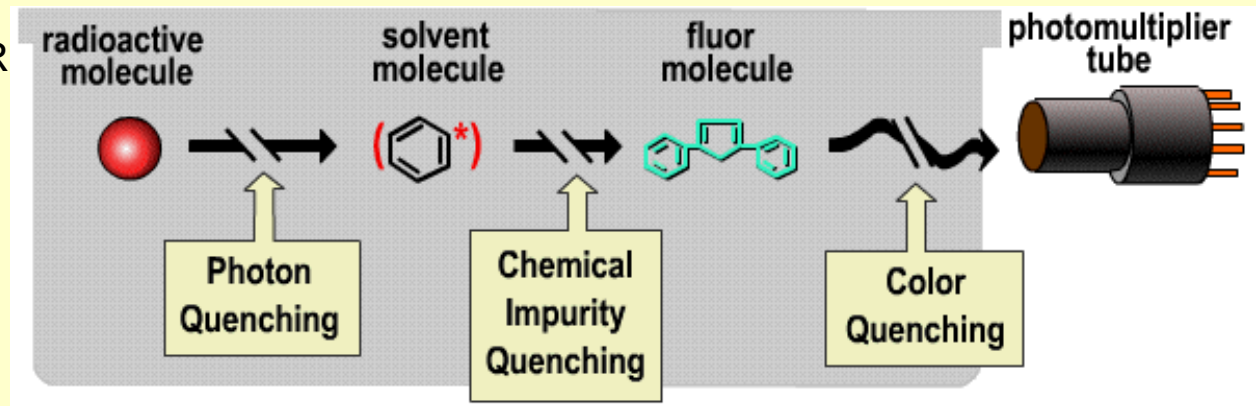
(b) Automatically via quench curve correction

Three window Sr-isotope counting



Quenching

- Quenching within a sample refers to any mechanism which reduces the amount of light being emitted from the vial.
- Reducing the amount of light reaching the PMT's results in a reduction of the pulse height.
- Any factor, which reduces the efficiency of the energy transfer or causes the absorption of photons (light), results in quenching in the sample.



■ Chemical Quenching

... occurs during the transfer of energy from the solvent to the scintillator.

Chemical agents (e.g. water and other solvents) added to the cocktail with the radioactive sample interfere with the transfer of kinetic energy between the solvent and the fluor(s).

The results are:

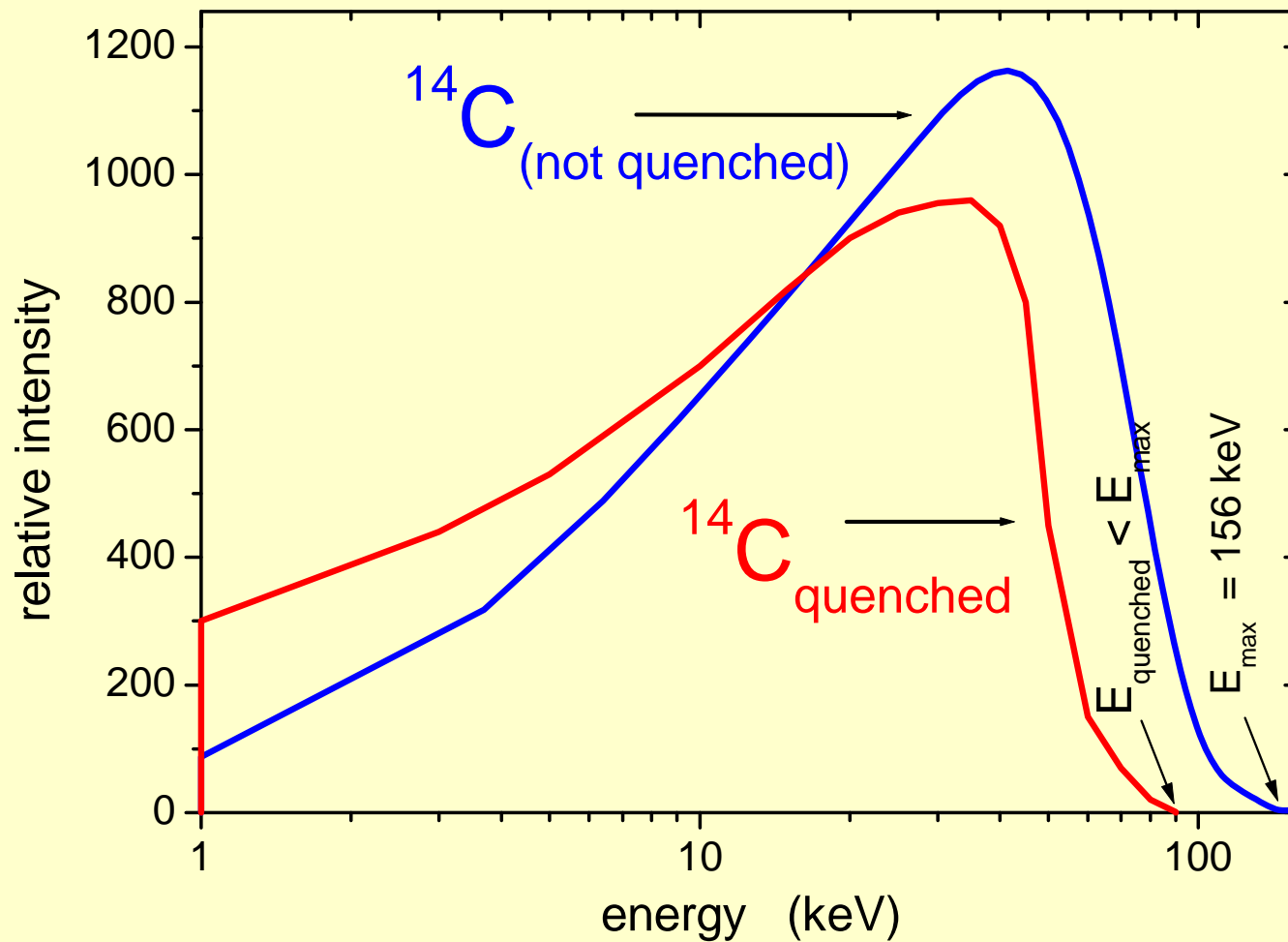
- Reduction and loss of light
- Reduced counting efficiency

■ Colour Quenching

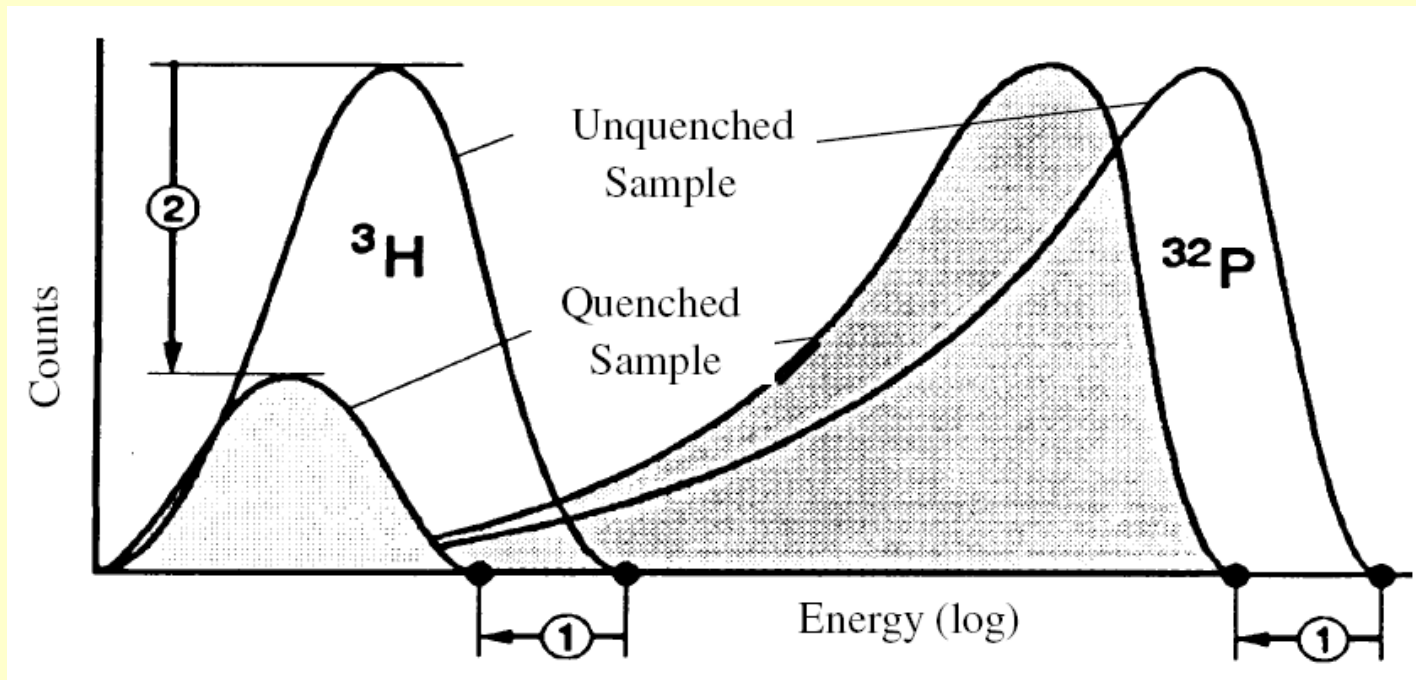
...is an attenuation of the photon of light.

The photons produced are absorbed or scattered by the colour in the solution, resulting in reduced light output available for measurement by the PMT's.

^{14}C spectrum of waste water: examples for not quenched filtrated water and a quenched spectrum (direct measurement)



Effects of Quenching



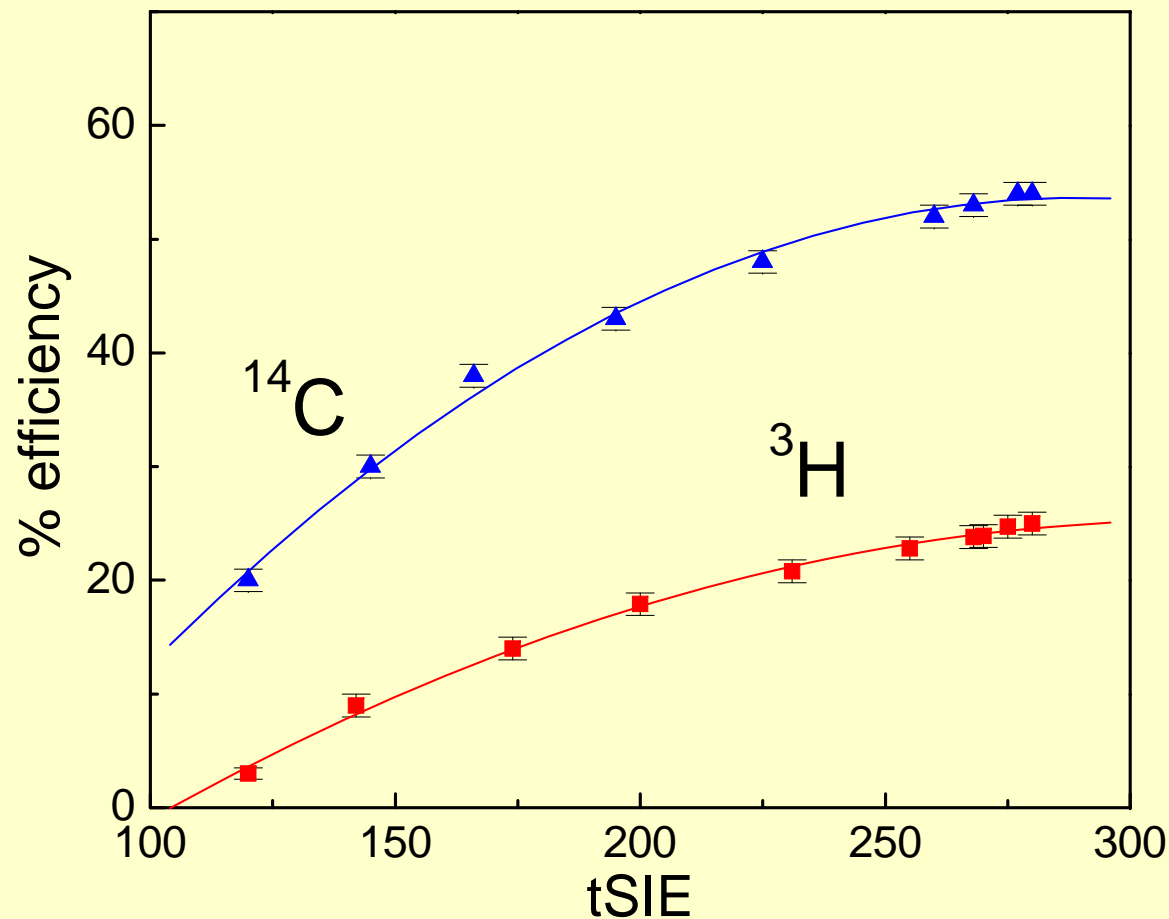
- 1) A shift in the pulse height spectrum of the particles to lower energy
- 2) A reduction in the measured CPM of the sample (loss of counting efficiency). This effect occurs especially with low energy particles.

Quench parameter calculation

$$QPES = k \cdot \frac{\sum_{i=1}^k X_i \cdot I(X_i)}{\sum_{i=1}^k I(X_i)}$$

QPES or tSIE = quenching parameter (or center of gravity or spectral index) of the external standard
 X_i and $I(X_i)$ refer to the channel numbers and the count rates of the external standard in each channel number.

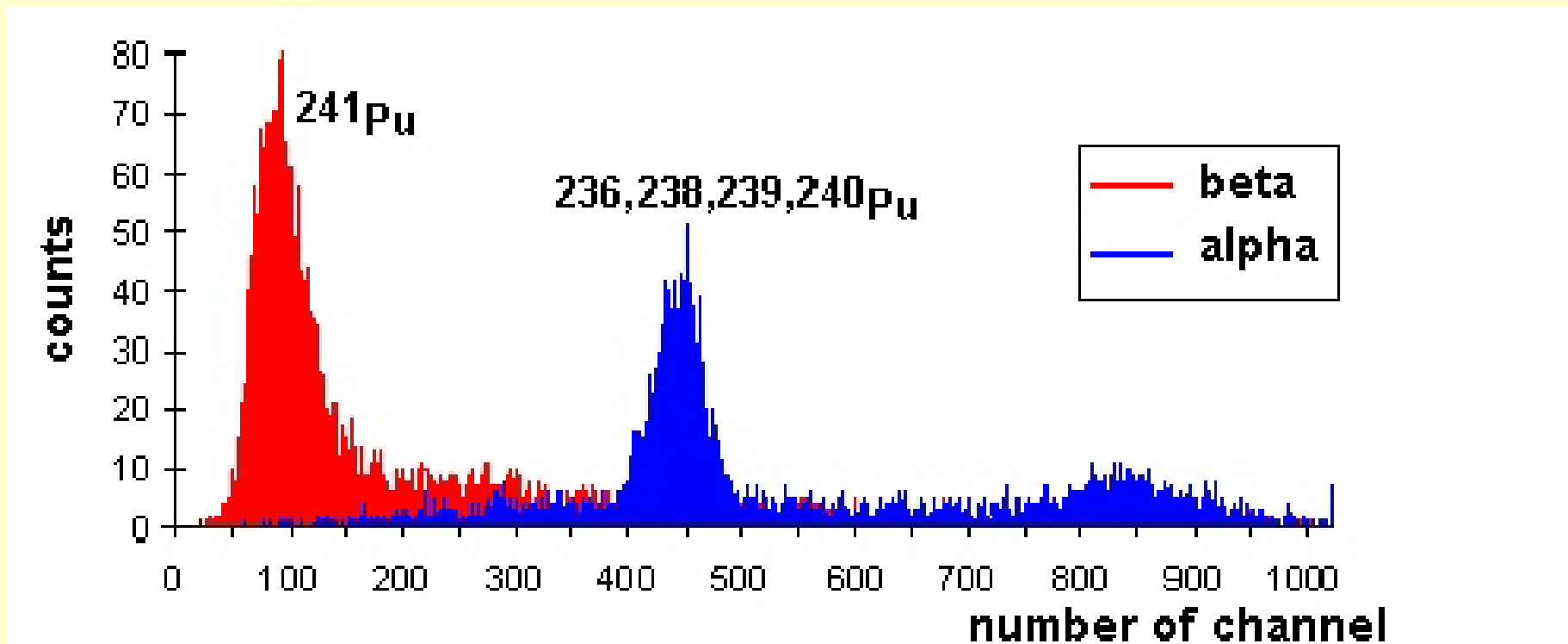
^3H , ^{14}C quench curves: efficiency in dependency of the spectral index from the external standard



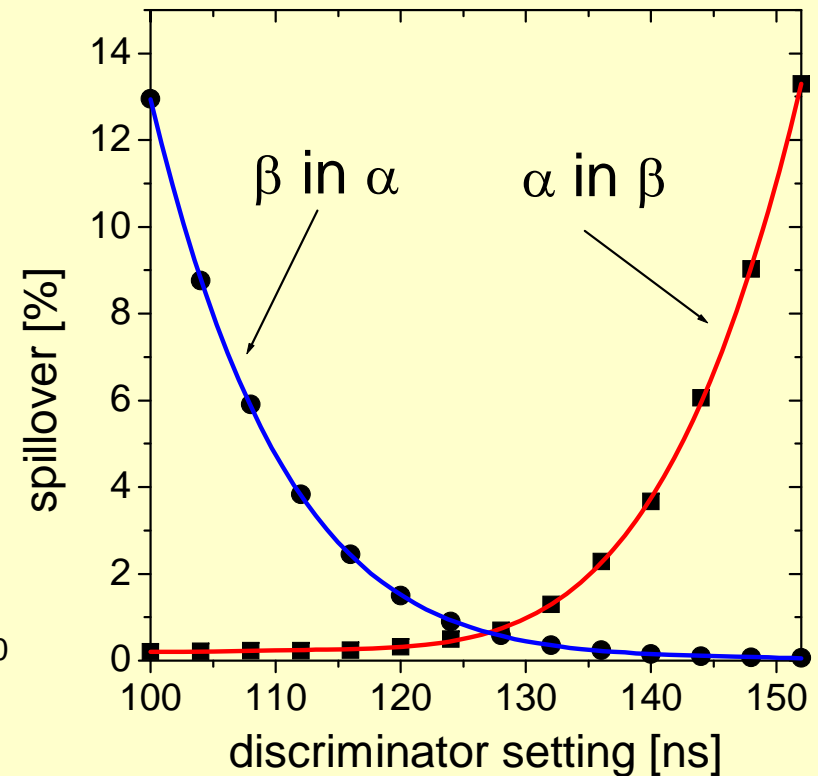
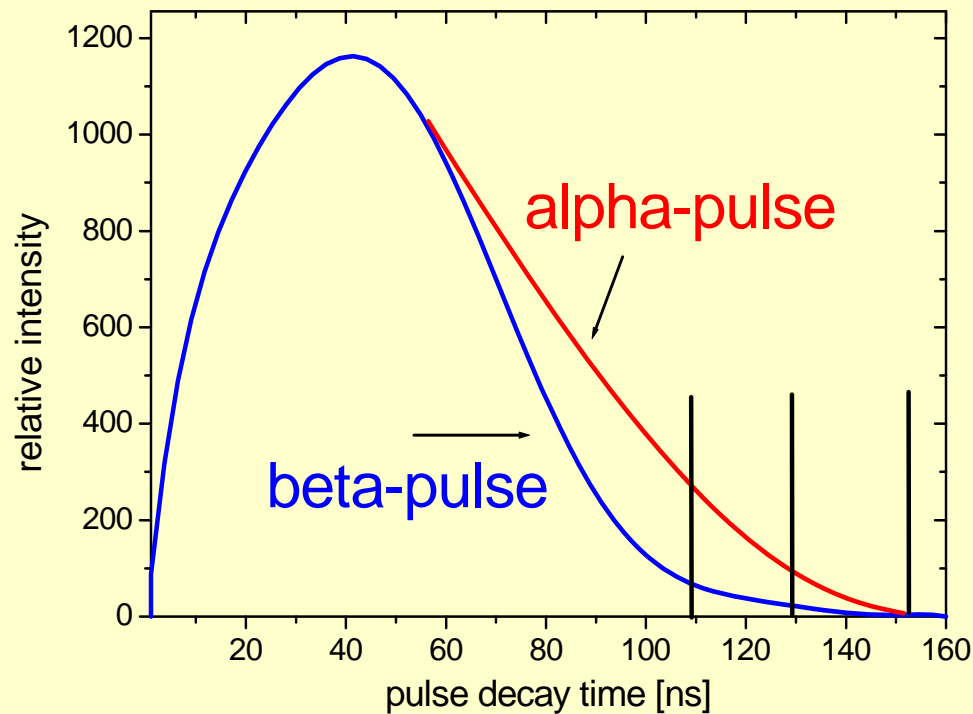
Alpha/Beta Separation

- Classical: use of spill-over curves and pulse shape analysis (PSA)
- TDCR (Hidex 300 SL): use of pulse length index (PLI) and energy differentiation

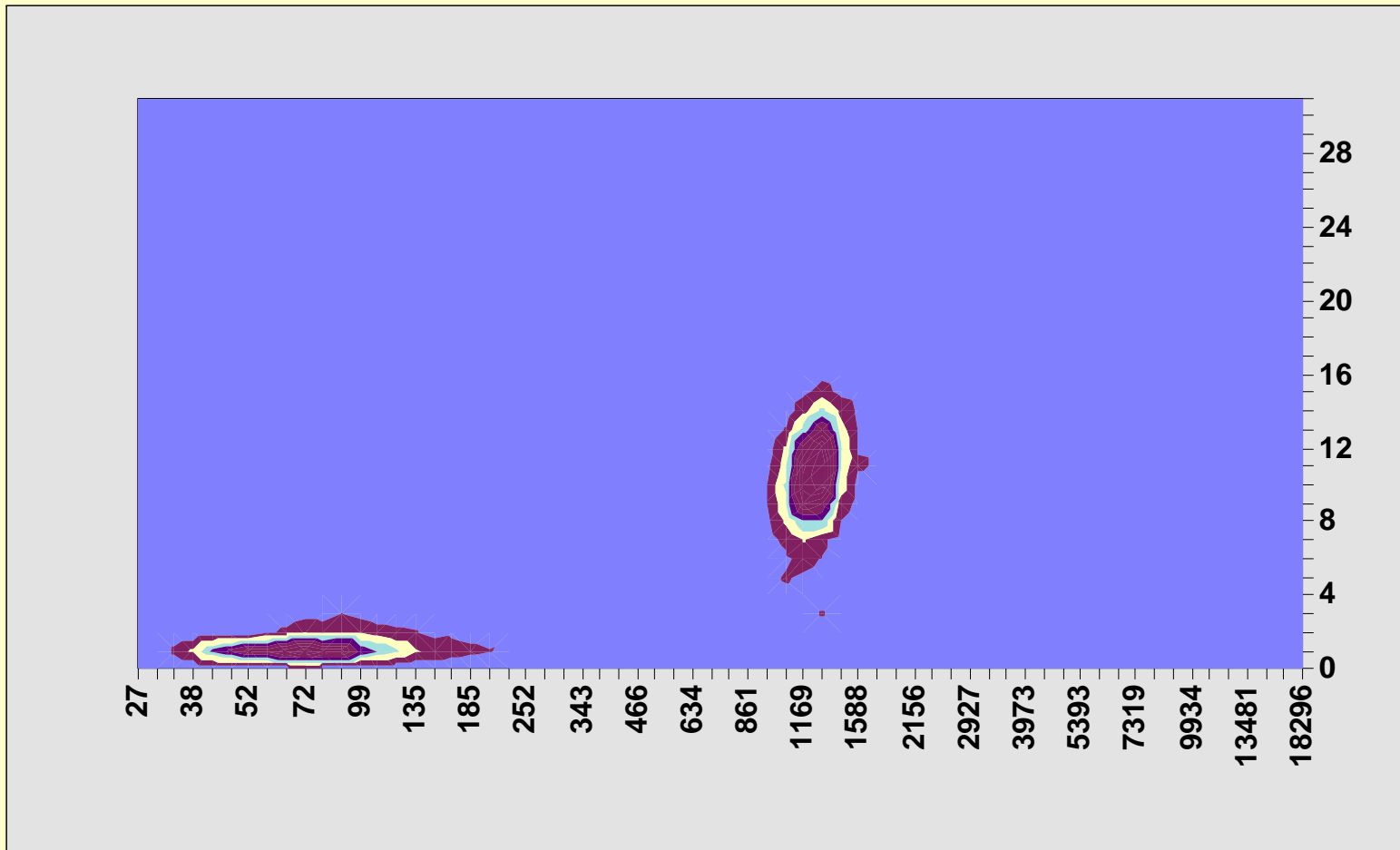
Alpha/Beta spectrum of Pu-isotopes



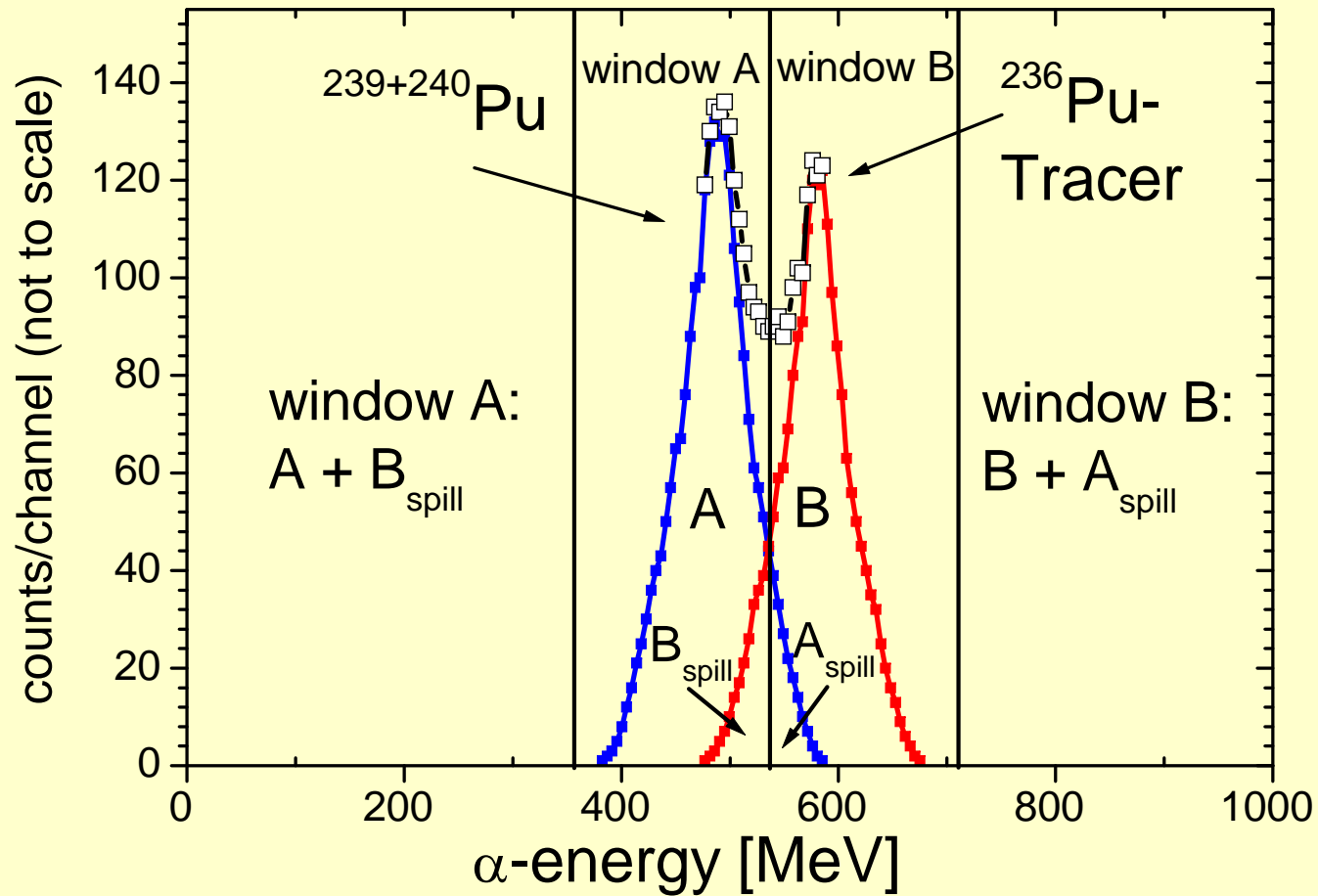
(iii) Alpha LSC counting alpha/beta-discrimination, PSA, Pulse Shape Analysis)



Pulse Length Index (PLI) discrimination with HIDEX SL 300



Analytical separation of two interfering α -peaks



mathematical equations: 2-window counting

$$V_1 = \frac{A_{spill}}{A}$$

$$V_2 = \frac{B_{spill}}{B}$$

$$N_A = A + B_{spill}$$

$$N_B = B + A_{spill}$$

$$N_{239} = A + A_{spill} = \frac{(1 + V_1) \cdot (N_A - V_2 \cdot N_B)}{1 - V_1 \cdot V_2}$$

$$N_{236} = B + B_{spill} = \frac{(1 + V_2) \cdot (N_B - V_1 \cdot N_A)}{1 - V_1 \cdot V_2}$$

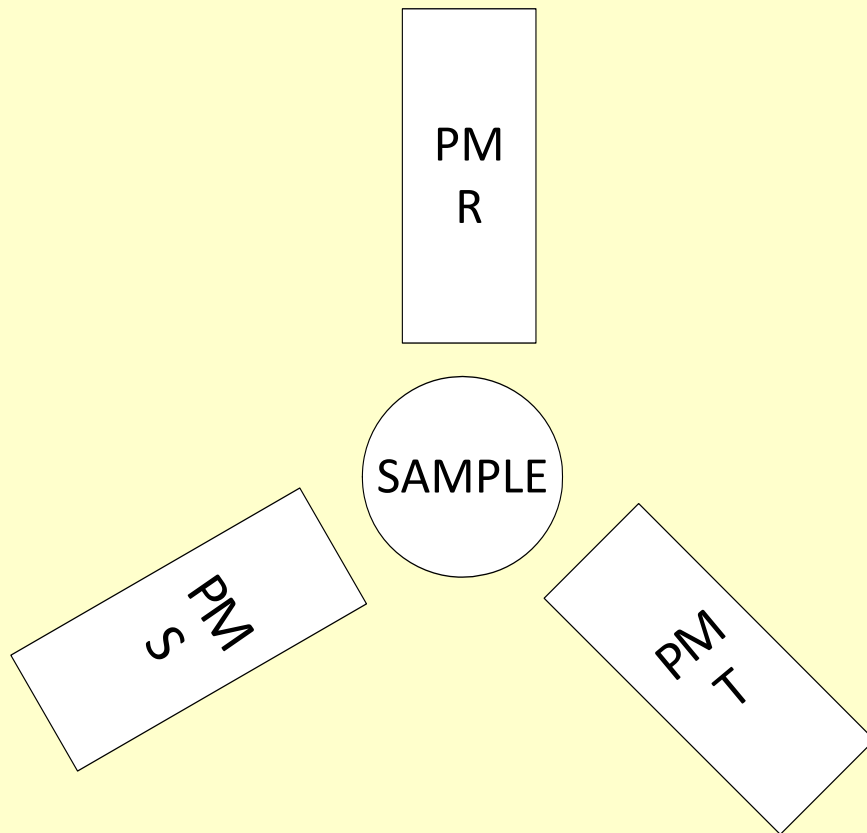
Isotope Spiking

$$A_{239(s)} = \frac{N_{239(s)}}{Y_{Pu} \cdot \varepsilon \cdot \eta}$$

$$A_{236(t)} = \frac{N_{236(t)}}{Y_{Pu} \cdot \varepsilon \cdot \eta}$$

$$A_{239(s)} = \frac{N_{239(s)}}{N_{236(t)}} \cdot A_{236(t)}$$

The triple coincidence to double coincidence ratio (TDCR) counting technique



The theory of TDCR

In counting statistics the number of events (x) that are detected from a mean number of (n) events follows a discrete probability or Poisson distribution provided that the events occur with a known average rate and independently of the time since the last event i.e.

$$P(x, n) = \frac{n^x}{x!} \cdot e^{-n} \quad (9-53)$$

From equation (9-53) it follows for the extreme case of no detection

$$x \rightarrow 0: \frac{n^x}{x!} \rightarrow 1 \cdot \quad (9-54)$$

Therefore, for case of no detection or zero detection (Z) it follows for 1 photomultiplier, for instance for “R”:

$$Z = P(0, n) = e^{-n} \quad (9-55)$$

And, for the detection probability or detection efficiency (ε):

$$\varepsilon = 1 - Z = 1 - e^{-n} \quad (9-56)$$

Equation (9-56) shows that the value for the detection efficiency varies between 0 (no interaction between the decaying isotope and the scintillation cocktail) and 1 (i.e. when high energetic beta particles undergo strong interaction with the cocktail medium, i.e. produce a very high number of photons that are detected via LSC). From equation (9-56) it is obvious that for 2 photomultipliers (R+S) connected in coincidence, the total coincidence efficiency is:

$$\varepsilon = (1 - e^{-n}) \cdot (1 - e^{-n}) = (1 - e^{-n})^2 \quad (9-57)$$

And, consequently, for three photomultipliers (R, S, T) connected in a coincidence circuit:

$$\varepsilon = (1 - e^{-n}) \cdot (1 - e^{-n})^2 = (1 - e^{-n})^3 \quad (9-58)$$

In the following the possible quantity of coincidences is listed for the one case of triple coincidences tubes (R-S-T) and the other three cases of double coincidences, i.e. (R-S, R-T, S-T).

3-coincidences: $RST = (1 - e^{-n})^3 \quad (9-59)$

2-coincidences: $RS = (1 - e^{-n})^2 \cdot e^{-n} \quad (9-60)$

Equation (9-60) shows the coincidence probability for the R-S couple with zero detection from the T-tube. In analogy it can be written for the combination of the R-T-tubes (with zero detection from the S-tube):

2-coincidences: $RT = (1 - e^{-n})^2 \cdot e^{-n} \quad (9-62)$

And, finally for the combination S-T (with zero detection from the R-tube):
2-coincidences:

$$ST = \left(1 - e^{-n}\right)^2 \cdot e^{-n} \quad (9-62)$$

The logical sum of these 4 possible combinations, i.e. the sum of all coincidences is:

$$all = \left(1 - e^{-n}\right)^3 + 3 \cdot \left(1 - e^{-n}\right)^2 \cdot e^{-n} \quad (9-63)$$

This expression can be rewritten by reducing both terms in equation (9-63) with $(1 - e^{-n})^2$ i.e.,

$$all = \left(1 - e^{-n}\right)^2 \cdot \left(1 - e^{-n} + 3 \cdot e^{-n}\right) \quad (9-64)$$

$$all = \left(1 - e^{-n}\right)^2 \cdot \left(1 + 2 \cdot e^{-n}\right) \quad (9-65)$$

Multiplying these terms and converting the result in binominal expressions yields finally:

$$all = 3 \cdot (1 - e^{-n})^2 - 2 \cdot (1 - e^{-n})^3 \quad (9-66)$$

Therefore the ratio of triple coincidences to all coincidences, referred in the literature as TDCR, is in reality:

$$TDCR = \frac{triplecoincidences}{doublecoincidences} = \frac{triple}{all} = \frac{(1 - e^{-n})^3}{3 \cdot (1 - e^{-n})^2 - 2 \cdot (1 - e^{-n})^3} \quad (9-67)$$

In the following, two extreme cases have to be regarded, i.e. the number of photoelectrons produced in the multiplier (n) tends to a) an unlimited high number and, b) tends to zero value, i.e.

$$n \rightarrow \infty : (1 - e^{-n}) \rightarrow 1 \text{ i.e. } TDCR \rightarrow 1 \quad (9-68)$$

$$n \rightarrow 0 : (1 - e^{-n})^3 \ll (1 - e^{-n})^2 \text{ i.e. } TDCR \rightarrow 0 \quad (9-69)$$

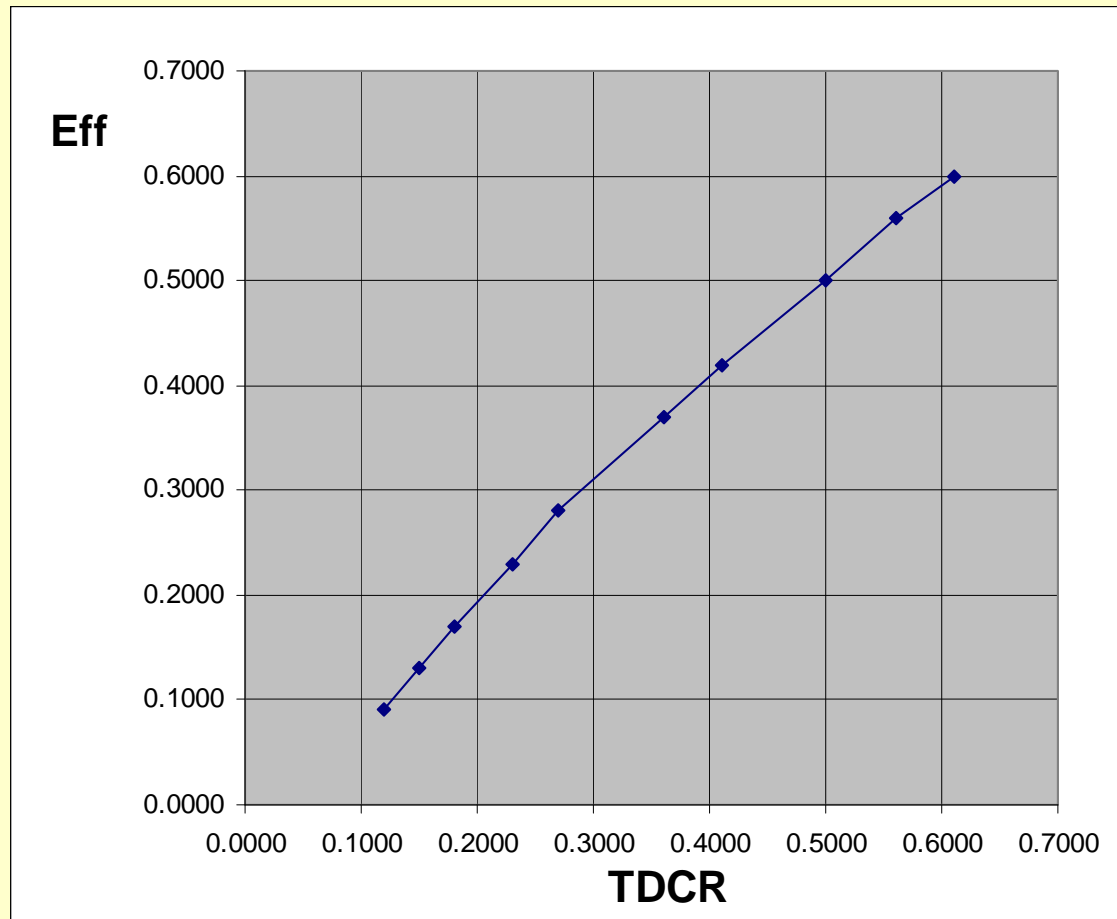
For a high number of events the measured ratio TDCR is a function of the counting probability detection, i.e. the efficiency.

With common pure β -emitting radionuclides and less quenched cocktail medium (e.g. ^{14}C in organic compounds such as benzene mixed with a high aromatic scintillation liquid) the TDCR value approximates roughly the counting efficiency.

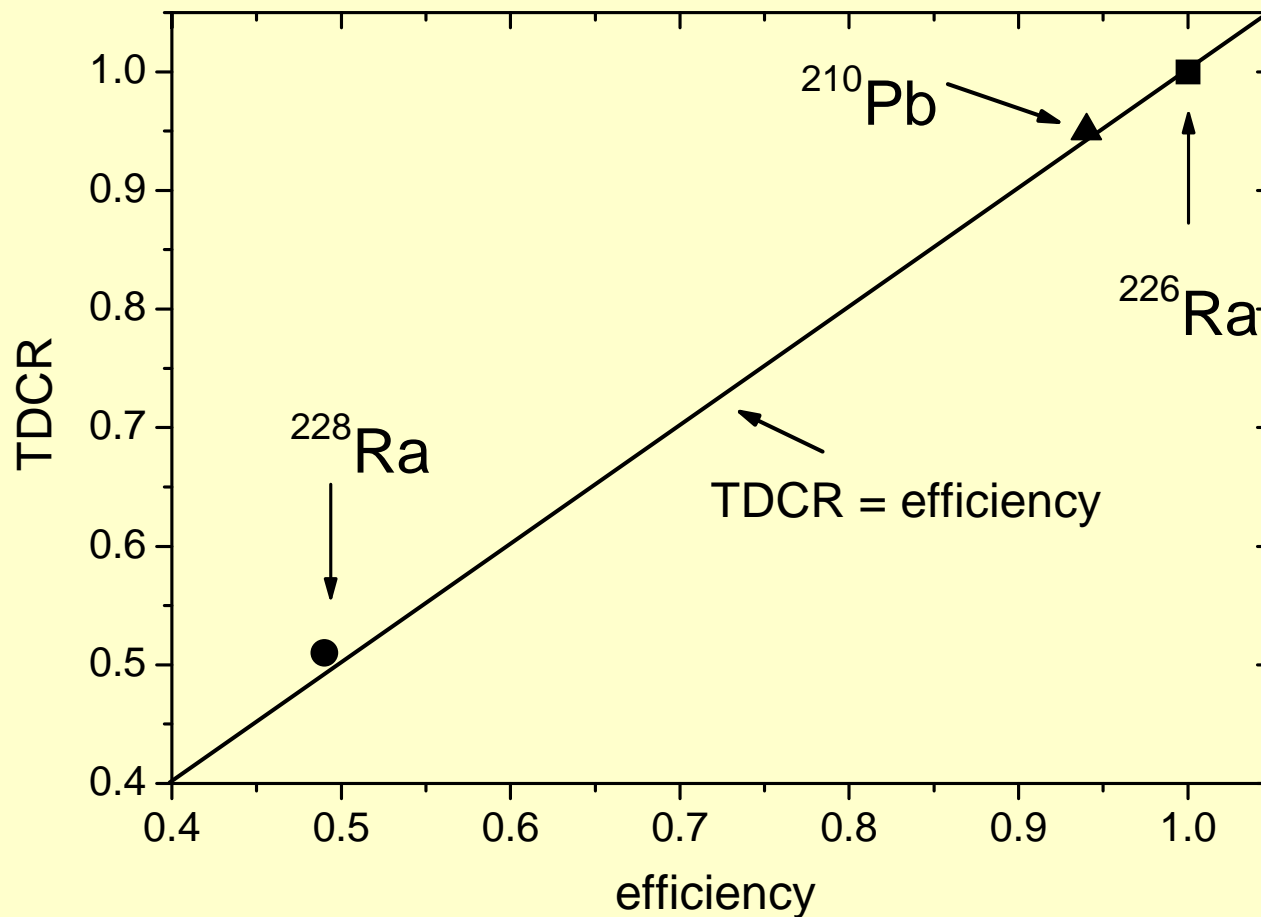
For the Hidex 300 SL LS-spectrometer the efficiency is given as linear function of the TDCR-value or,

$$\varepsilon = m \cdot TDCR \quad \text{with } m = 1 \quad (9-73)$$

The first approximation linear relationship between the counting efficiency and the TDCR



TDCR vs. Efficiency using high purity radionuclide standard solutions



TDCR blank correction

For linear systems the following mass relationship hold for mixtures (m) of two components, M_1 and M_2 with the concentrations C_1 and C_2

$$C_m \cdot M_m = C_1 \cdot M_1 + C_2 \cdot M_2$$

This relationship can be transferred directly to TDCR measurements and the true or net-TDCR ($TDCR_n$) has to be calculated from the brut-TDCR („mixture“) ($TDCR_b$) and the TDCR-value of a blank measurement ($TDCR_0$).

$$r_b \cdot TDCR_b = r_n \cdot TDCR_n + r_0 \cdot TDCR_0$$

with: $r_n = r_b - r_0$

follows: $r_b \cdot TDCR_b = (r_b - r_0) \cdot TDCR_n + r_0 \cdot TDCR_0$

$$TDCR_n = \frac{r_b \cdot TDCR_b - r_0 \cdot TDCR_0}{r_b - r_0}$$

for pure beta emitters holds: $TDCR_n \approx \varepsilon_n$

with $A = \frac{r_n}{\varepsilon_n} = \frac{r_b - r_0}{\varepsilon_n}$

follows for the activity calculation

$$A = \frac{(r_b - r_0)^2}{r_b \cdot TDCR_b - r_0 \cdot TDCR_0}$$



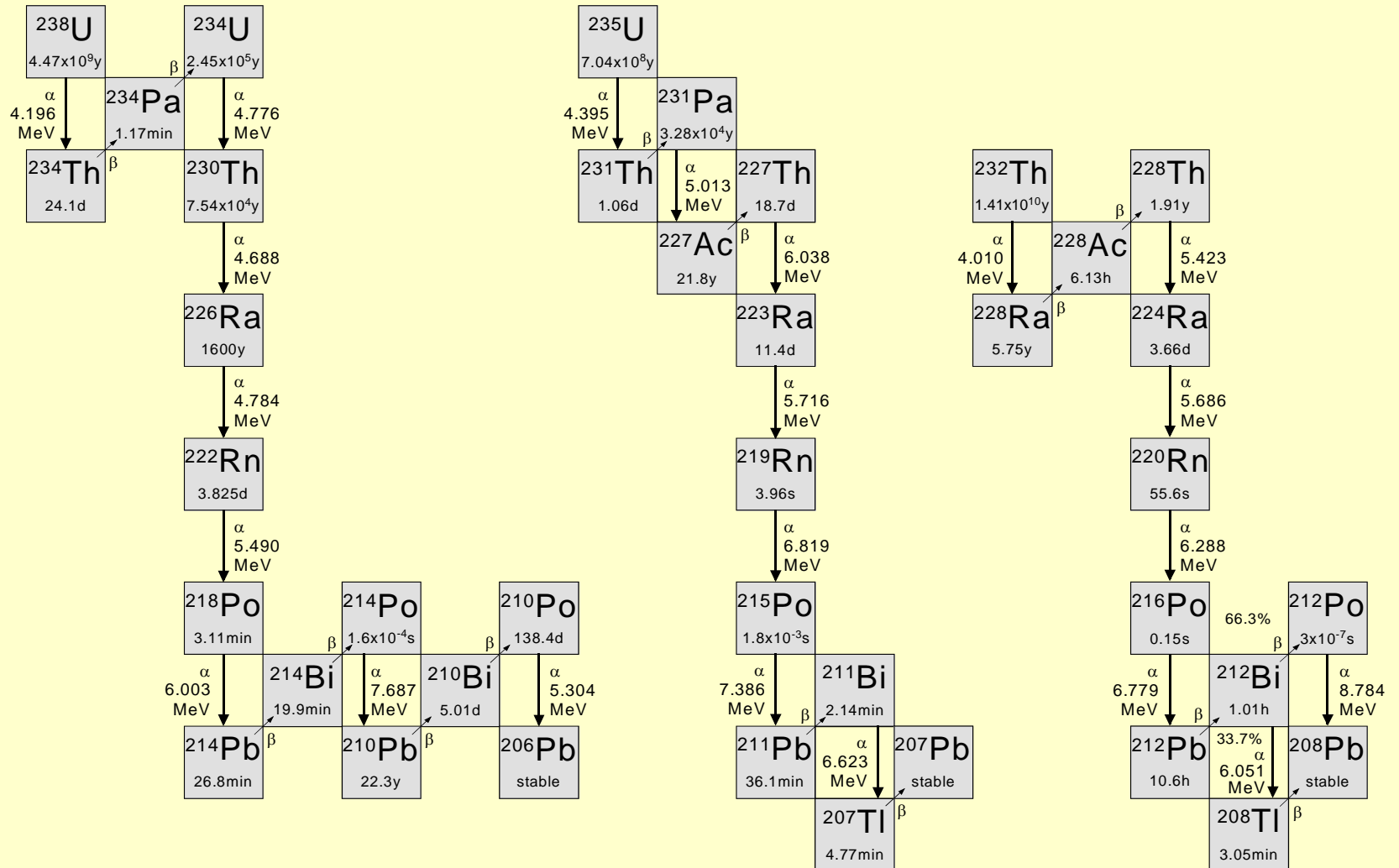
Terrestrial
radioisotopes:
 ^{238}U -series
 ^{235}U -series
 ^{232}Th -series

^{238}U -Series

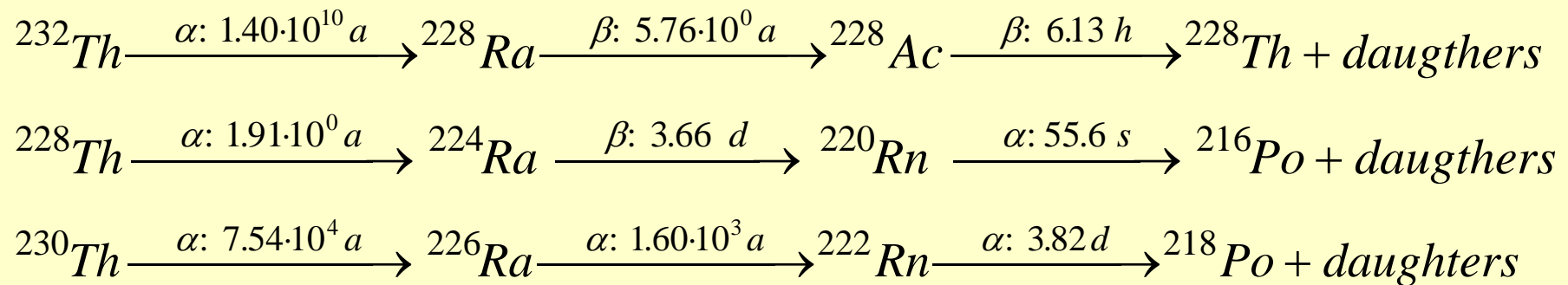
 ^{235}U -Series

 ^{232}Th -Series

U
Pa
Th
Ac
Ra
Fr
Rn
At
Po
Bi
Pb
Tl



Th-Ra relationship in the ^{232}Th and ^{238}U decay series



Continental water: relevant isotopes

- Alpha-emitter: U-238, U-234
- Beta-emitter: Ra-228 (with fast ingrowing Ac-228)
- Alpha-emitter: Ra-226 (with Rn-222 progenies)
- Beta-emitter: Pb-210 (with ingrowing Bi-210)
- Alpha-emitter: Po-210

relevant isotopes in continental water and their measurement methods at PSI

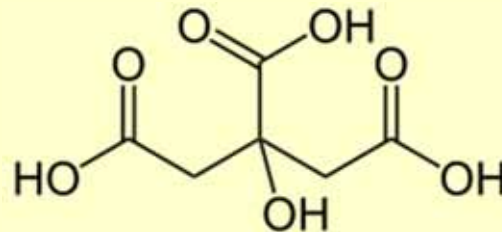
radionuclide	analytical technique
^{234}U , (^{235}U), ^{238}U	U/TEVA separation, electro-deposition, α -spectrometry
^{226}Ra , ^{228}Ra , ^{210}Pb	filtration (RadDisc), OptiPhase Hisafe3 cocktail, LSC
^{210}Po	spontaneous deposition on silver disc, α -spectrometry

Relationship parent / daughter

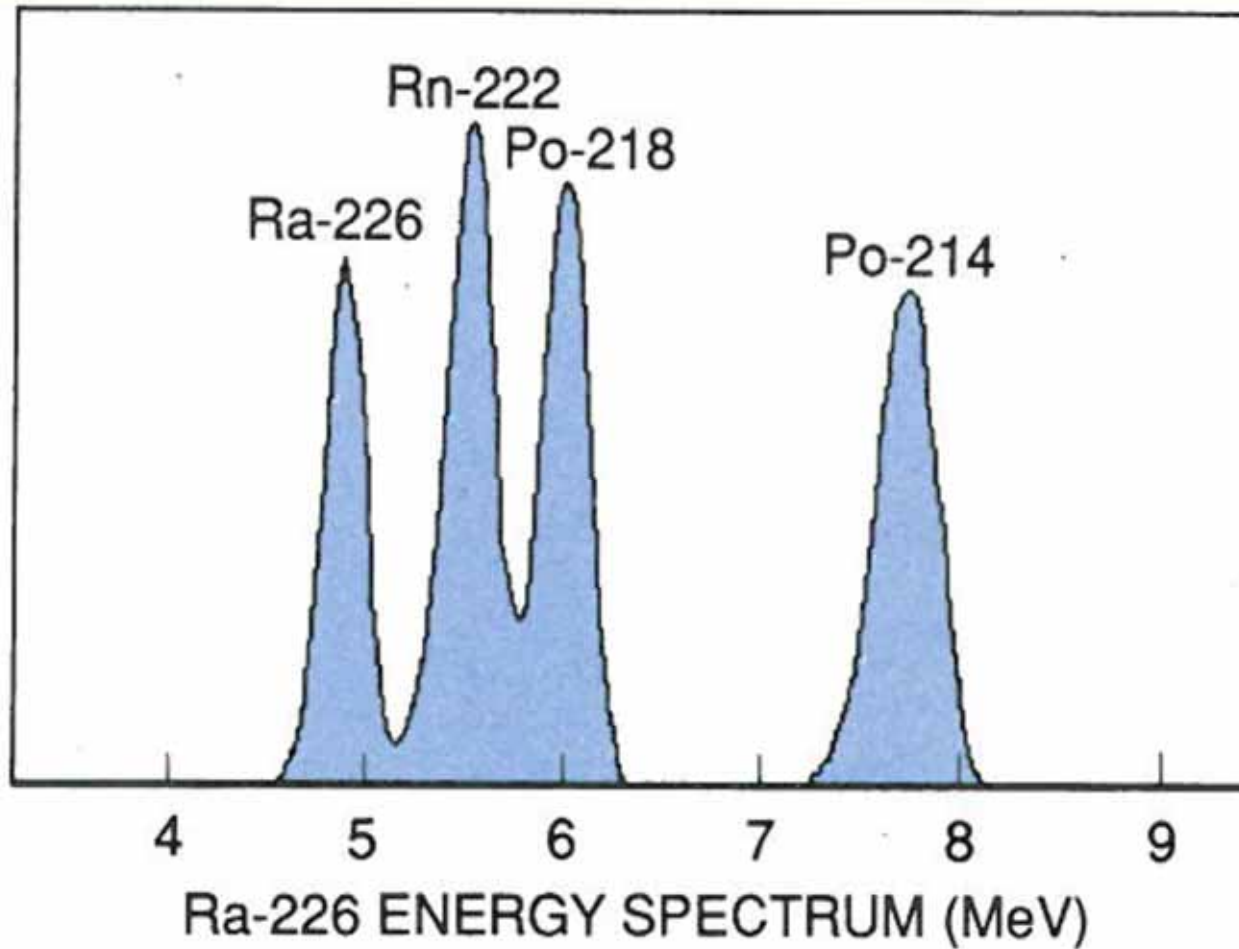
parent isotope	half-life parent	ingrowing daughter	half-life daughter
^{210}Pb (β)	22.3 years	^{210}Bi (β)	6.02 days
^{226}Ra (α)	1602 years	^{222}Rn (α)	3.82 days
^{228}Ra (β)	5.76 years	^{228}Ac (β)	6.13 hours

Method implementation: low level determination of ^{210}Pb , $^{226}\text{Ra}+^{228}\text{Ra}$ in drinking water

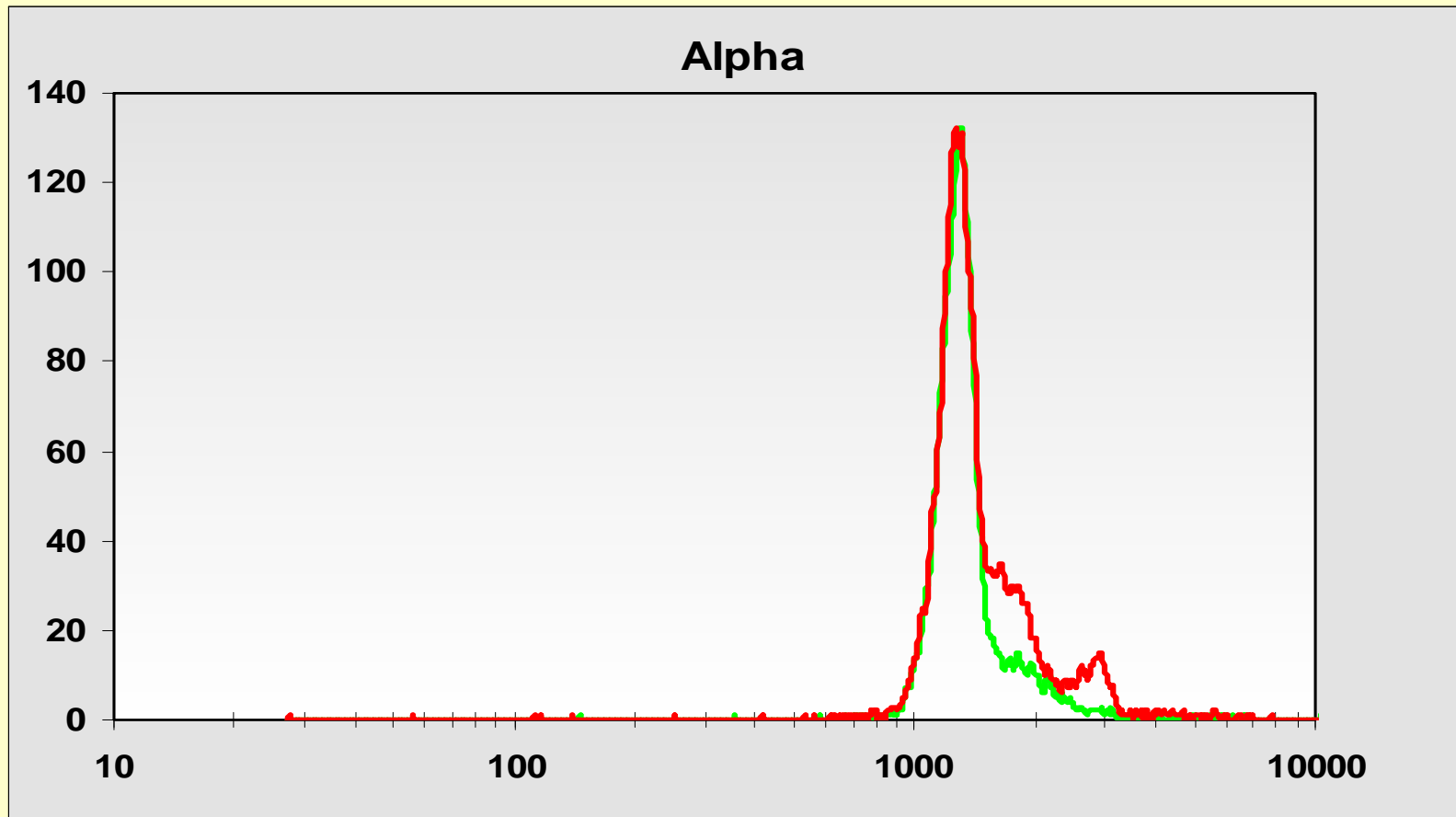
- Filtration of the sample (2 liter) through 3 Empore RadDisc (Mn-oxide impregnated) membrane filters
- Elution of Pb with Diammonium Hydrogen Citrate
- Elution of Ra with alkaline Na-EDTA solution
- Measuring via LSC with optimized α/β -discrimination



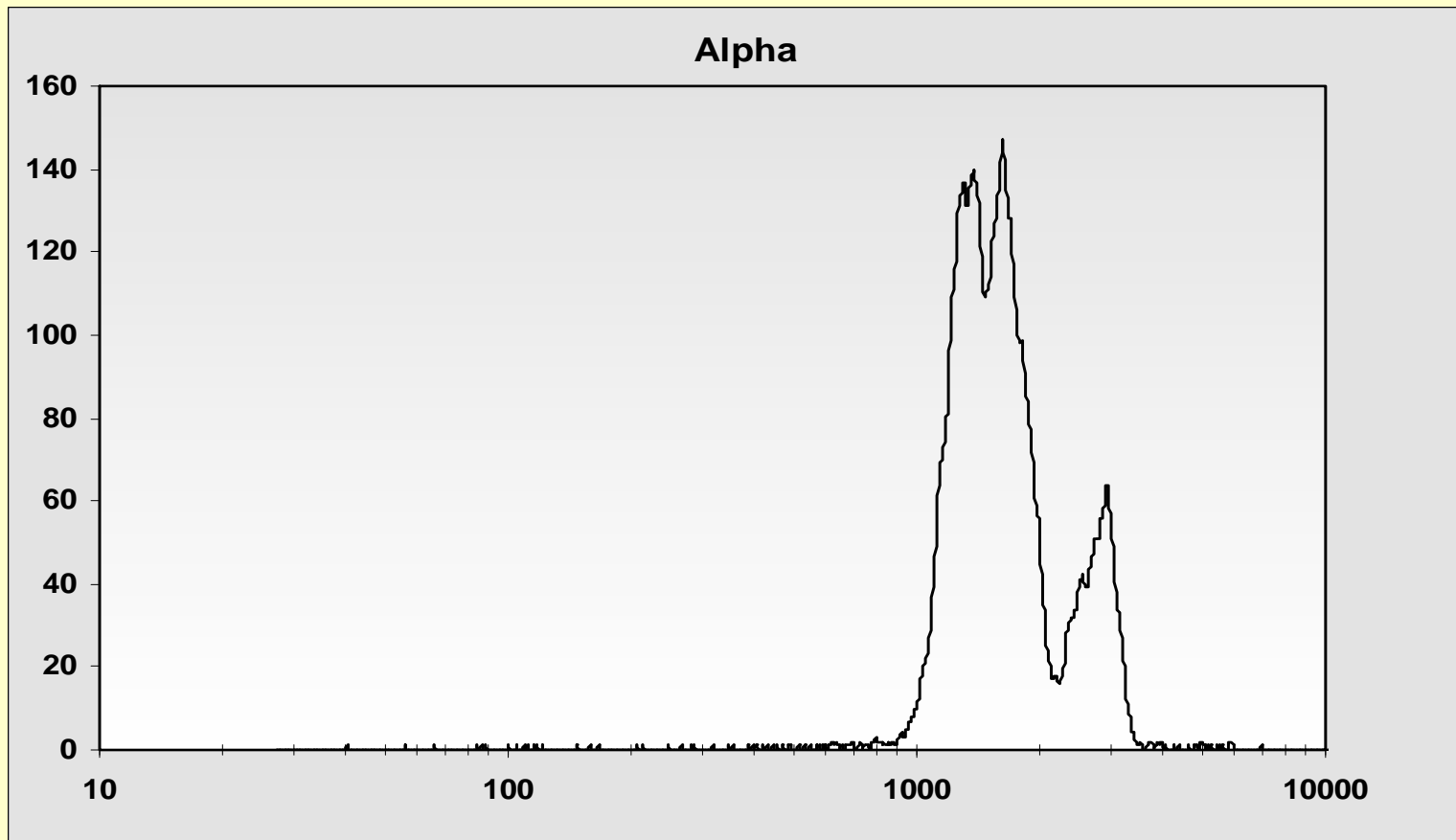
α -spectrum of Radium-226: PERALS-LSC



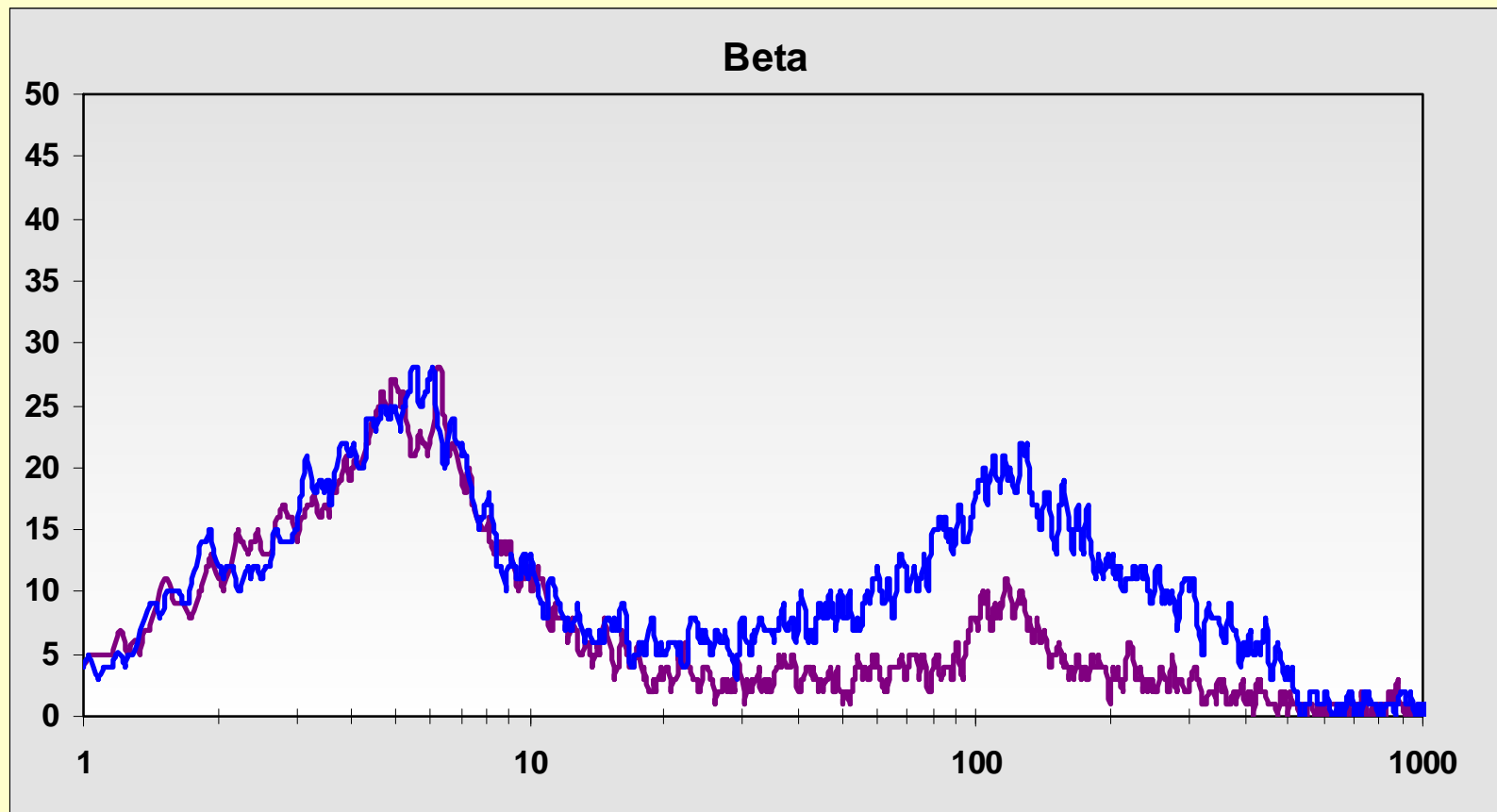
α -spectrum of ^{226}Ra with ingrowing daughters 2 h and 8 h after separation using HIDEX 300 SL LSC



α -spectrum of ^{226}Ra with ingrowing daughters obtained 6 days after separation



β -spectrum of ^{228}Ra with ingrowing ^{228}Ac 1 h and 8 h after separation using HIDEX 300 SL LSC



long lived mother – short lived daughter relationship

$$A_y(t) = A_x(0) \cdot \frac{\lambda_y}{\lambda_y - \lambda_x} \cdot (e^{-\lambda_x t} - e^{-\lambda_y t}) + A_y(0) \cdot e^{-\lambda_y t}$$

$$A_y(t) = A_x(0) \cdot \frac{\lambda_y}{\lambda_y - \lambda_x} \cdot (e^{-\lambda_x t} - e^{-\lambda_y t})$$

$$\lambda_x \ll \lambda_y \Rightarrow \frac{\lambda_y}{\lambda_y - \lambda_x} \rightarrow 1$$

$$A_y(t) = A_x(0) \cdot (1 - e^{-\lambda_y t})$$

LS-spectrum interference correction

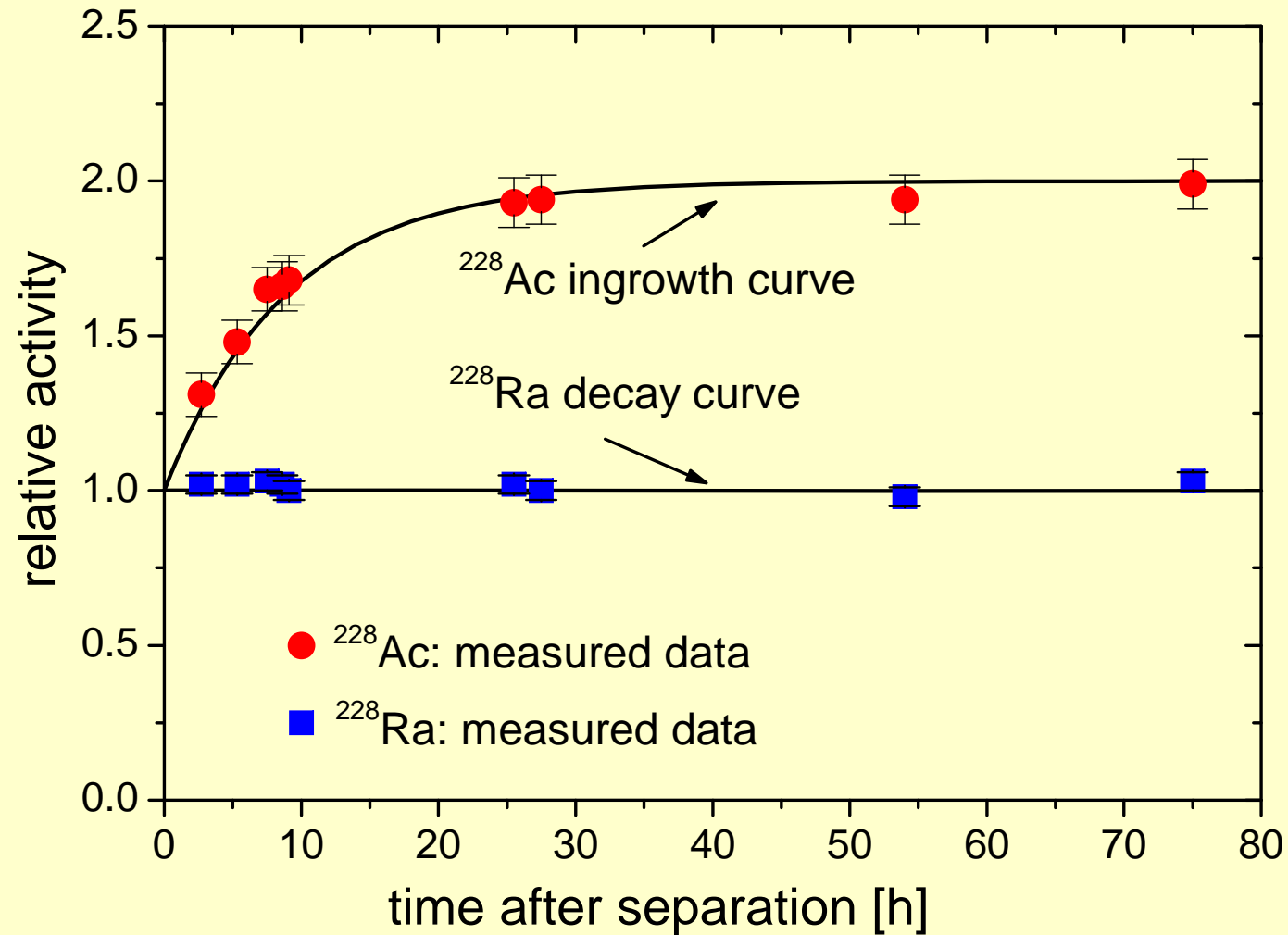
$$R_{Ac-228} = \left(\frac{\varepsilon^A}{\varepsilon^B} \right)_{Ac-228}$$

$$r_{n,cor}^A(^{228}Ra) = r_{n,m}^A - R_{Ac-228} \cdot r_n^B(^{228}Ac)$$

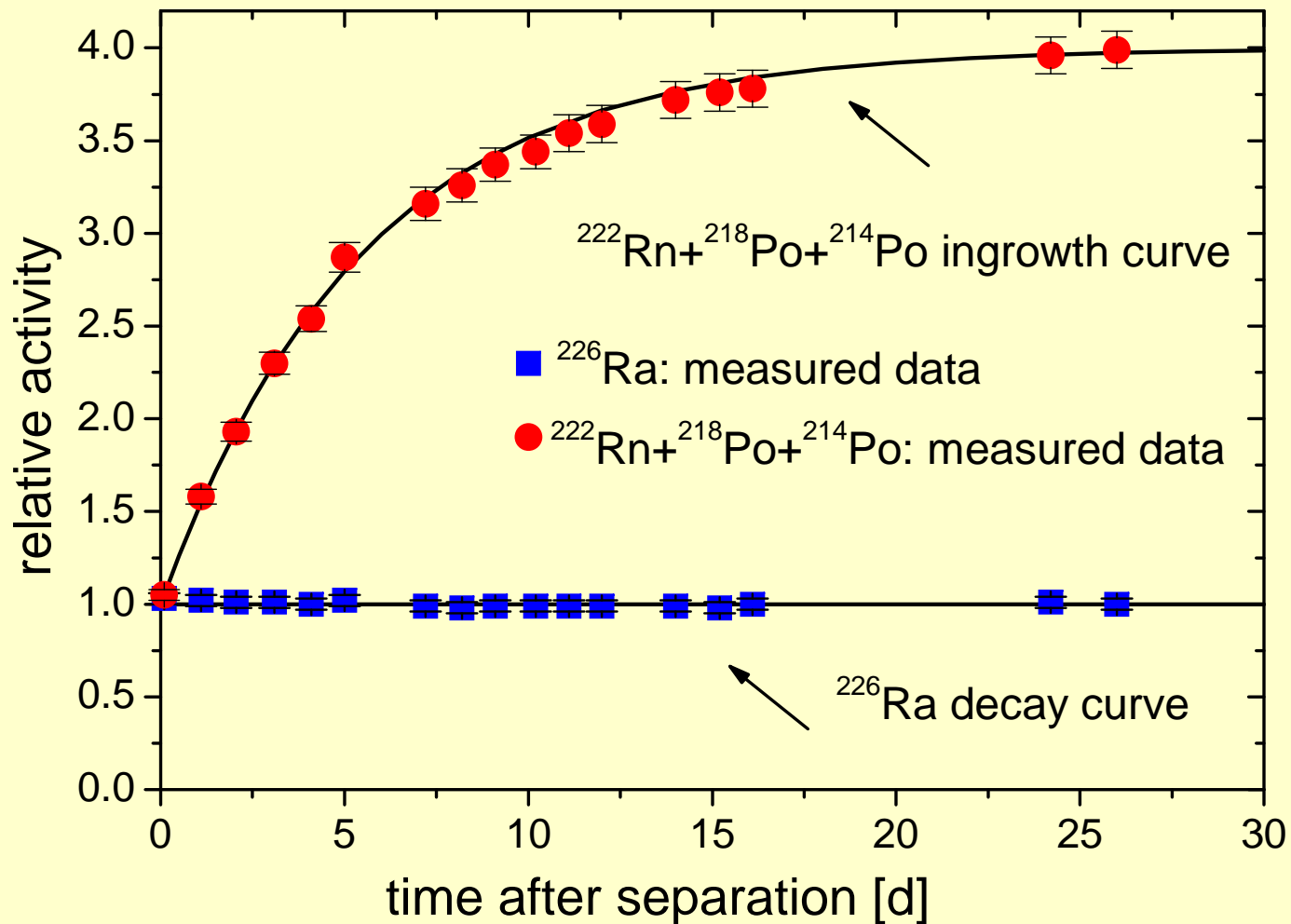
$$A_{Ra-228} = \frac{r_{n,cor}^A(^{228}Ra)}{\varepsilon_{Ra-228}^A}$$

$$A_{Ac-228} = \frac{r_n^B(^{228}Ac)}{\varepsilon_{Ac-228}^B}$$

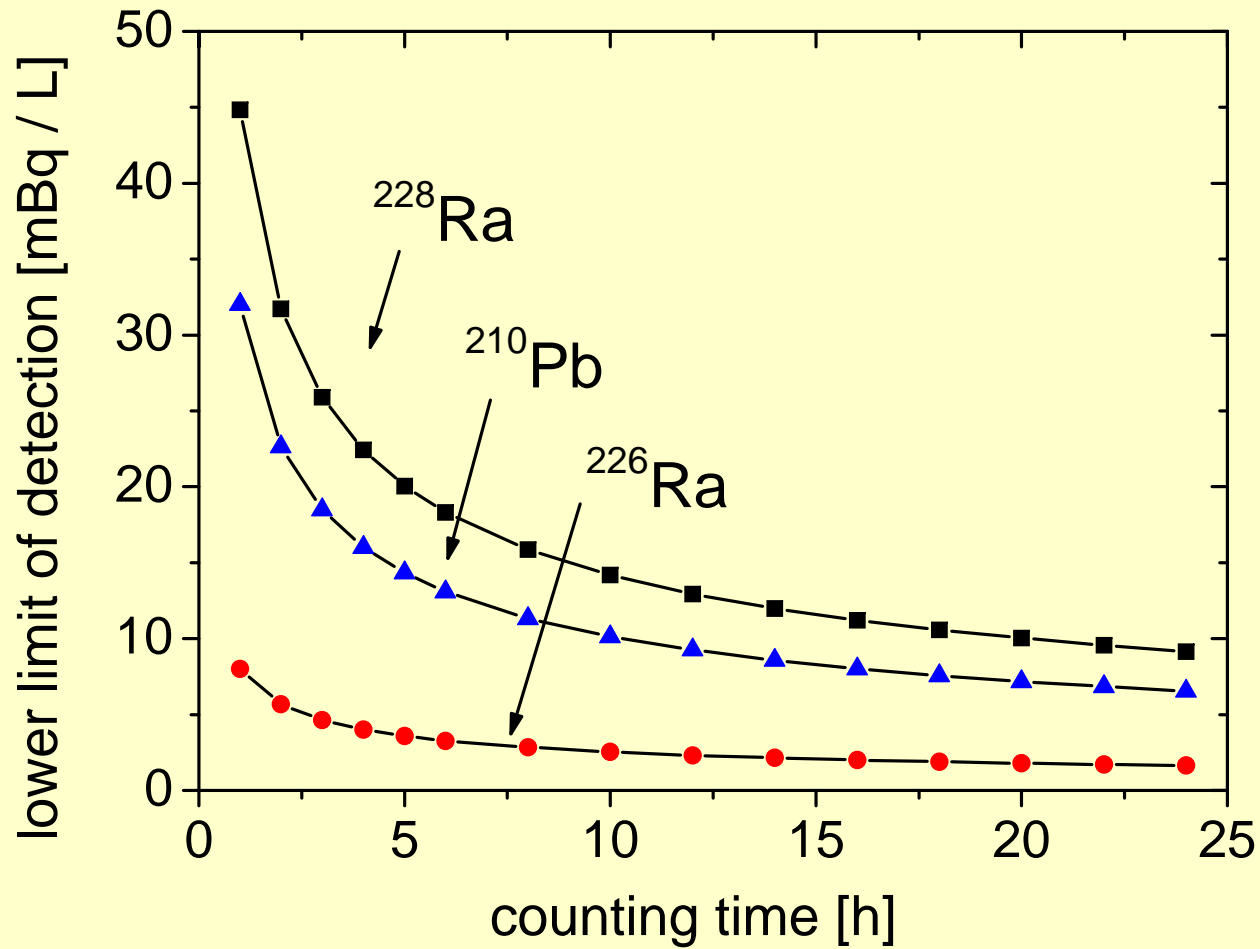
Comparison of measured ^{228}Ra and ^{228}Ac activities with calculated decay/ingrowth curves



Comparison of measured ^{226}Ra and the progeny isotopes ^{222}Rn , ^{218}Po and ^{214}Po with calculated decay/ingrowth curves



$$A^* = k_{1-\alpha} \cdot \frac{1}{\varepsilon \cdot V_s} \cdot \sqrt{2} \cdot \sqrt{\frac{r_0}{t_m}}$$



LSC detection limits, 2 l aliquot,
quantitative adsorption on RadDisc filter,
counting time 6 h

- Ra-226: 3 mBq/liter
- Ra-228: 20 mBq/liter
- Pb-210: 15 mBq/liter

Conclusions

- LSC is a powerful method to detect particle radiation (alpha / beta) without the need of applying extensive sample preparation procedures
- LSC is highly useful to measure potentially volatile isotopes such as ^3H and ^{14}C
- New counter developments allow almost quantitative activity concentration determinations without (internal) standardization, i.e. application of TDCR-measurements using triple to double coincidence ratio measurements



**Thank you for your
attention**