Practical Approaches using TDCR Measurements and Alpha/Beta Separation

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Overview / Topics

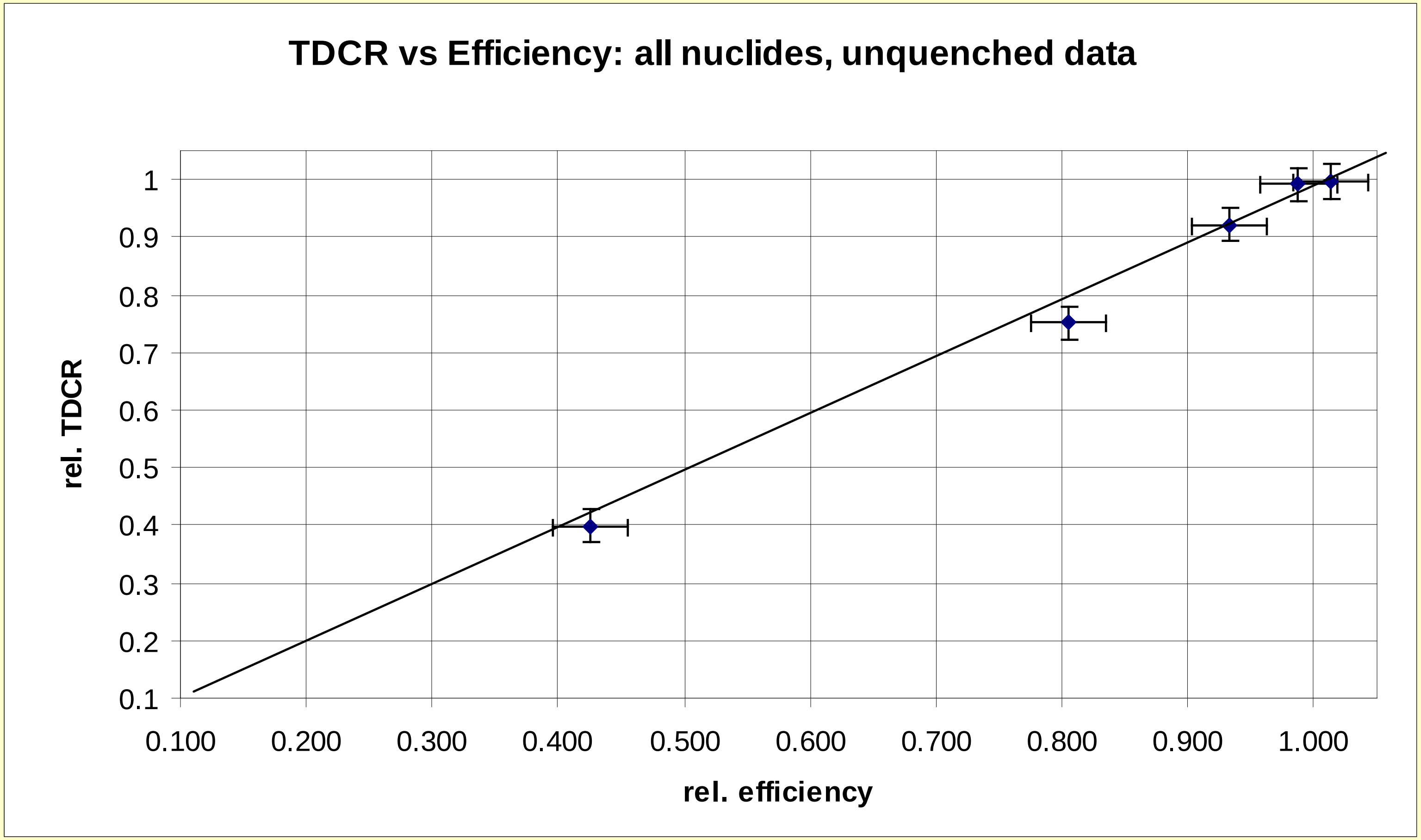
- TDCR standardization measurements with typical isotopes from the nuclear fuel cycle
- Presentation of a radiochemical method for simultaneous determination of ^{210}Pb and ^{226}Ra+^{228}Ra
- Simultaneous determination of ^{241}Pu (β-emitter) and ^{238}Pu, ^{239}Pu+^{240}Pu (α-emitter) in nuclear materials

TDCR standardization measurements

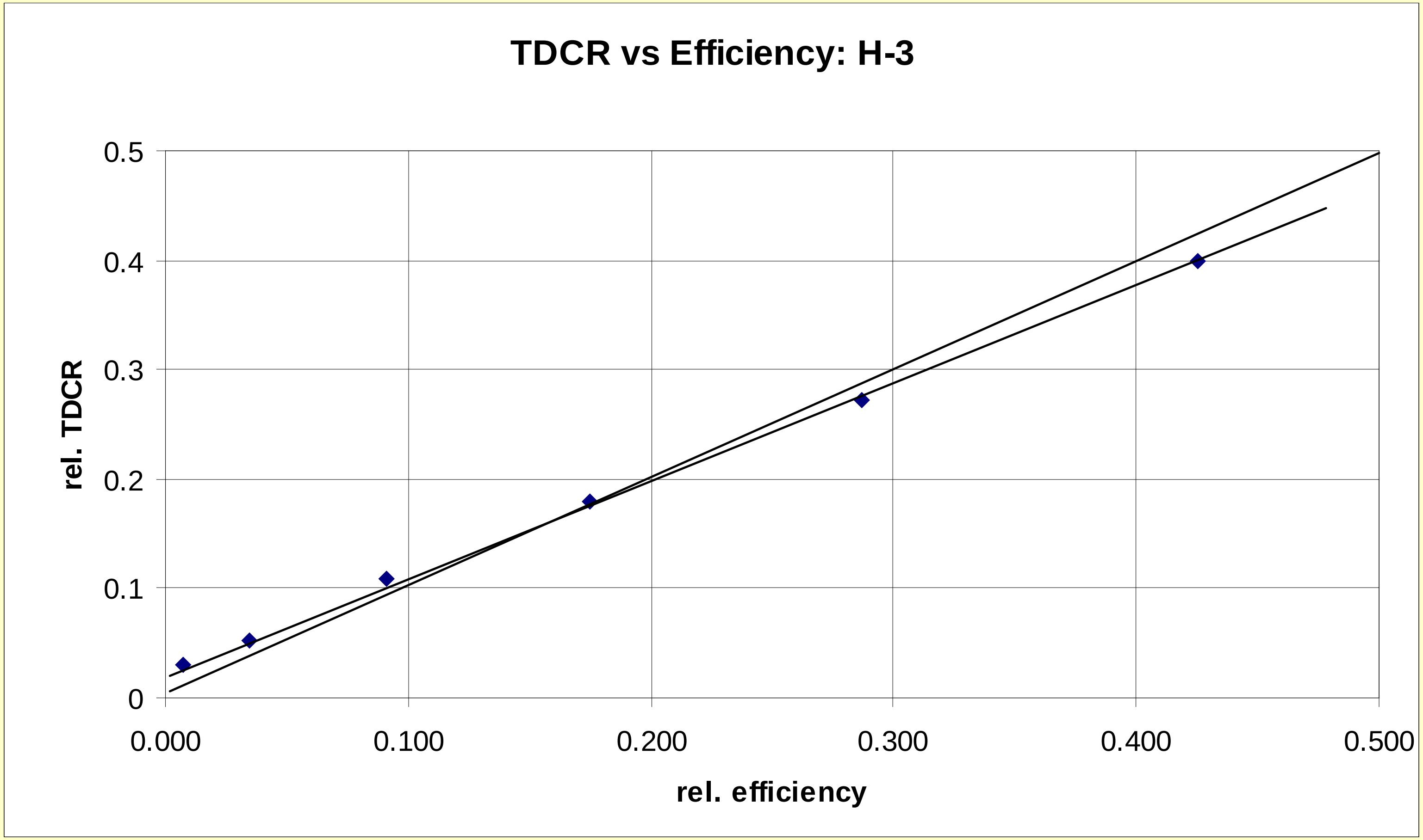
- LSC measurements using pure β-emitting isotopes: ^{3}H, ^{63}Ni, ^{14}C, ^{36}Cl and ^{90}Sr/^{90}Y (isotopes in the order of increasing β-energy)

- Presentation of unquenched vs. quenched data

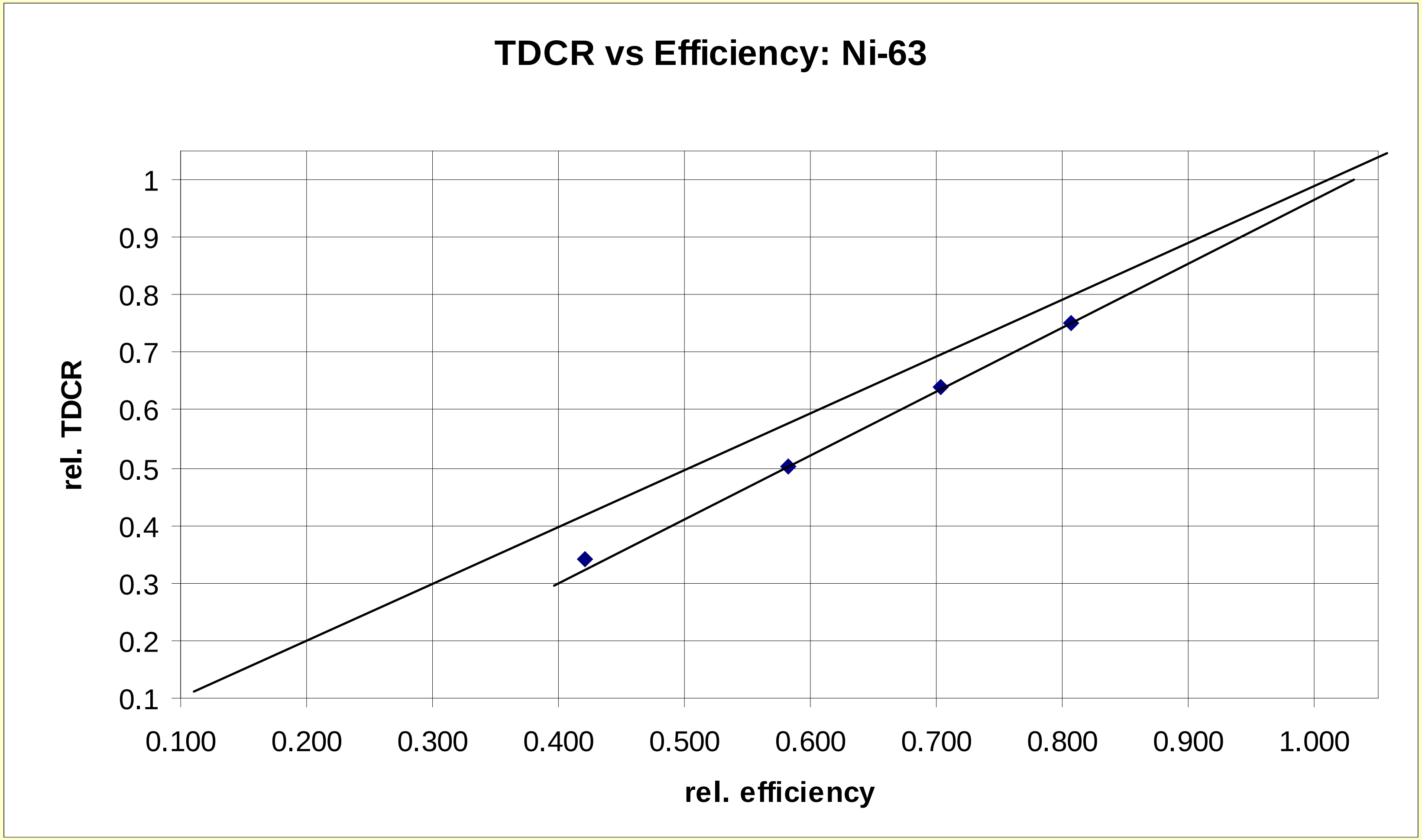
TDCR vs. Efficiency: all isotopes



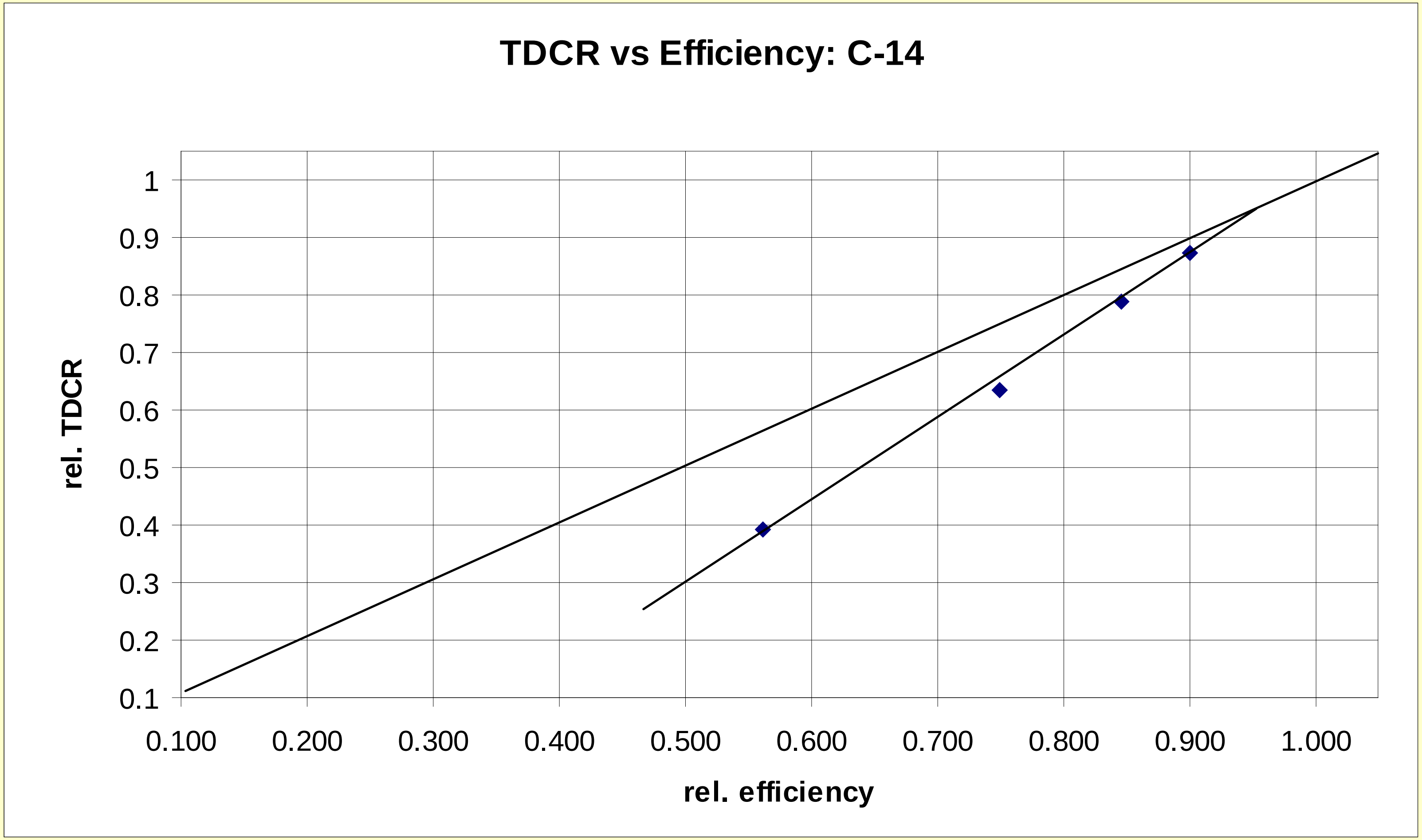
Tritium: ^{3}H (E_{max}: 18.6 keV)



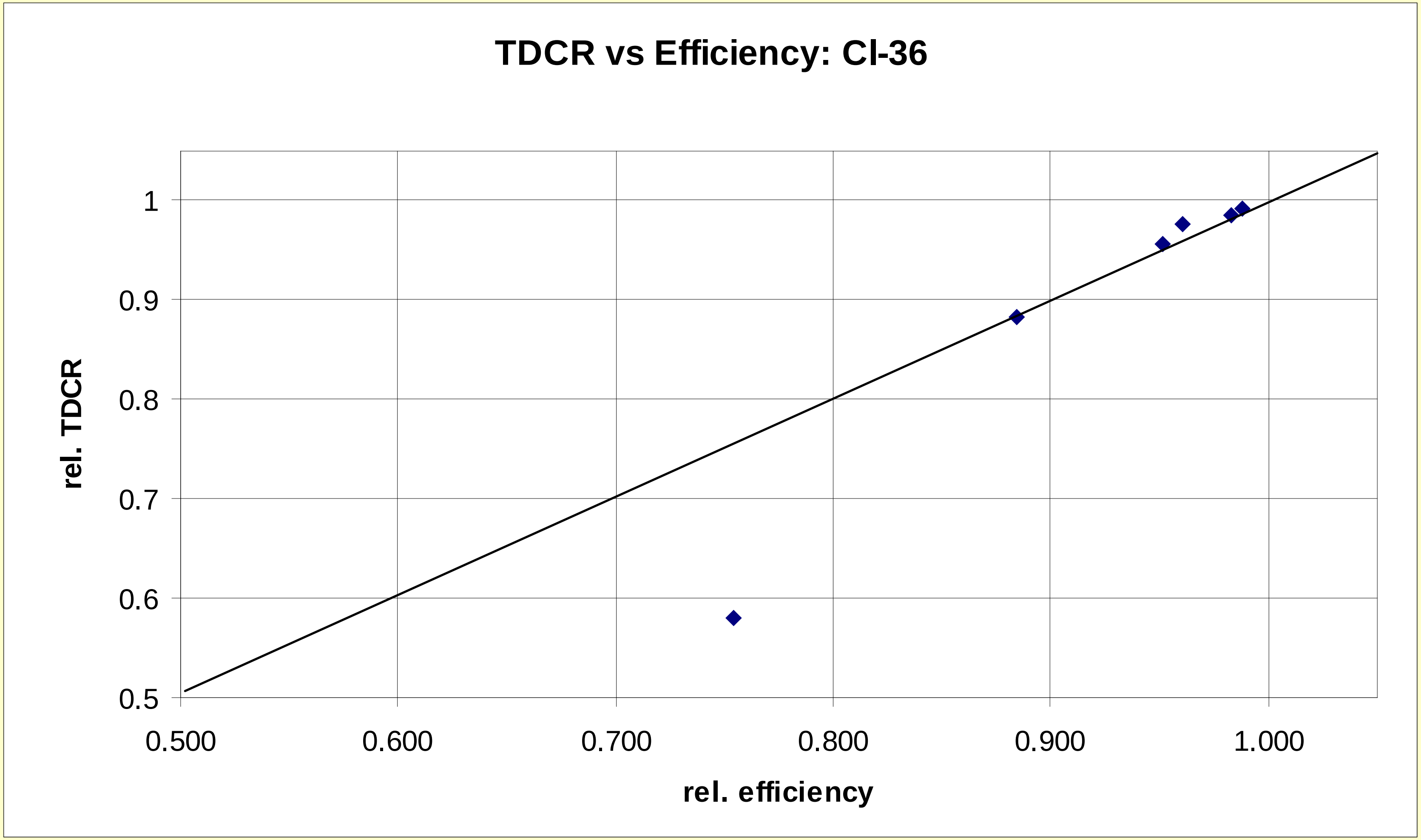
^{63}Ni (E_{max}: 65.9 keV)



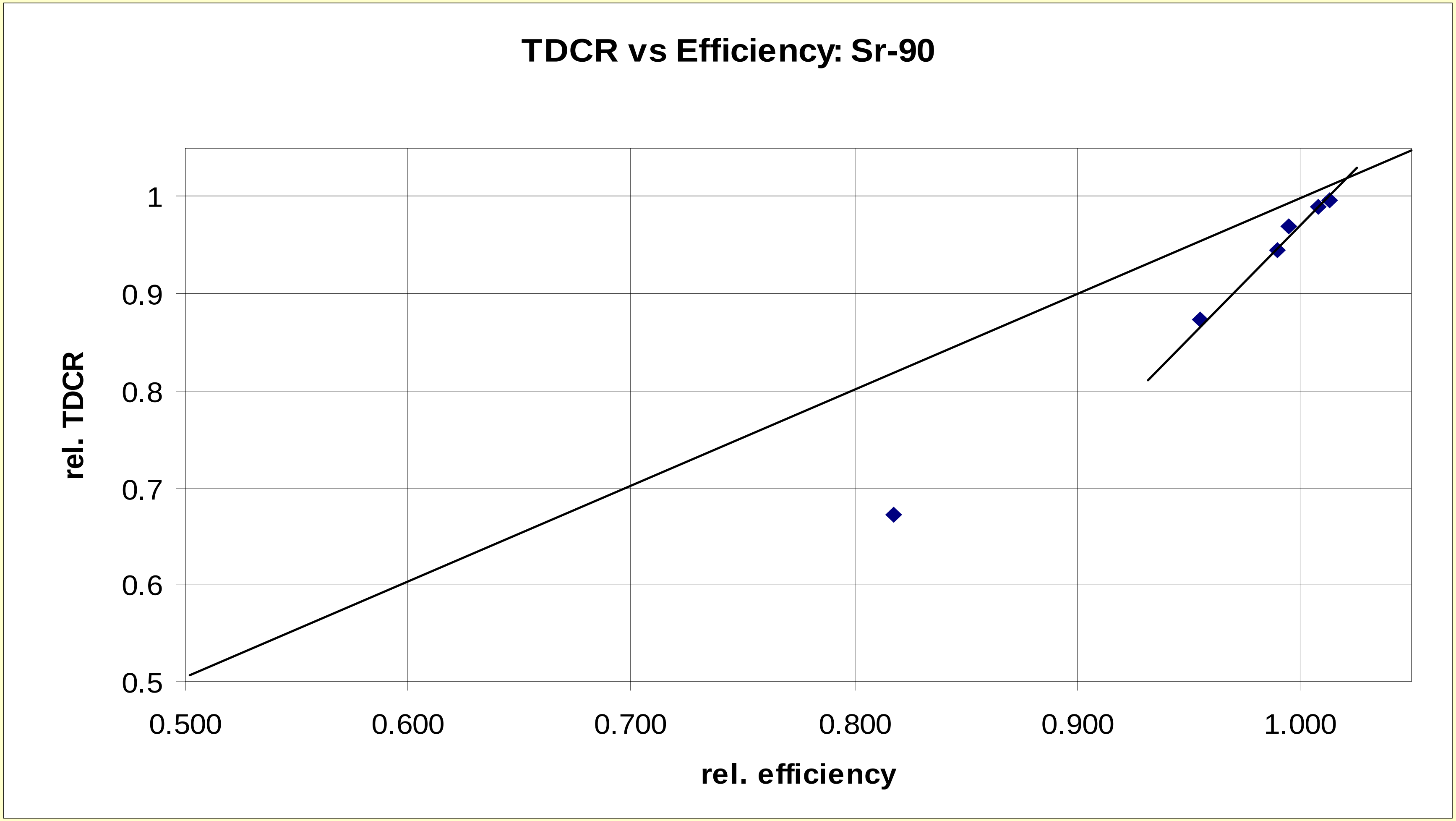
Radiocarbon: ^{14}C (E_{max}: 156 keV)



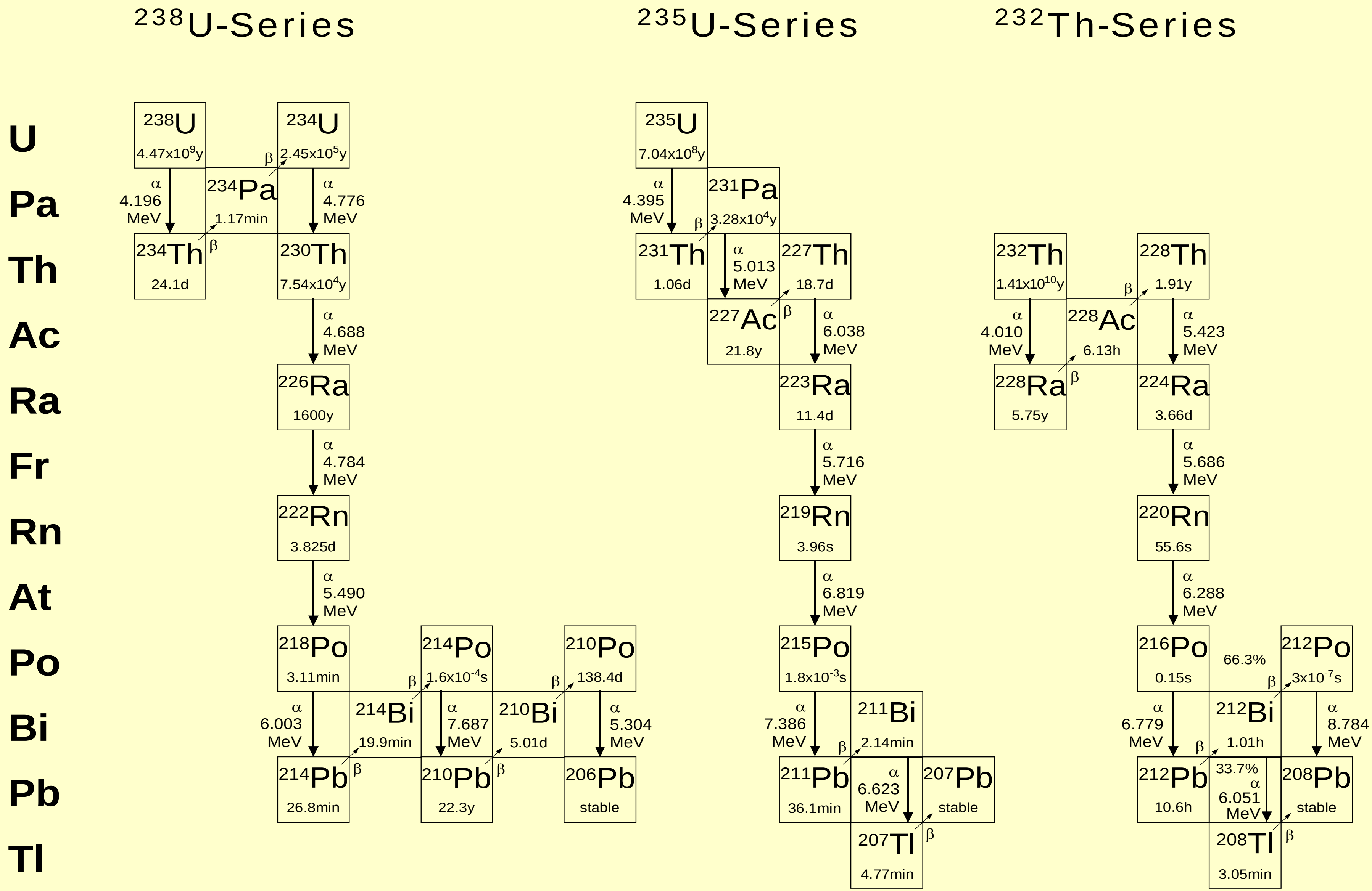
^{36}Cl: (E_{max}: 709 keV)



$^{90}Sr/^{90}Y$ (E_{max}: 546/2280 keV)



Environmental application: determination of ^{228}Ra, ^{226}Ra and ^{210}Pb in aqueous samples using TDCR measurement technique and α/β-separation


^{238}U-Series
^{235}U-Series
^{232}Th-Series
U
Pa
Th
Ac
Ra
Fr
Rn
At
Po
Bi
Pb
Tl
238U 4.47x10^9y
α 4.196 MeV
234Th 24.1d
β
234Pa 1.17min
β
234U 2.45x10^5y
α 4.776 MeV
230Th 7.54x10^4y
α 4.688 MeV
226Ra 1600y
α 4.784 MeV
222Rn 3.825d
α 5.490 MeV
218Po 3.11min
α 6.003 MeV
214Pb 26.8min
β
214Bi 19.9min
β
214Po 1.6x10^-4s
α 7.687 MeV
210Pb 22.3y
β
210Bi 5.01d
β
210Po 138.4d
α 5.304 MeV
206Pb stable
235U 7.04x10^8y
α 4.395 MeV
231Th 1.06d
β
231Pa 3.28x10^4y
α 5.013 MeV
227Ac 21.8y
β
227Th 18.7d
α 6.038 MeV
223Ra 11.4d
α 5.716 MeV
219Rn 3.96s
α 6.819 MeV
215Po 1.8x10^-3s
α 7.386 MeV
211Pb 36.1min
β
211Bi 2.14min
α 6.623 MeV
207Tl 4.77min
β
207Pb stable
232Th 1.41x10^10y
α 4.010 MeV
228Ra 5.75y
β
228Ac 6.13h
β
228Th 1.91y
α 5.423 MeV
224Ra 3.66d
α 5.686 MeV
220Rn 55.6s
α 6.288 MeV
216Po 0.15s
α 6.779 MeV
212Pb 10.6h
β
212Bi 1.01h
66.3%
β
212Po 3x10^-7s
α 8.784 MeV
33.7%
α 6.051 MeV
208Tl 3.05min
β
208Pb stable

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

$$^{232}Th \xrightarrow{\alpha:\ 1.40\cdot 10^{10}\,a} {}^{228}Ra \xrightarrow{\beta:\ 5.76\cdot 10^{0}\,a} {}^{228}Ac \xrightarrow{\beta:\ 6.13\ h} {}^{228}Th + daugthers$$

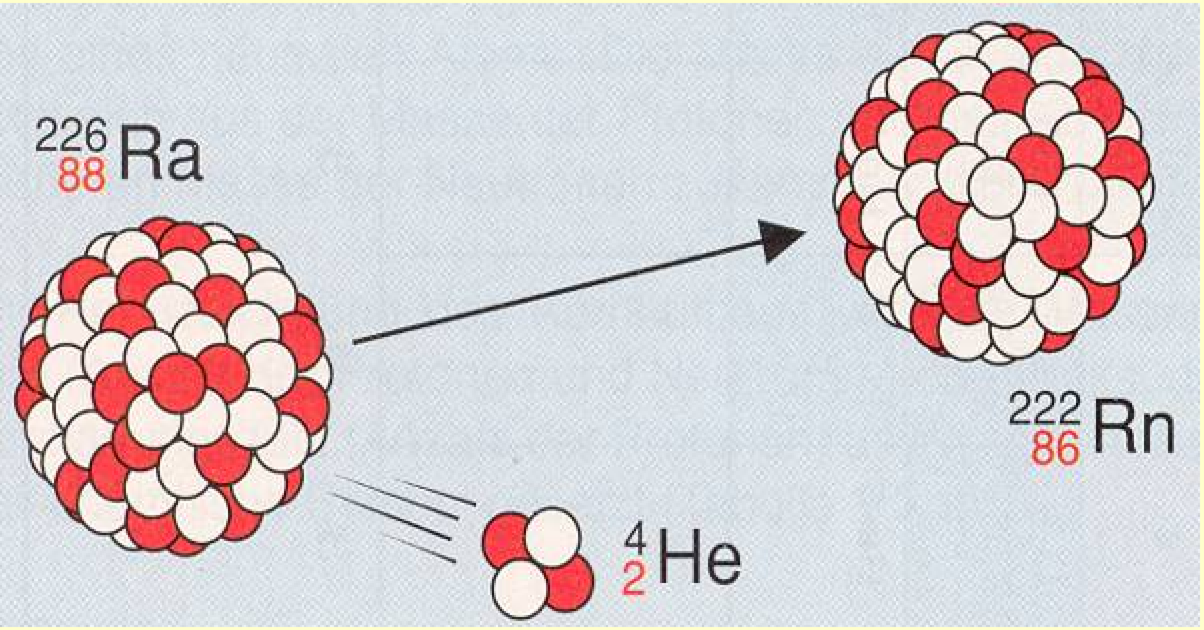
$$^{228}Th \xrightarrow{\alpha:\ 1.91\cdot 10^{0}\,a} {}^{224}Ra \xrightarrow{\beta:\ 3.66\ \ d} {}^{220}Rn \xrightarrow{\alpha:\ 55.6\ s} {}^{216}Po + daugthers$$

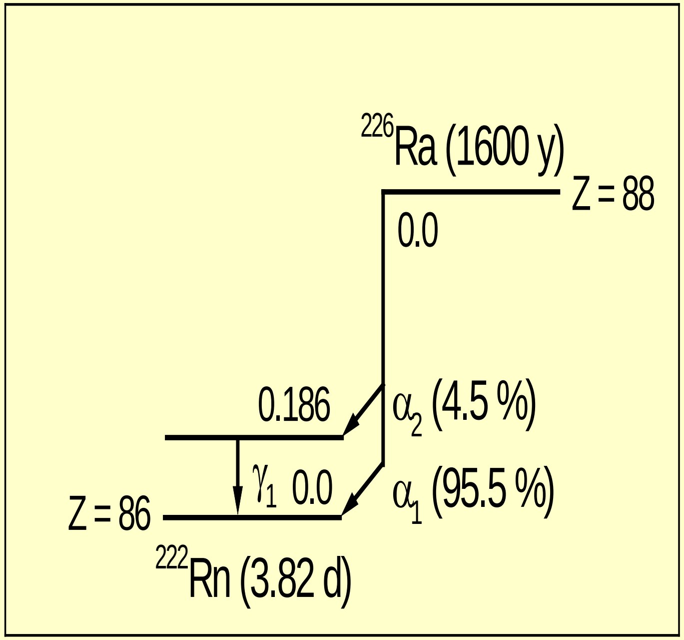
$$^{230}Th \xrightarrow{\alpha:\ 7.54\cdot 10^{4}\,a} {}^{226}Ra \xrightarrow{\alpha:\ 1.60\cdot 10^{3}\,a} {}^{222}Rn \xrightarrow{\alpha:\ 3.82\,d} {}^{218}Po + daugthers$$

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 prognies)
- Beta-emitter: Pb-210 (with ingrowing Bi-210)
- Alpha-emitter: Po-210

Schematic view of radioactive transformation





$$^{226}_{88}Ra \rightarrow ^{222}_{86}Rn + ^{4}_{2}He + 4.78\,MeV$$

relevant isotopes in continental water and their measurement methods at PSI

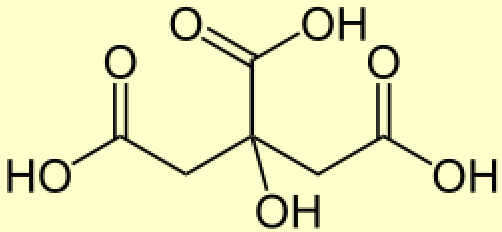
radionuclide	analytical technique
^{234}U, (^{235}U), ^{238}U	U/TEVA separation, electro-deposition, α-spectrometry
^{226}Ra, ^{228}Ra, ^{210}Pb	filtration (RadDisc), OptiPhase Hisafe3 cocktail, LSC
^{210}Po	spontaneous deposition on silver disc, α-spectrometry

Relationship parent / daughter

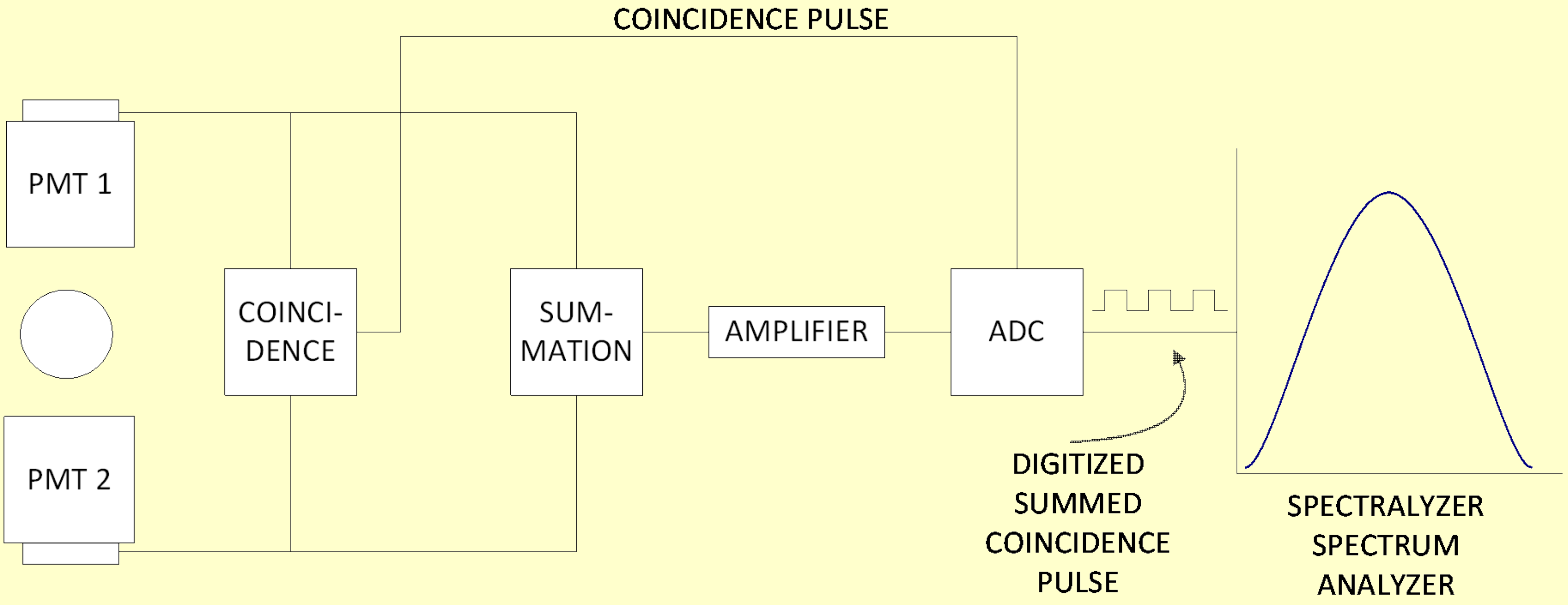
parent isotope	half-life parent	ingrowing daughter	half-life daughter
^{210}Pb (β)	22.3 years	^{210}Bi (β)	6.02 days
^{226}Ra (α)	1602 years	^{222}Rn (α)	3.82 days
^{228}Ra (β)	5.76 years	^{228}Ac (β)	6.13 hours

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

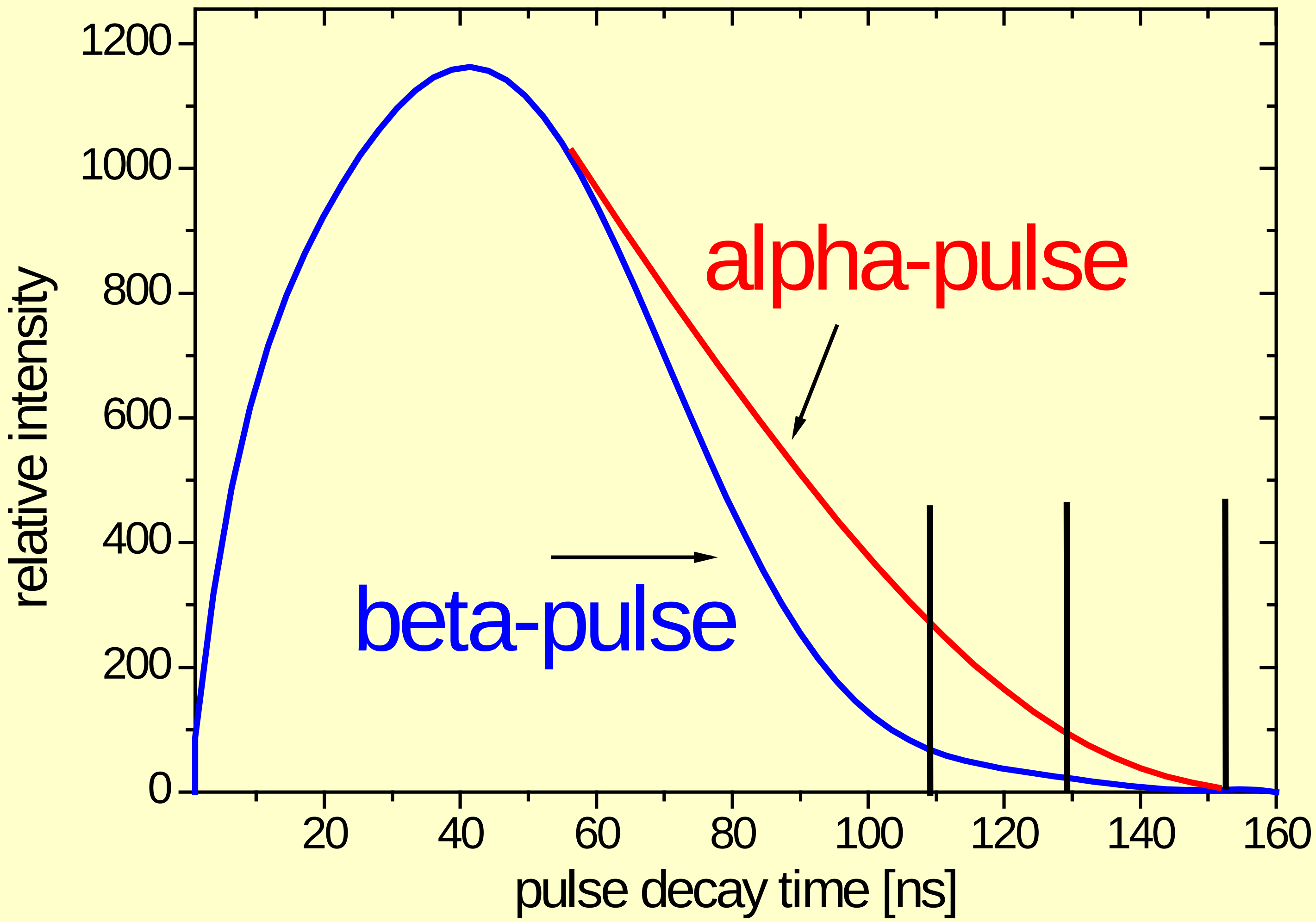
- Filtration of the sample (2 liter) through 3 Empore RadDisc (Mn-oxide impregnated) membrane filters
- Elution of Pb with Diammonium Hydrogen Citrate
- Elution of Ra with alkaline Na-EDTA solution
- Measuring via LSC with optimized α/β-discrimination



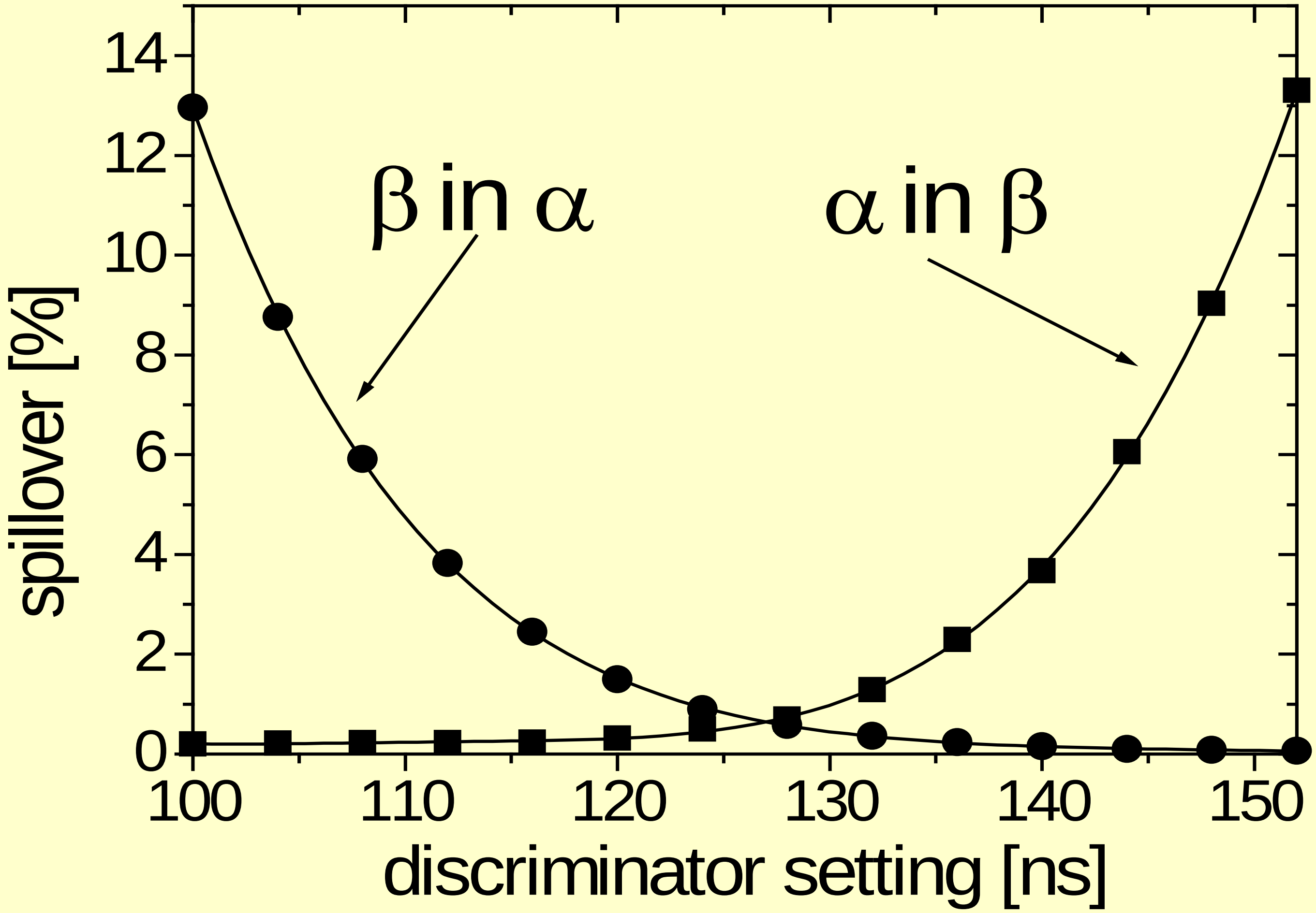
Classical two photomultiplier LS electronic set-up



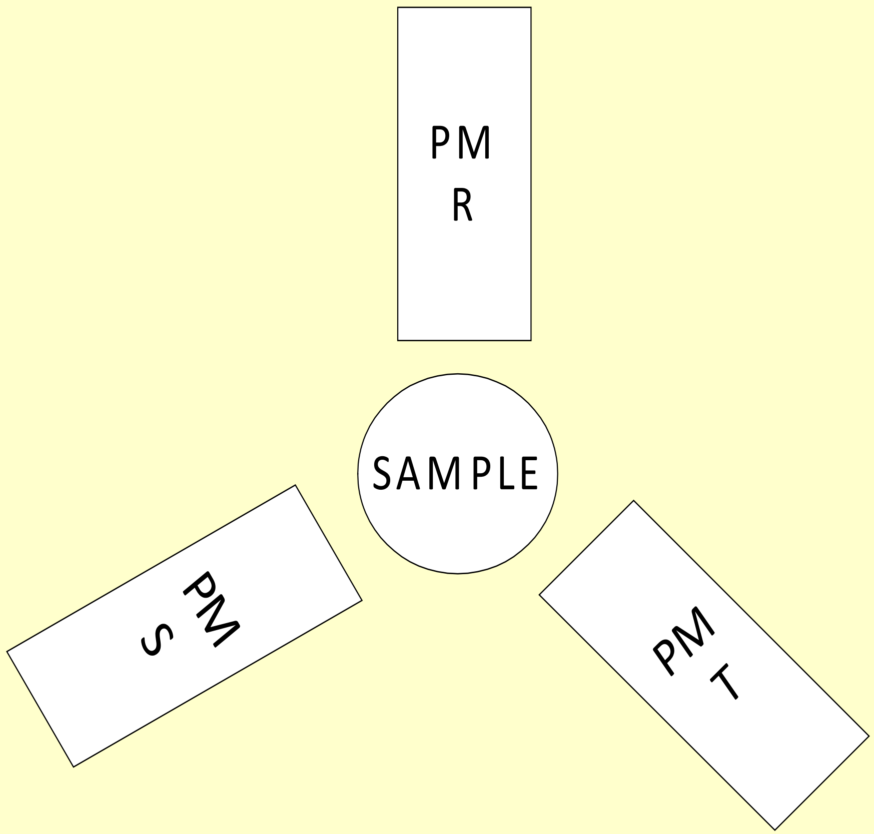
Pulse shape α/β discrimination



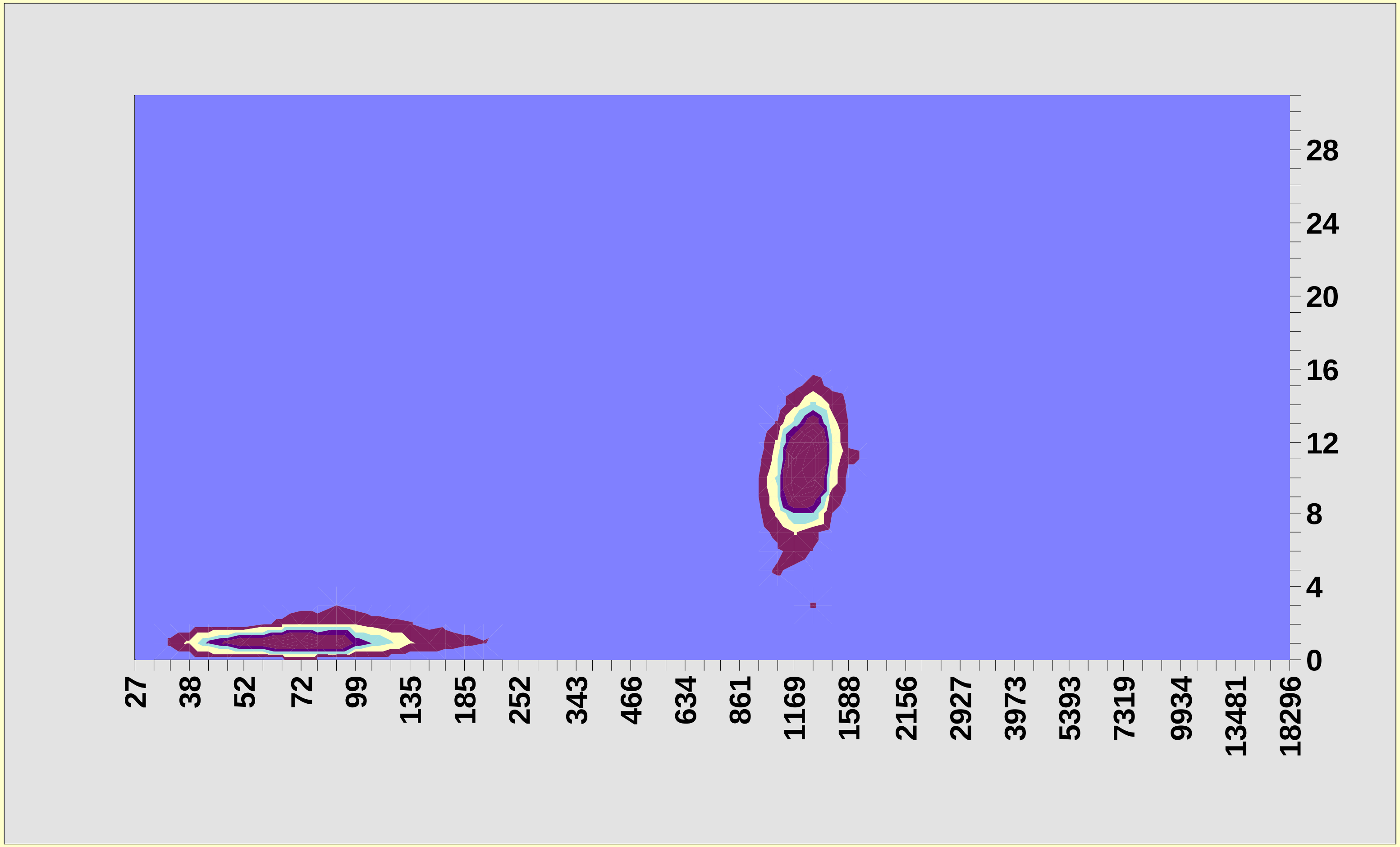
Spill-over α/β determination



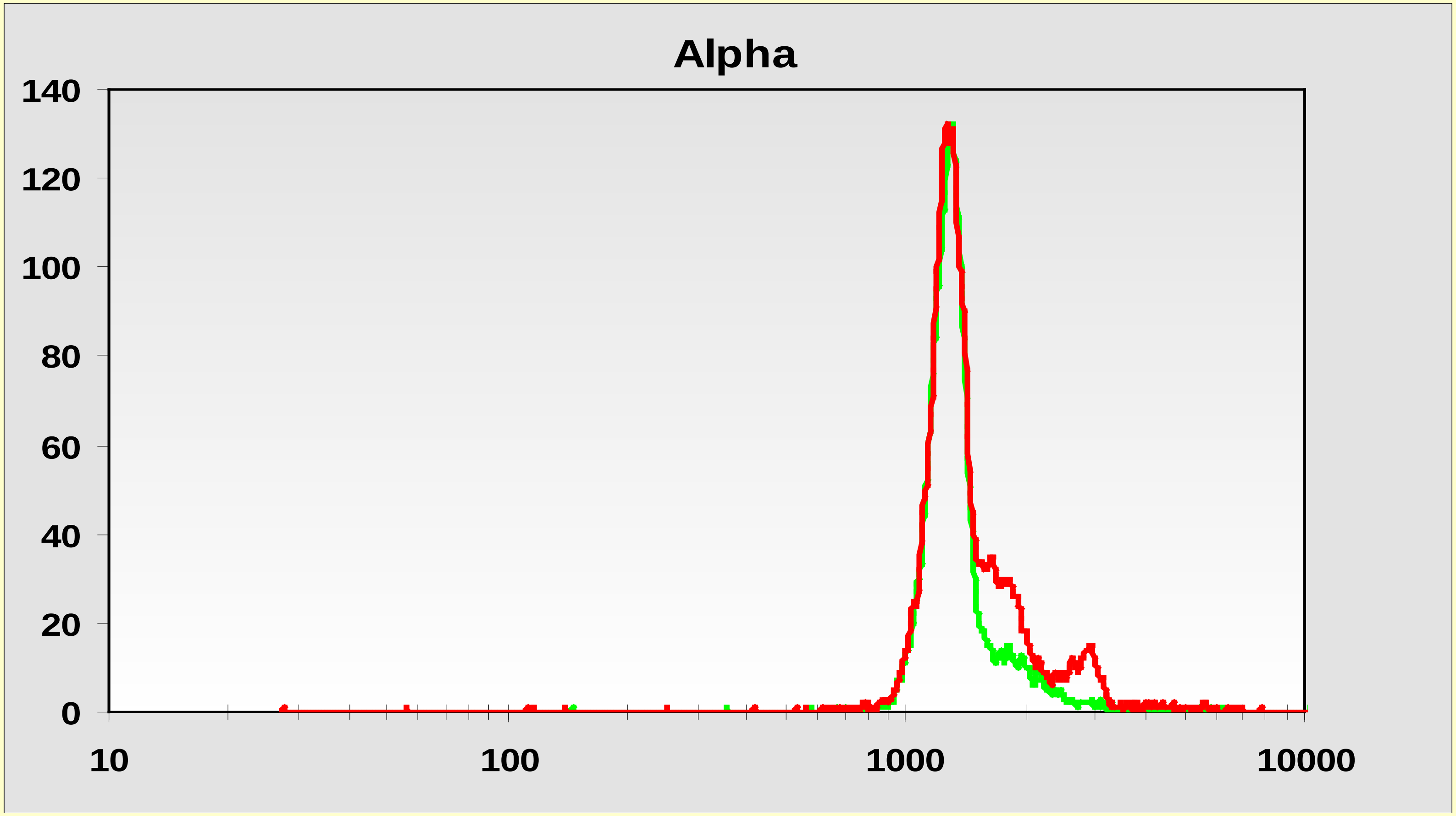
The triple coincidence to double coincidence ratio (TDCR) counting technique



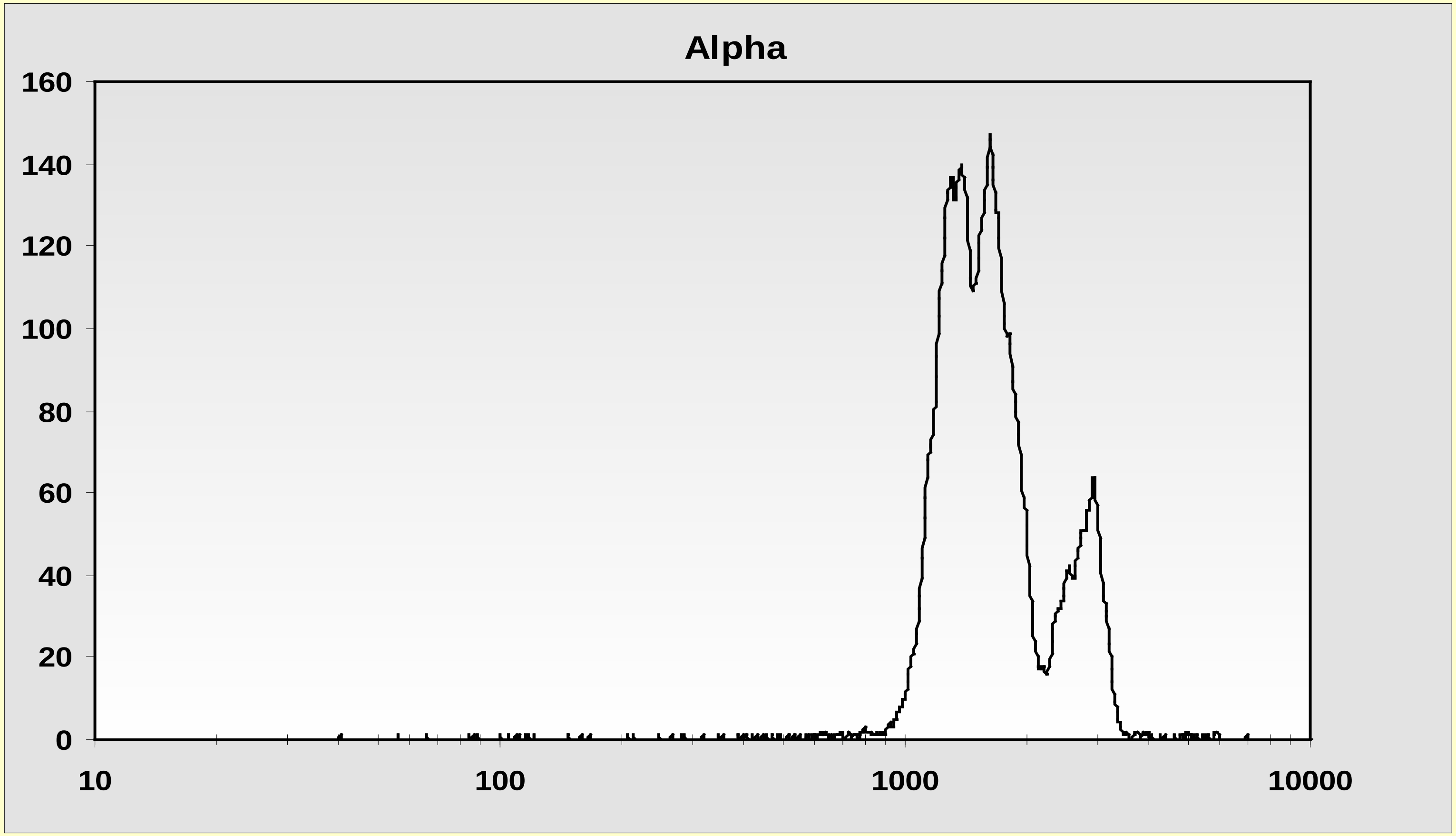
Pulse Length Index (PLI) discrimination with HIDEX SL 300



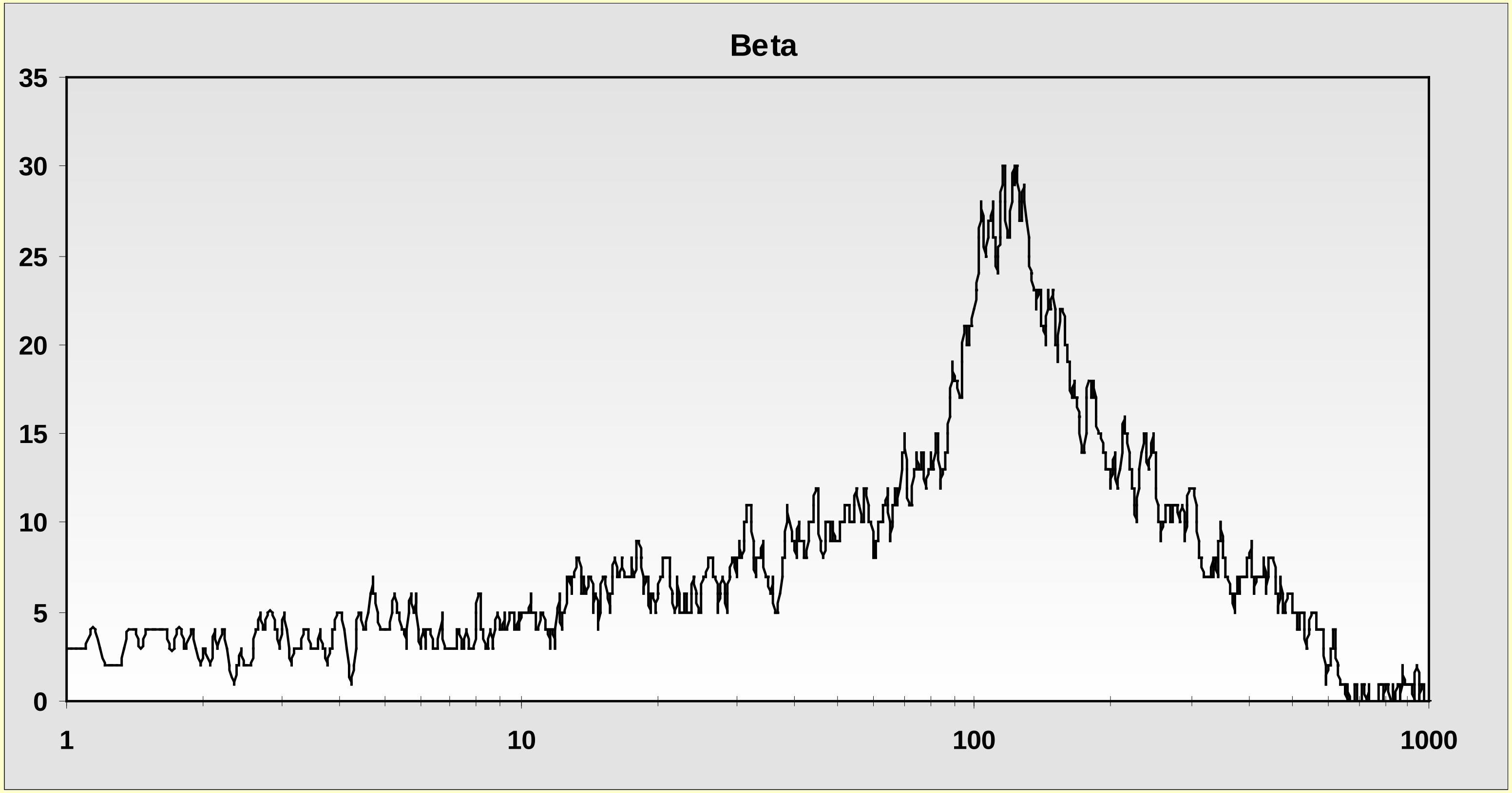
α-spectrum of ^{226}Ra with ingrowing daughters 2 h and 8 h after separation using HIDEX 300 SL LSC



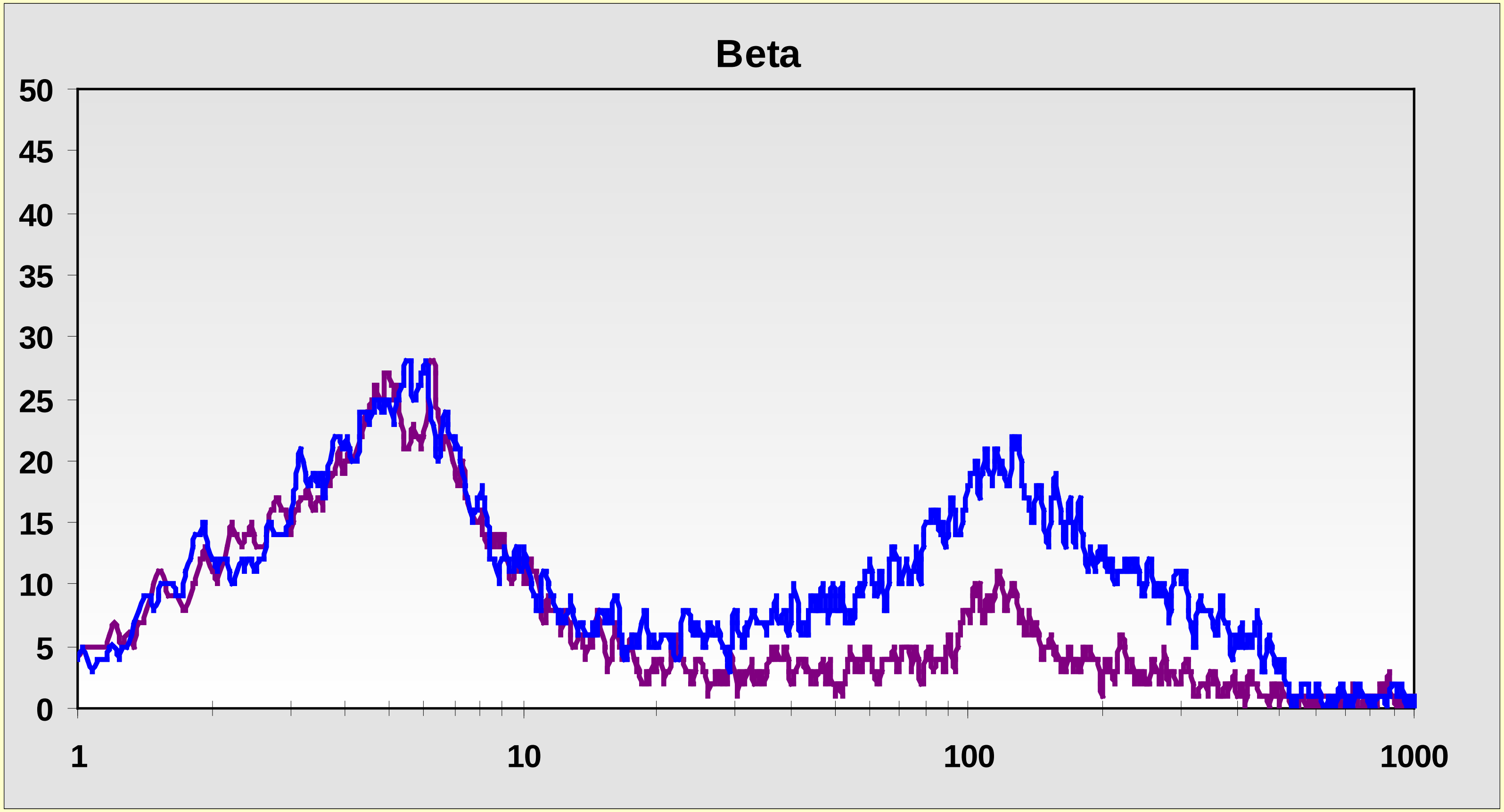
α-spectrum of ^{226}Ra with ingrowing daughters obtained 6 days after separation



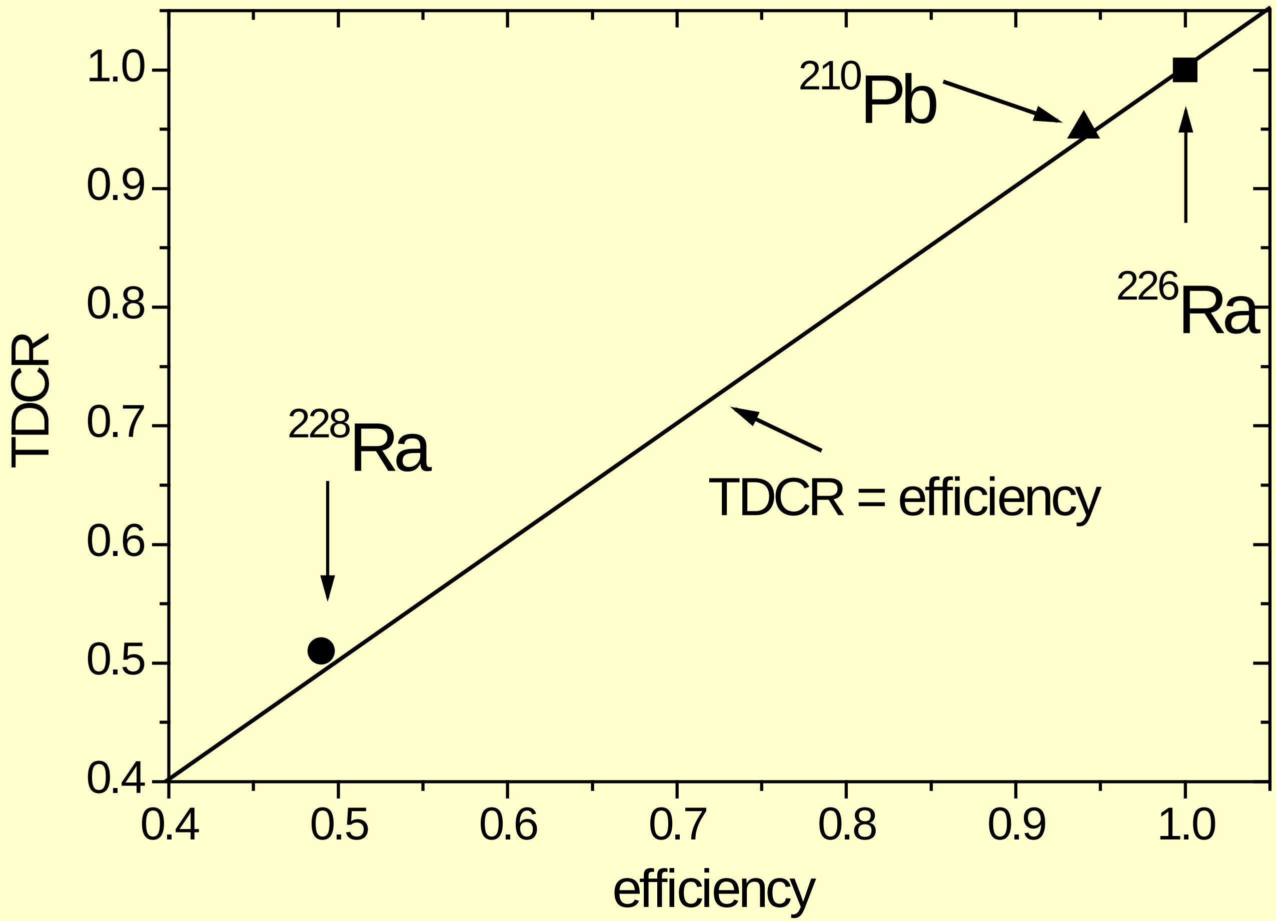
β-spectrum of ^{214}Bi/^{214}Pb obtained 6 days after separation (^{226}Ra/^{222}Rn decay series products)



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



TDCR vs. Efficiency using high purity radionuclide standard solutions



long lived mother – short lived daughter relationship

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

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

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

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

LS-spectrum interference correction

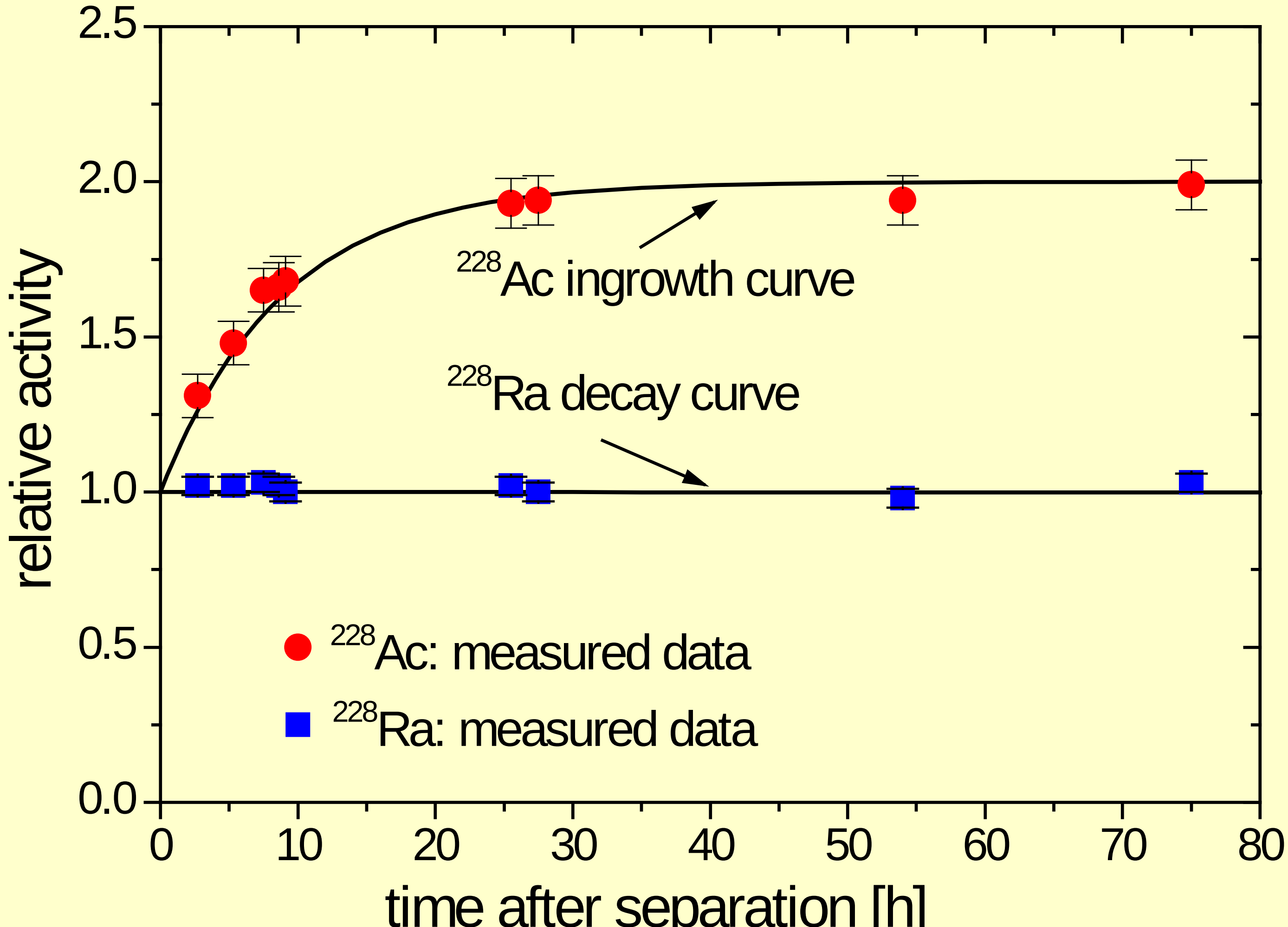
$$R_{Ac-228} = \left(\frac{\varepsilon^{A}}{\varepsilon^{B}} \right)_{Ac-228}$$

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

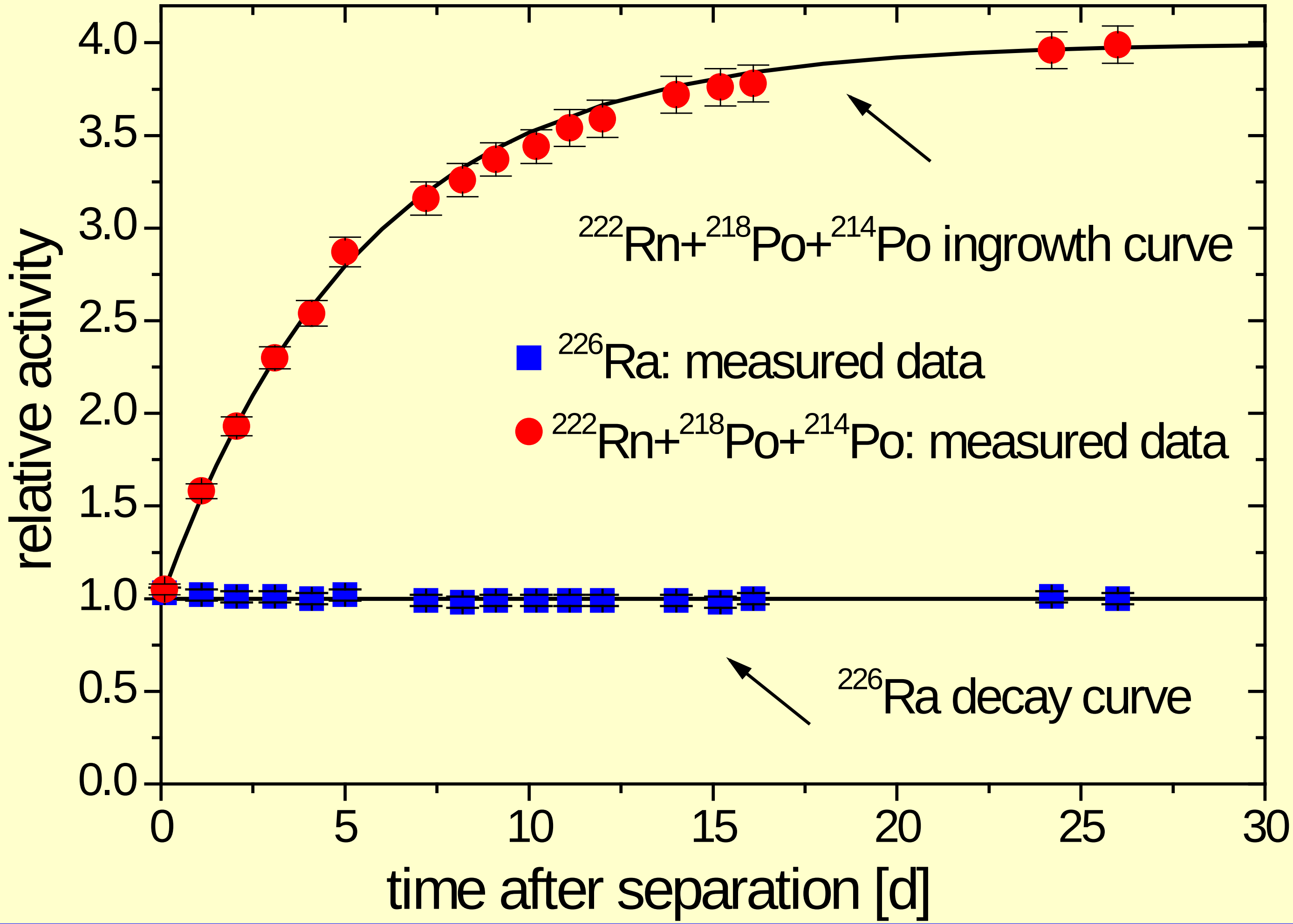
$$A_{Ra-228} = \frac{r_{n,cor}({}^{228}Ra)}{\varepsilon^{A}_{Ra-228}}$$

$$A_{Ac-228} = \frac{r^{B}_{n}({}^{228}Ac)}{\varepsilon^{B}_{Ac-228}}$$

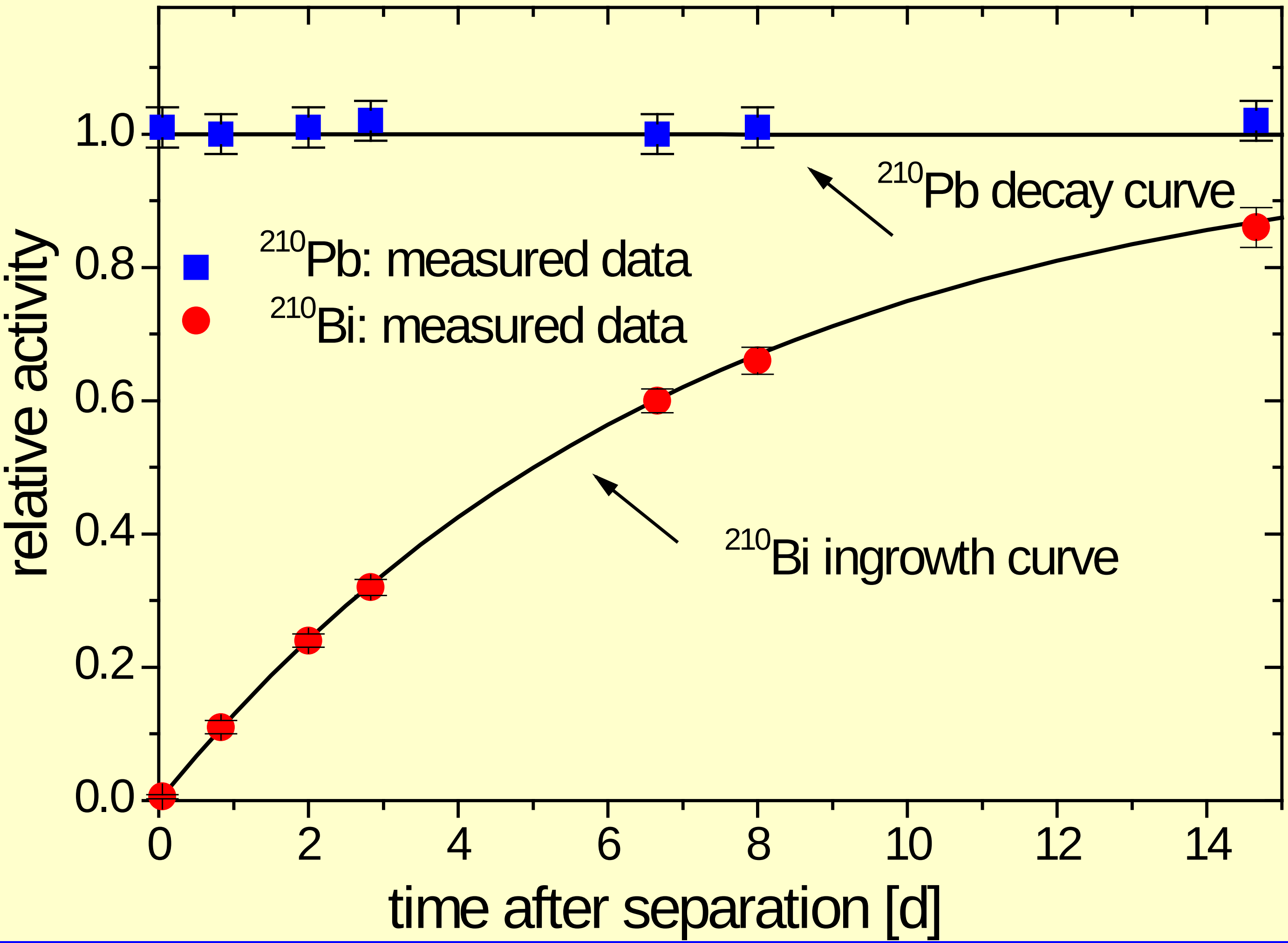
Comparison of measured ^{228}Ra and ^{228}Ac activities with calculated decay/ingrowth curves



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



Comparison of measured ^{210}Pb and ^{210}Bi activities with calculated decay/ingrowth curves



Minimizing the interferences: ^{210}Pb

- ^{210}Pb: start counting not before 3 hours after separation because ^{226}Ra unsupported progeny products (i.e. ^{214}Pb/^{214}Po) have to decay prior to the measurement (β-spectrum interferences)

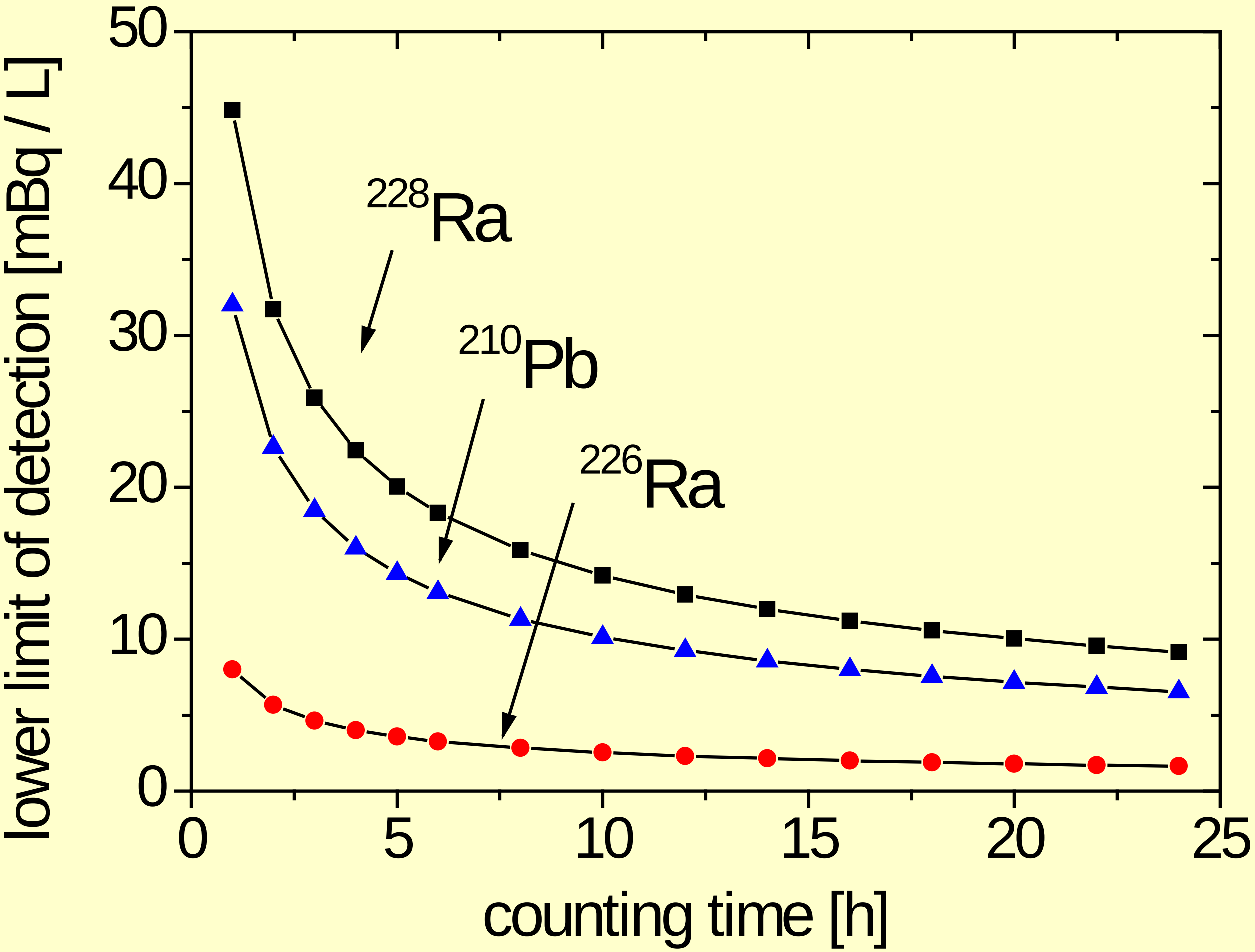
Minimizing the interferences: ^{226}Ra

- ^{226}Ra: ^{224}Ra [($t_{1/2}$) = 3.66 days] and its short lived progeny products should have been decayed prior to measurement, i.e. the sampled water should set aside for about 10 days before radiochemical separation (support from ^{228}Th has to be checked !). The same holds for ^{210}Pb (interference with 10 h half live decaying pure β-decaying ^{212}Pb)

Minimizing the interferences: ^{228}Ra

- The samples should be measured during the first 24 hours after chemical separation, i.e. when the ingrowth of the ^{226}Ra/^{222}Rn couple decay products (i.e. ^{214}Pb, ^{214}Bi) is not of large concern. These isotopes interfere strongly with the β-spectrum of ^{228}Ac, which has to be taken to correct the low energy spectrum of ^{228}Ra

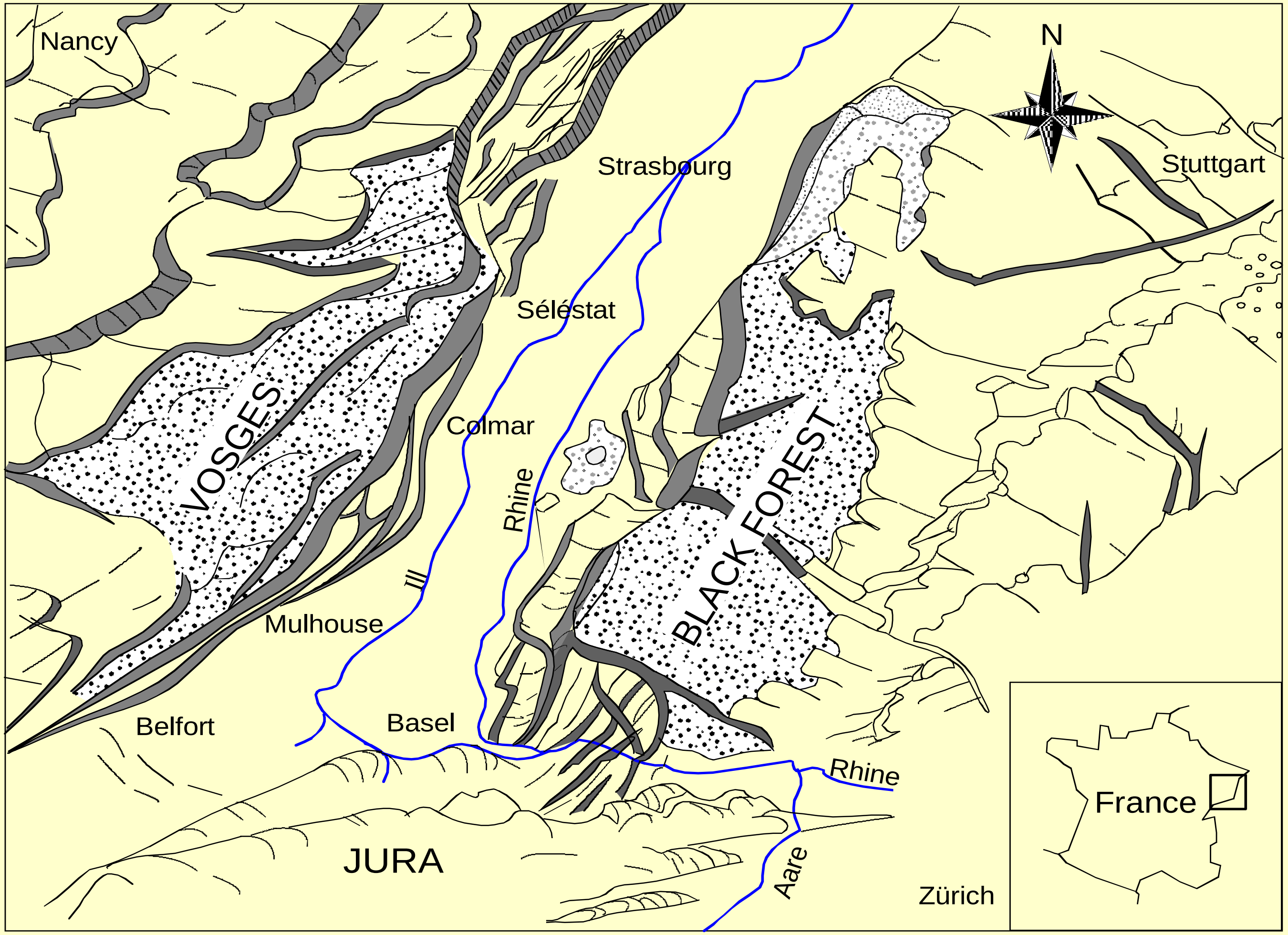
$$A^* = k_{1-\alpha} \cdot \frac{1}{\varepsilon \cdot V_s} \cdot \sqrt{2} \cdot \sqrt{\frac{r_0}{t_m}}$$



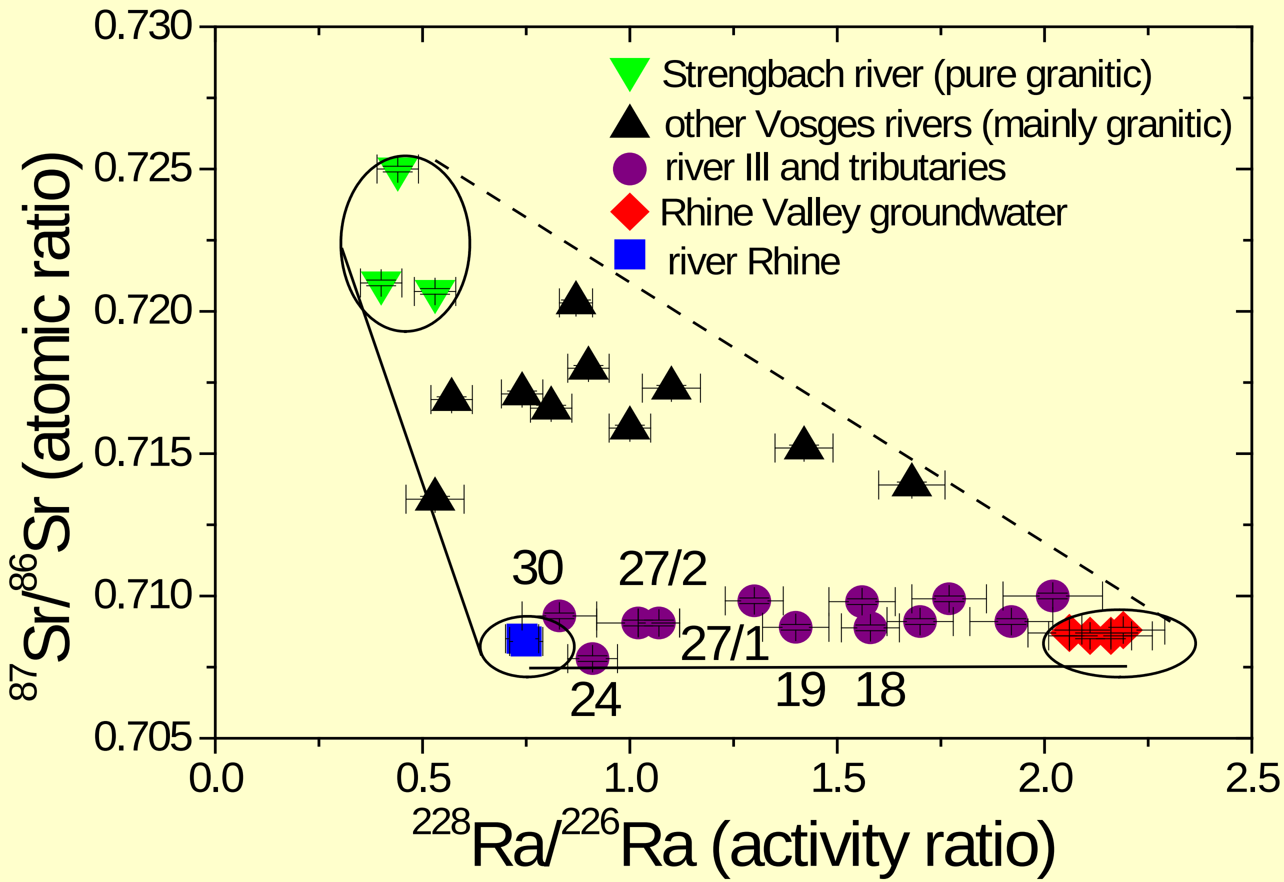
LSC detection limits, 2 l aliquot, quantitative adsorption on RadDisc filter, counting time 6 h

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

Field study: use of Ra-isotopes as natural tracers: isotopic signatures for determining mixing between waters from different source regions



Calculating mixing/exchange between river and ground water using $^{228}Ra/^{226}Ra$ and $^{87}Sr/^{86}Sr$



TDCR blank correction

For linear systems the general mass balance equation holds for mixtures of two components M_1 and M_2 with the concentrations C_1 und C_2

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

This relationship can be directly transferred to TDCR-measurements, i.e. the „true“ or net-TDCR ($TDCR_n$) value has to be obtained via the brut-TDCR („mixture“) ($TDCR_b$) and the TDCR-result of a blanc measurement ($TDCR_0$) .

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

with: $r_n = r_b - r_0$

It 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 β-emitter holds: $TDCR_n \approx \varepsilon_n$

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

It results for the activity calculation

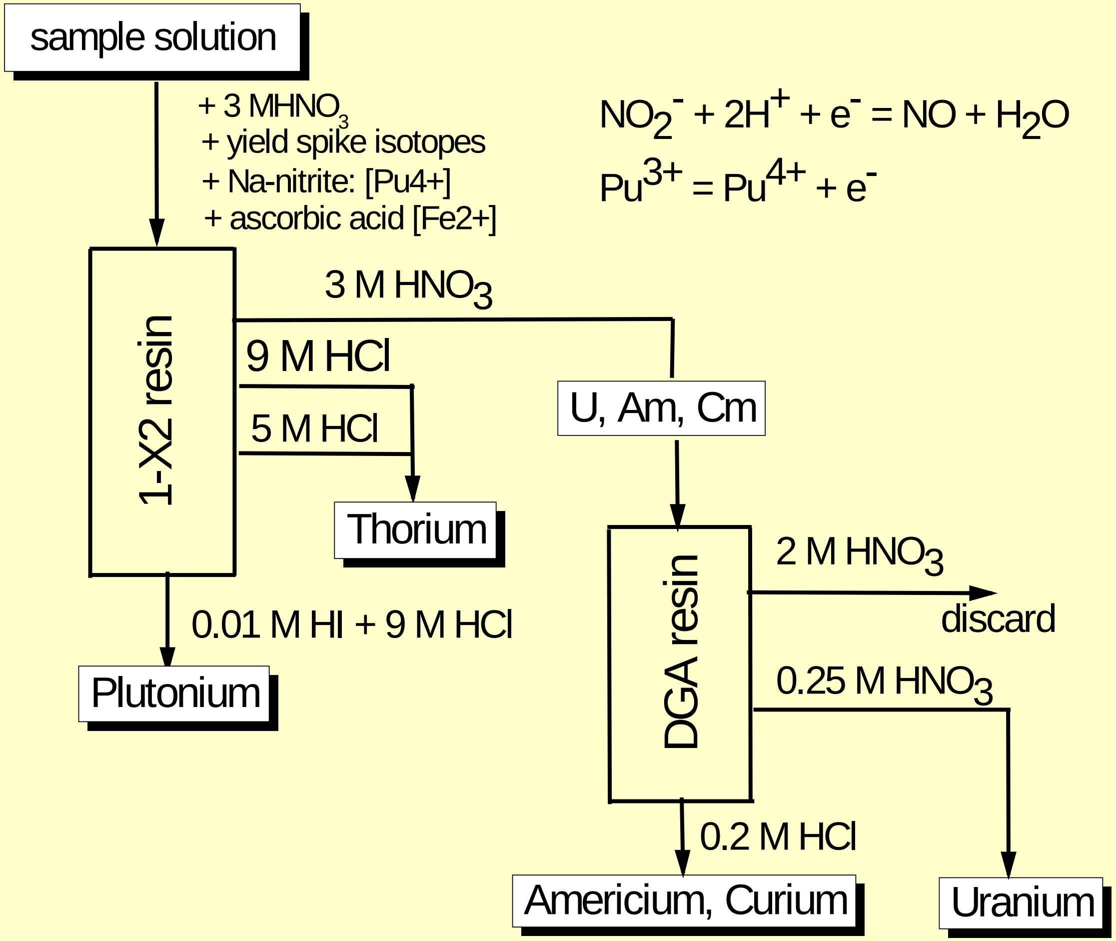
$$A = \frac{(r_b - r_0)^2}{r_b \cdot TDCR_b - r_0 \cdot TDCR_b}$$

Simultaneous determination of ^{241}Pu (β-emitter) and ^{238}Pu, ^{239}Pu+^{240}Pu (α-emitter) in nuclear materials

- Application of extraction chromatography: adsorption onto BioRad 1X2 anion exchange resin
- Elution of the Pu-fraction using a HI/HCl acidic reduction solution
- Electrodeposition onto a stainless steel planchet, α-spectrometric measurement
- Dissolution from the sample planchet, cocktail preparation
- α/β-measurement via LSC

				^{241}Am α 433 a 5.5 MeV		**^{243}Am** α 7370 a 5.3 MeV
^{236}Pu α 2.8 a 5.8 MeV		**^{238}Pu** α 88 a 5.5 MeV	**^{239}Pu** α $2.4\ 10^4$a 5.2 MeV	**^{240}Pu** α 6550 a 5.2 MeV	**^{241}Pu** β 14.4 a 0.021 MeV	**^{242}Pu** α $3.7\ 10^5$ a 4.9 MeV

Actinide analysis: 1-X2 / DGA separation



$NO_2^- + 2H^+ + e^- = NO + H_2O$

$Pu^{3+} = Pu^{4+} + e^-$

redox reactions and equilibria

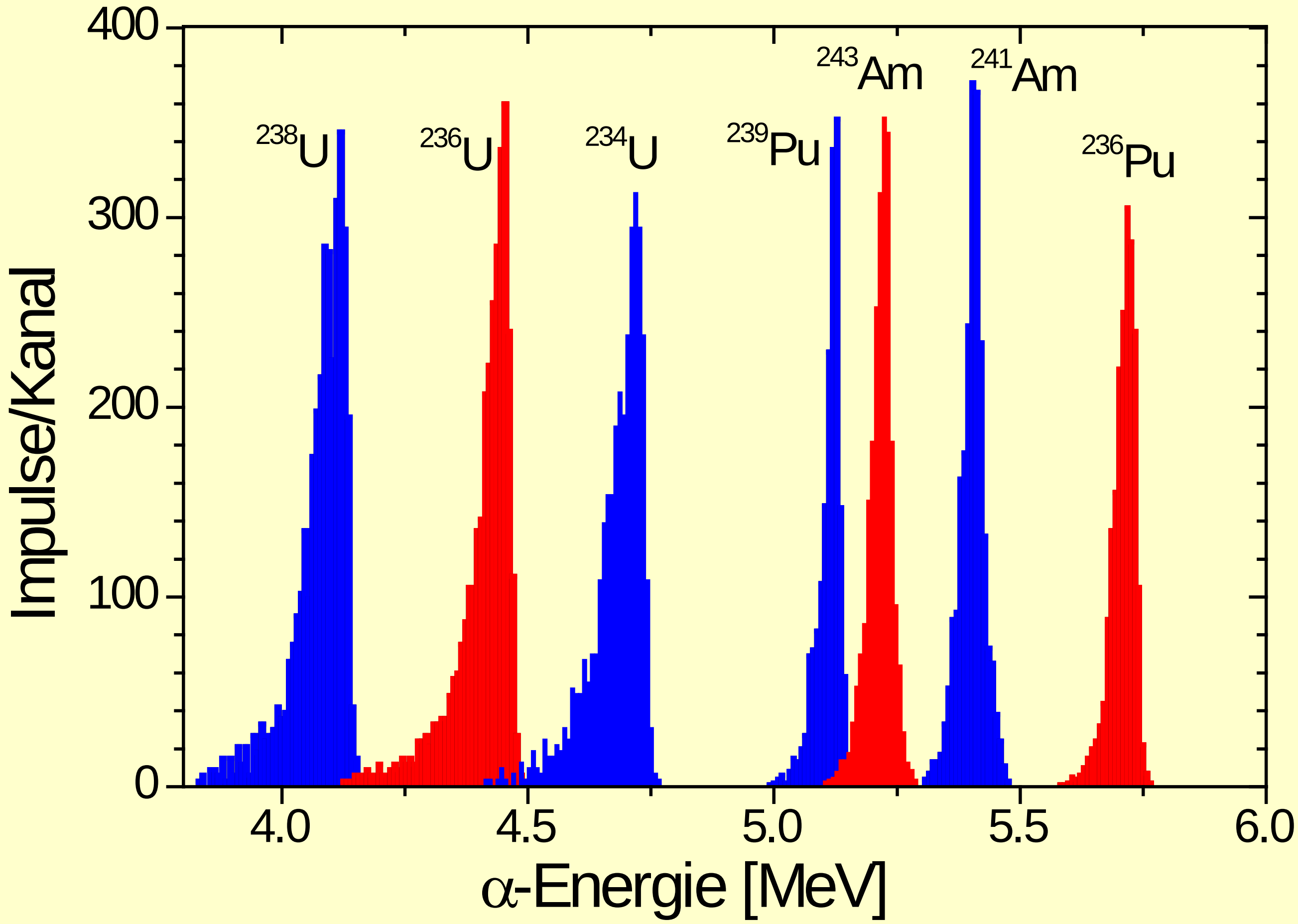
reduction of Pu(vi) to Pu(iii)

$$2I^{-} \rightarrow I_2^0 \uparrow + 2e^{-}$$

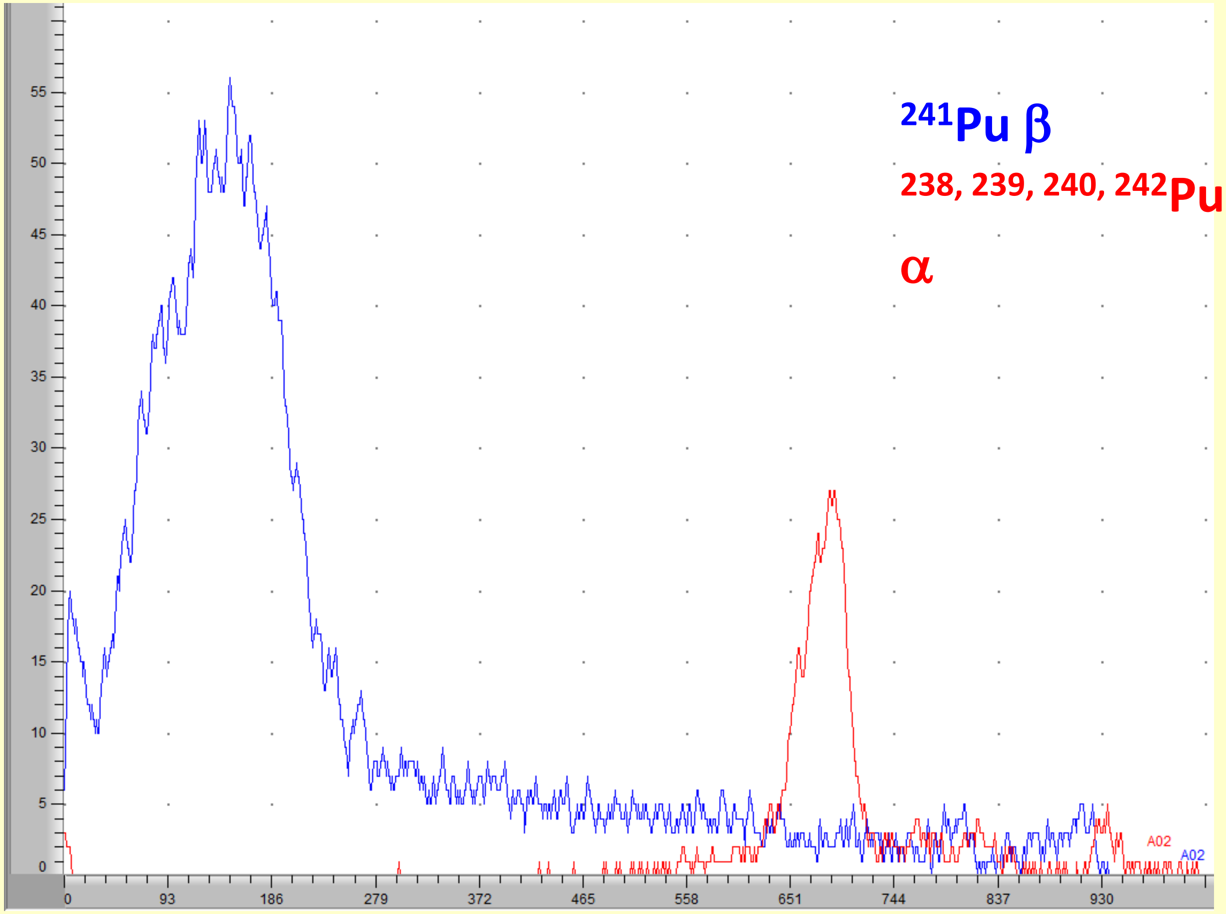
$$2Pu^{4+} + 2e^{-} \rightarrow 2Pu^{3+}$$

$$2I^{-} + 2Pu^{4+} \rightarrow I_2^0 \uparrow + 2Pu^{3+}$$

α-spectrum of U, Pu and Am (blue sample isotopes to be analyzed; red added spike isotopes)



a/b-LSC with optimized α/β separation (pulse index and energy), α-spill in β < 1%, β-spill in α < 0.1%



Conclusions

- TDCR measurement of non or weakly quenched samples yield sufficiently precise results for radionuclide analysis in the frame of decommissioning projects.
- Environmental application: LSC with optimized alpha/beta separation is a powerful tool to determine almost pure α-emitting ^{226}Ra besides weak β-emitting ^{228}Ra
- Determination of Pu-isotopes in materials from the nuclear fuel cycle: optimized α/β-separation yields precise results for measurement of pure beta emitting ^{241}Pu

Thank you for your attention