School of Nuclear Science and Technology

A method for ^{237}Np determination with LSC in the experiment of neptunium sorption onto bentonite

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OUTLINE OF THE TALK

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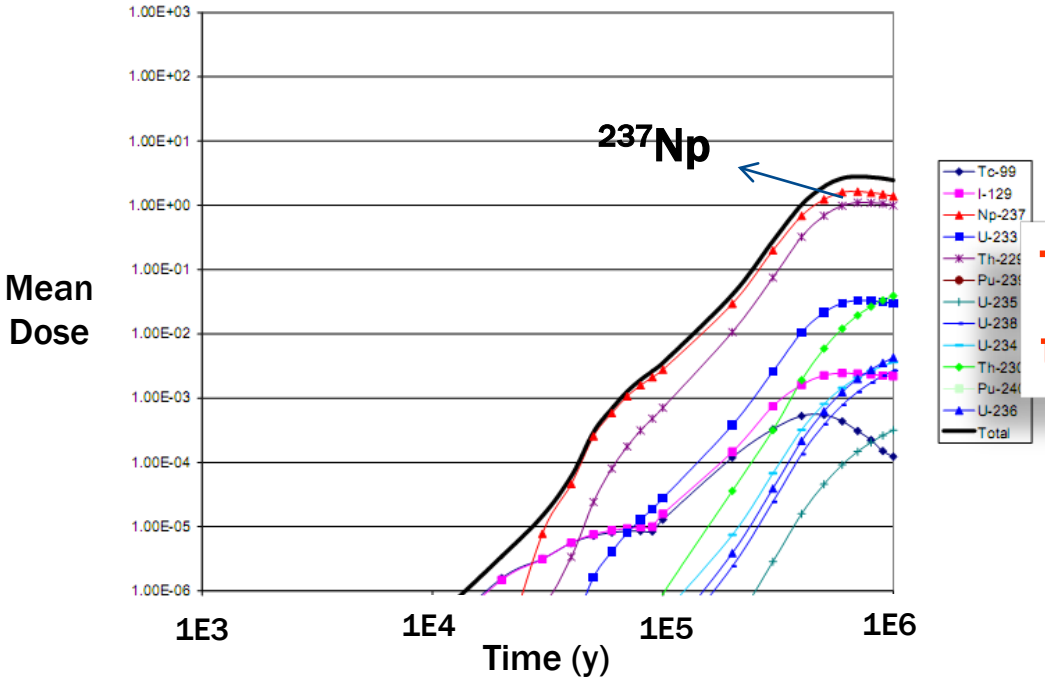
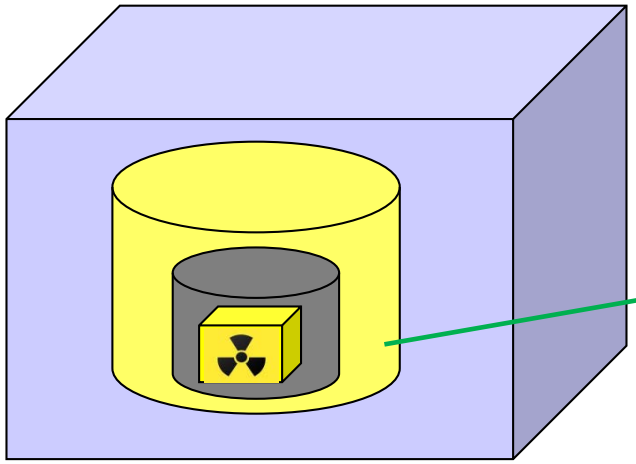
Introduction – Background

^{237}Np will be a major contributor to environmental radioactivity from the disposal of high- or intermediate-level radioactive waste because of its long half-life ($t_{1/2}$ = 2.14×10^6 yr), suspected high radiotoxicity and low affinity for many geological minerals. (usually present as the pentavalent NpO_2^+ cation under several environmental conditions)



The so-called “key nuclide” in the HLW disposal repository

Introduction – Background



- *Waste*
- *Metallic containers*
- *Buffer and backfill*
- *Natural barriers*

System of Multiple Barriers

However, determination of ^{237}Np is rather a complicated task because of its low specific activity and lack of a suitable yield tracer such as high purity ^{236}Np.

Introduction – Methods for determination of ^{237}Np

However,

- Both alpha and NAA methods require tedious chemical separations of analytes and long counting times. Both methods suffer from potential interferences from the presence of high levels of uranium, thorium, polonium, etc., in environmental samples, as well as the influence of self-adsorption.
- ^{239}Np tracer has a too short half-life ($T_{1/2}$ = 2.36 d).
- In PERALS system, a process of extraction is needed.
- Peak tailing of ^{238}U and molecular interferences (e.g. $^{235}U^{1}H^{2+}$, $^{236}U^{1}H^{+}$) in the method of ICP-MS.
- ……

Introduction – Determination by LSC

LSC is widely used in the field of radionuclide metrology, because of its numerous advantages over conventional techniques:

- Virtually 100% counting efficiency;
- simple sample preparation;
- Large sample capacity;
- high throughput-automatic, multiple sample counting;
- no disturbance from the self-adsorption;
- Low backgrounds and great sensitivity for alpha counting, etc.

Very proper for samples determination in batch sorption experiment.

Introduction – Determination by LSC

However,

$$^{237}\mathrm{Np} \xrightarrow[T_{1/2} = 1.6 \times 10^5\ \mathrm{a}]{\alpha} {}^{233}\mathrm{Pa} \xrightarrow[T_{1/2} = 27\ \mathrm{d}]{\beta^-} {}^{233}\mathrm{U} \xrightarrow[T_{1/2} = 1.4 \times 10^6\ \mathrm{a}]{\alpha}$$

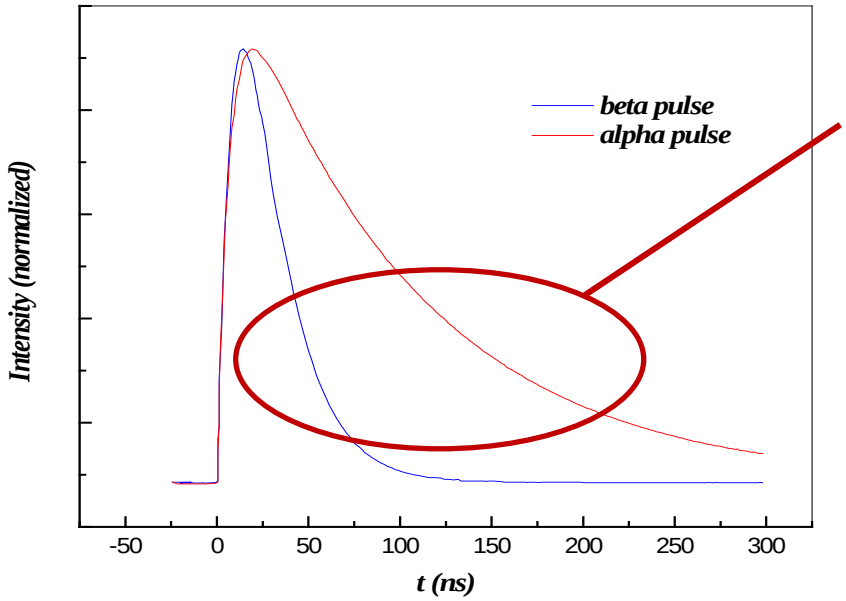
The β active daughter ^{233}Pa ($t_{1/2}$ = 27.00 d) has a radioactivity 2.89×10^7 times higher than ^{237}Np.

To solve this problem:

The use of a pulse shape analysis (PSA) technique.

Introduction – Determination by LSC

Theory:



De-excite of alpha particles to the ground state slower than singlet states produced by beta particles.

Measurement of the pulse decay time or length allows identification of the particle which caused it and enables simultaneous recording of pure alpha and beta spectra, respectively.

By optimizing the PSA setting, a high efficiency 98% for alpha counting and a discrimination of beta emitters of 99.9% could be achieved.

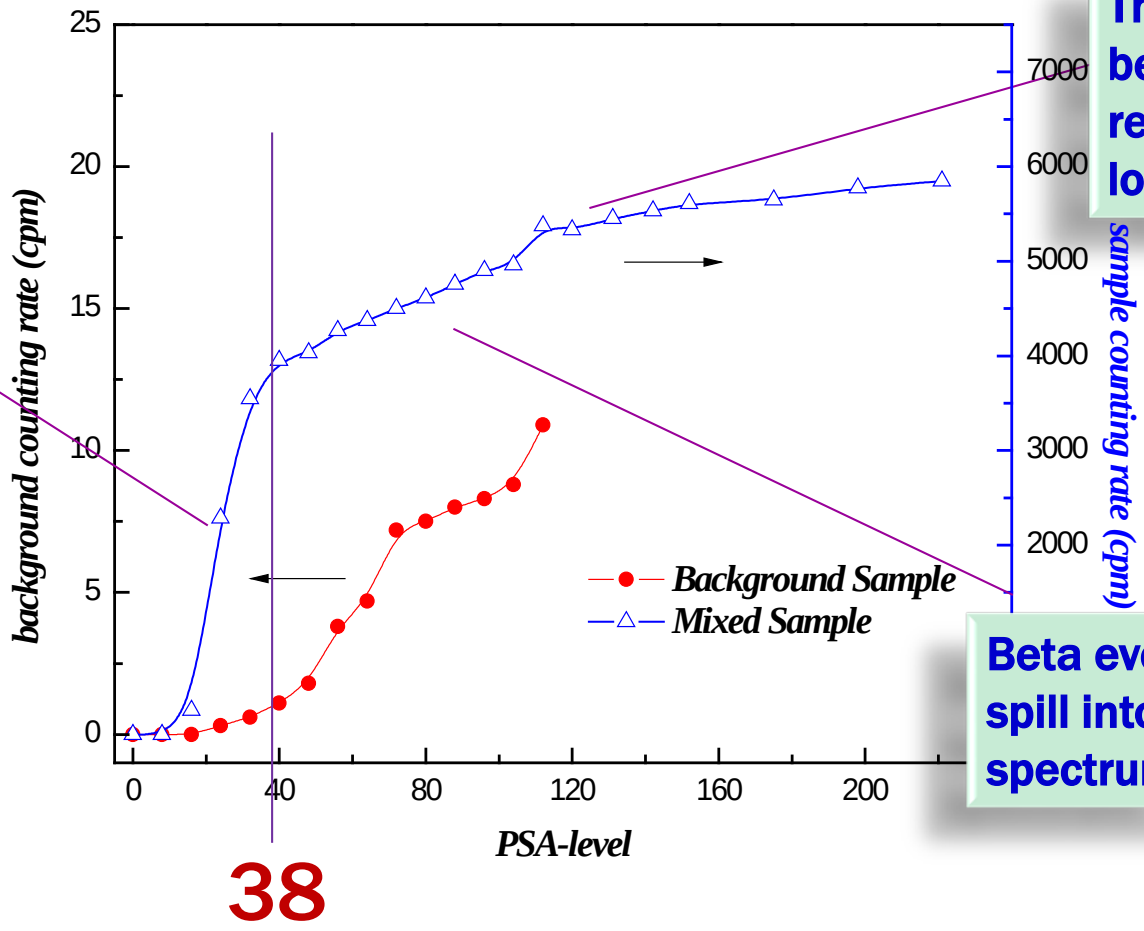
Results and Discussion – PSA-level Optimization

Usually, **a pure α emitter and a pure β emitter are needed.** The best pure α and β emitters should be the same nuclides as are present in the sample. Otherwise, some alternative nuclides with the same energy distribution could be used practically. **Nevertheless, in some cases such as the determination of ^{237}Np/^{233}Pa, it is not convenient to obtain a pure α emitter or a pure β emitter with the same energy distribution as ^{233}Pa.**

Therefore, we set the optimum PSA by measuring the sample itself of mixed α/β emitters as well as a background sample.

Results and Discussion – PSA-level Optimization

The true alpha events are regarded as alpha pulses

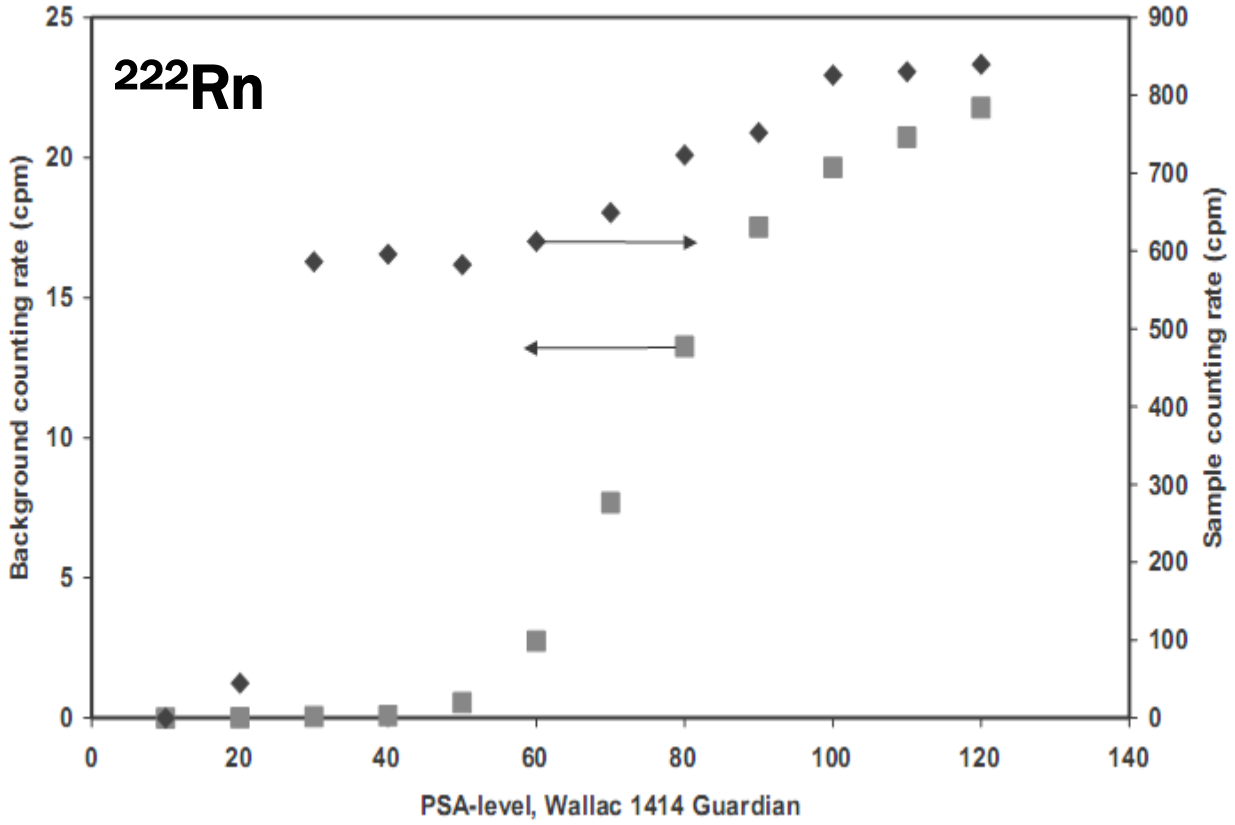


The bulk of beta events are regarded as long pulses

Beta events start to spill into the alpha spectrum

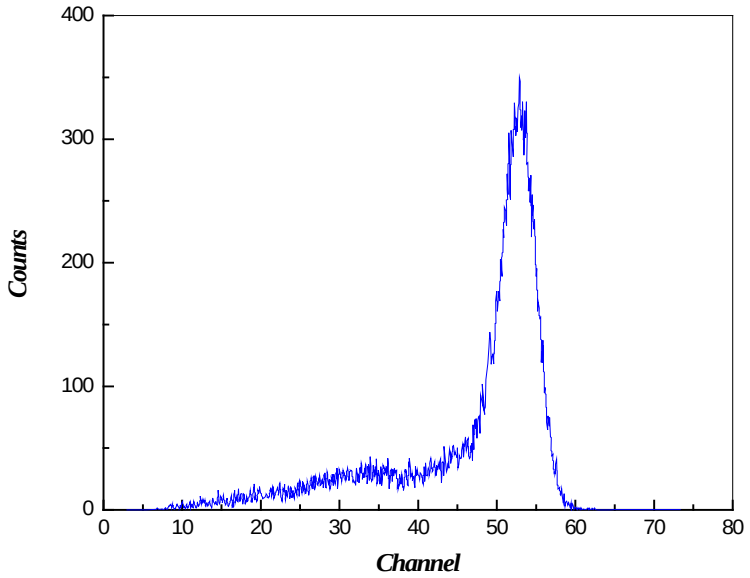
Results and Discussion – PSA-level Optimization

This is similar to the measurement of ^{222}Rn:

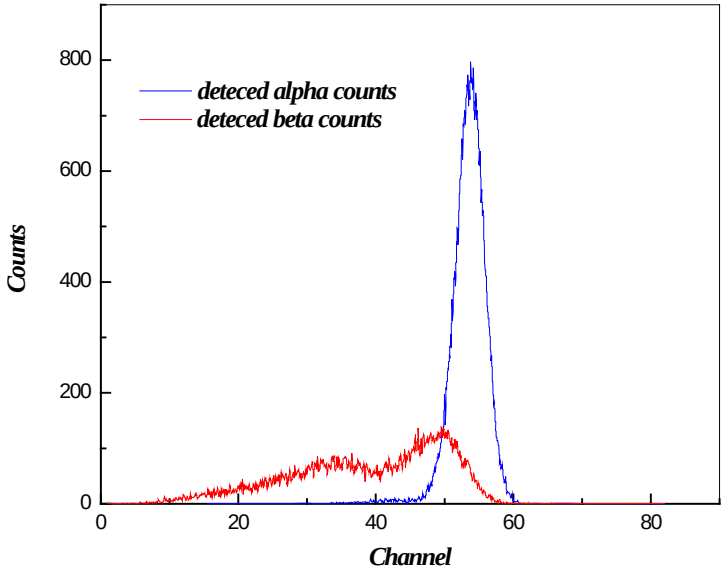


Byegård J, Ramebäck H, Widestrand H. International Progress Report IPR-02-68. 2002

Results and Discussion – PSA-level Optimization



Without PSA-level



Use PSA-level=38

Reasonable ?

Results and Discussion – Validation of the selected PSA-level

If the PSA-level is set higher than the optimum, many of the pulses originating from β-activity will be falsely accepted as α-decay.

The misclassified β events of ^{233}Pa into α-MCA will greatly influence the results of neptunium sorption experiment since Pa^{5+} exhibits very different sorption ability to NpO_2^+.

Use the mathematic method of Aupiais et al. to validate:

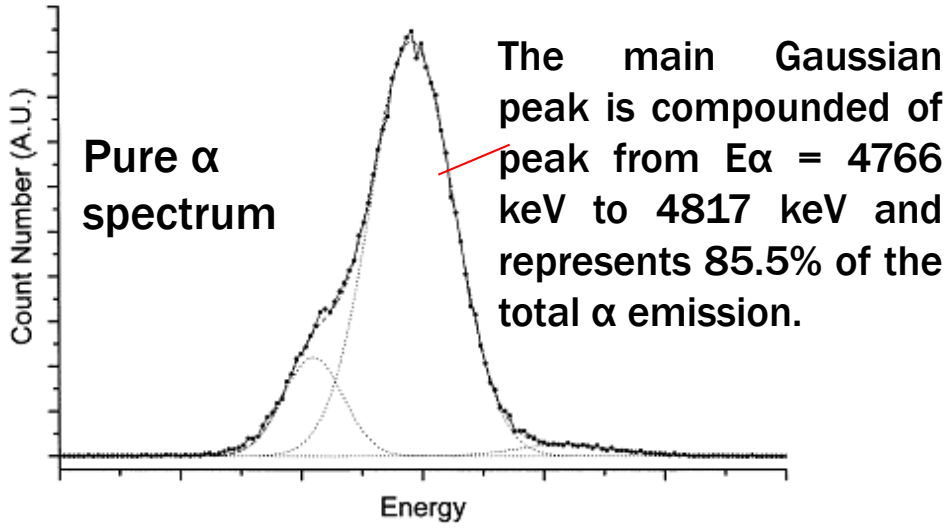
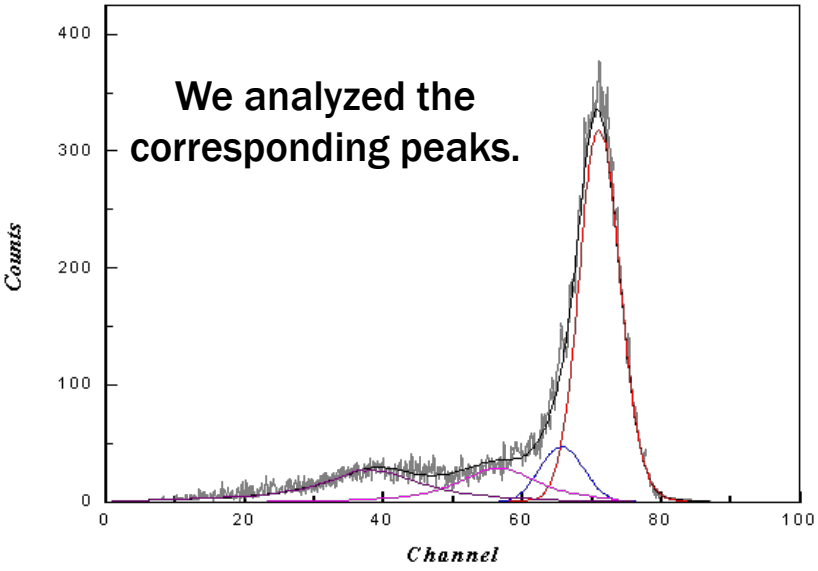
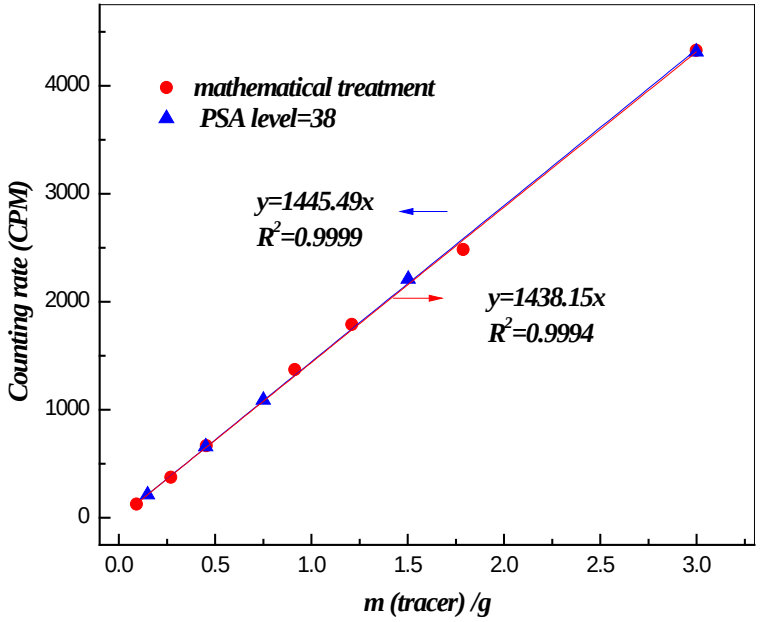


Fig. 1. ^{237}Np spectrum by alpha liquid scintillation. Condition of extraction: oxidation by AgO and extraction by POLEX in 0.1 M HNO_3 + 3.9 M NH_4NO_3.



Results and Discussion – Validation of the selected PSA-level

A series of samples are determined at PSA-level=38 as well as analyzed by the mathematic method. The results are compared:



APSA-level=38, the detected α emission accounts for ~86% of the total ^{237}Np α emission and ~14% of α emission is misclassified into β-MCA.

The selected PSA-level is slightly lower than the optimum.
We can then obtain the optimum PSA-level by increasing PSA-level until the exact value of total ^{237}Np α emission is reached.

Results and Discussion – Validation of the selected PSA-level

However, the PSA-level is not further optimized on account of the fact that in the experiment of neptunium sorption onto bentonite, sorption percentages of neptunium can be obtained by:

$$Sorption\% = \frac{CPM_t - CPM_s}{CPM_t}$$

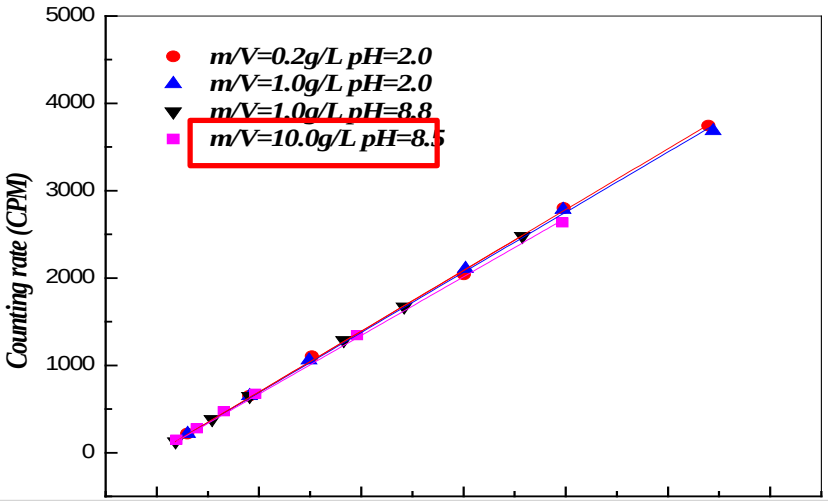
where CPM_t is the total α emission of the sample in batch sorption experiment; CPM_s is the α emission in supernatant.

Inferring from the equation, the calculated sorption percentage does not change while ~86% of true CPMt and CPMs is detected, i.e. the misclassified ~14% of α emission has no influence on the sorption results.

PSA-level=38 is suitable for the determination of ^{237}Np samples.

Results and Discussion – Quenching of bentonite

Almost ~50% of $^{237}Np(V)$ is adsorbed on betonite under this condition, but no obvious influence was observed, the measurement was not influenced.



Therefore, suspension samples can be directly determined.

In conclusion, the second mode is more suitable for the determination of batch experiment samples.

Solid to Volume ratio (g/L)	Solution pH	Linear relationship between the detected α emission and ^{237}Np tracer content at PSA-level=38	R^2
0.2	2.0	y=1391.96x	0.9997
1.0	2.0	y=1377.03x	0.9996
1.0	8.8	y=1389.98x	0.9999
10.0	8.5	y=1342.53x	0.9995

Summary

PSA-level Optimization

- ^{237}Np samples were well measured on Wallac Guardian 1414 at PSA-level = 38. At this PSA-level, practically all pulses from β-activity of ^{233}Pa are discarded and ~86% of total α emission was detected.

Determination Modes

- Bentonite solid particles in sample have no influence on ^{237}Np sample measurement by LSC. As a result, sorption percentage can be calculated by counting suspension and equivalent supernatant from the same sample.

Notice

- The numerical setting of the PSA-levels works on the Wallac Guardian 1414 is defined in a different way than the corresponding settings on some other LSC such as Wallac Rackbeta 1219 (Chalmers). Therefore, the selected PSA-level in this study cannot be directly applied to ^{237}Np measurement on some other LSCs.

Thanks for your attention!

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