# APPLICATIONS OF NEUTRON ACTIVATION ANALYSIS IN DETERMINATION OF NATURAL AND MAN-MADE RADIONUCLIDES, INCLUDING PA-231

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Neutron activation analysis (NAA), being essentially an isotopic and not an elemental method of analysis, is capable of determining a number of important radionuclides of radioecological interest by transformation into another, more easily quantifiable radionuclide. The nuclear characteristics which favour this technique may be summarized in an advantage factor relative to radiometric analysis of the original radioanalyte. Well known or hardly known examples include $^{235}$U, $^{238}$U, $^{232}$Th, $^{230}$Th, $^{129}$I, $^{99}$Tc, $^{237}$Np and $^{231}$Pa; a number of these are discussed and illustrated in analysis of real samples of environmental and biological origin. In particular, determination of $^{231}$Pa by RNAA was performed using both postirradiation and preseparation methods. Application of INAA to enable the use of $^{238}$U and $^{232}$Th as endogenous (internal) radiotracers in alpha spectrometric analyses of uranium and thorium radioisotopes in radioecological studies is described, also allowing independent data sets to be obtained for quality control.

## 1 Introduction

In general, determination of radionuclides may be performed either by direct activity measurement, usually termed radiometric analysis, or by mass measurement. Mass measurement can in principle be accomplished by any suitable technique, but in practice the required sensitivity usually limits the choice to spectroscopic techniques and mass spectrometry; the latter are usually more favourable being isotopically based.

However, a third type of measurement is that based on neutron activation analysis (NAA), which is a form of isotopic mass measurement depending on a nuclear transformation reaction followed by a radiometric measurement of the newly- induced radionuclide (or its daughter products); it thus has affinities with both previous types of method, but also its own characteristics. Since in general quality assurance of analytical data, especially in measurements using or establishing reference materials demands the use of independent routes, NAA applied to radionuclides can play a useful if somewhat restricted role.

## 2 NAA for Radionuclide Determination

As is obvious from the fundamental relationship defining activity as the number of atoms (mass) divided by the half- life, radiometric methods become less favourable for longer lived, low specific activity radionuclides, while mass-based (»atom-counting«) techniques become more advantageous. NAA is thus also more favourable for low specific activity nuclides. NAA, however, only becomes worth considering when the nuclear characteristics are highly favourable, i.e. the nuclide has a large capture cross section for formation of a product nuclide of relatively short half-life with good measurement properties, preferably for gamma spectrometry (namely abundant λ-ray emission of suitable energy). In the most favourable cases instrumental (non-destruc-

tive) NAA (INAA) can be employed. For example, this is the case for determination of $^{238}$U and $^{232}$Th via $^{239}$Np and $^{233}$Pa, respectively, in many materials at natural levels. In cases where radiochemical separation of the induced radionuclide (i.e. RNAA) needs to be done after irradiation to improve the signal/noise ratio and the sensitivity, this radioactive measurement possesses some important advantages over normal radiometry of the original nuclide in that added carrier can be used to optimise and control chemical recovery, and crucially, the procedure is not subject to blank corrections. Indeed the blank becomes the factor limiting the ultimate sensitivity and accuracy of all other techniques, including mass spectrometry.

## 3 NAA for Long-lived Alpha Emitters, Including $^{231}$Pa

As described earlier [1,2] it is possible to quantify the advantages of NAA with respect to radiometry of the original radionuclide in terms of an advantage factor (A. F.) Thus the original activity is given by $A_1 = e_1 f_1 N_1 \lambda_1$ where e and f are the counting efficiency and the radiation emission probability. Neutron activation produces a new radionuclide 2 of activity $A_2$ given by

$$A_2 = e_2 f_2 . N_1 (\theta_{th}\sigma + \theta_{epi} I)(1 - e^{-\lambda_2 T})\, e^{-\lambda 2 t}$$

where $\theta_{th}$ and $\theta_{epi}$ are the thermal and epithermal neutron fluxes, $\sigma$ the thermal neutron cross section and I the resonance integral (barns), T the irradiation time and t the decay time (seconds). Hence the advantage factor AF is the ratio $A_2/A_1$:

$$A.F. = \frac{e_2 f_2}{\lambda_i e_1 f_1} (\theta_{th}\sigma + \theta_{epi} I)(1 - e^{-\lambda_2 T})\, e^{-\lambda_2 t} \qquad (1)$$

The second term on the right of Eq. 1 we term the neutron activation parameter (NAP) and the third the build-up and decay factor (BDF).

For the five long-lived alpha emitters $^{238}$U, $^{232}$Th, $^{230}$Th, $^{237}$Np and $^{231}$Pa, and their neutron induced product nuclides $^{239}$U or $^{239}$Np, $^{233}$Pa, $^{231}$Th, $^{238}$Np and $^{232}$Pa, the parameters contained in Eq. 1 and the resulting values of AF are given in Tables 1 and 2. (Values for $\sigma$ and I are taken from Erdtmann [3]).

It was assumed for radiometric measurements that the counting efficency $e_1$ of the major $\alpha$-line was 25 %, the gamma ray efficiencies $e_2$ were taken for a 5 ml volume in a well- type HP Ge detector, and that the radiochemical yields of the separation of $A_1$ and $A_2$ were approximately equal.

As shown in Table 2, extremely high values of AF are found for NAA of $^{238}$U and $^{232}$Th, and lower but still favourable values for $^{237}$Np, $^{231}$Pa and $^{230}$Th. There is of course a large literature on RNAA on U and Th; for example picogram levels of uranium [4] or of thorium [5, 6] in body fluids can be determined by RNAA. Alpha spectrometry at these levels is almost impossible, requiring kilogram sample sizes and concomitant blank problems. A recent value [7] for uranium in human blood of $\leq 2$ pg mL$^{-1}$ obtained in samples collected by state-of-the-art contamination-free procedures is the only experimental value approaching the very low value (0.6 pg mL$^{-1}$) which was derived from modelling of U uptake and dynamics by Leggett [8].

Before considering the other, less studied alpha emitters, we should point out that the AF is only a way of indicating the potential for RNAA relative to radiometry; important factors to consider are the sensitivity which can be obtained and the actual

Table 1. Nuclear parameters for radiometry and activation analysis of induced nuclides for some long-lived alpha emitters

| Original Nuclide | $T_{1/2(y)}$ | $E\alpha$ (MeV) | $e_1$ | $f_1$ | $e_1f_1$ | $\sigma_{barn}$ | $I_{barn}$ | NAP* |
|---|---|---|---|---|---|---|---|---|
| U-238 | $4.46 \times 10^9$ | 4.196 | 0.25 | 0.77 | 0.193 | 2.70 | 2.75 | $8.2 \times 10^{-11}$ |
| Th-232 | $1.40 \times 10^{10}$ | 4.010 | 0.25 | 0.77 | 0.193 | 7.4 | 72.4 | $8.85 \times 10^{-11}$ |
| Th-230 | $7.54 \times 10^4$ | 4.688 | 0.25 | 0.77 | 0.193 | 23 | 1010 | $4.32 \times 10^{-10}$ |
| Np-237 | $2.14 \times 10^6$ | 4.788 | 0.25 | 0.47 | 0.118 | 169 | 660 | $1.82 \times 10^{-9}$ |
| Pa-231 | $8.27 \times 10^4$ | 5.013 | 0.25 | 0.25 | 0.0625 | 210 | 1500 | $2.4 \times 10^{-9}$ |
| Induced nuclide | $T_{1/2}$ | $E\gamma$(keV) | $e_2$+ | $f_2$ | $e_2f_2$ | T | t | BDF |
| U-239 | 23.5 min | 75 | 0.55 | 0.59 | 0.325 | $1.t_{1/2}$ | $1.t_{1/2}$ | 0.25 |
| Np-239 | 2.36d | 228 | 0.26 | 0.095 | 0.025 | 1d | $1.t_{1/2}$ | 0.37 |
| Pa-233 | 27d | 312 | 0.20 | 0.38 | 0.076 | 1d | $t_{1/2}/2$ | 0.0179 |
| Th-231 | 25.5 h | 84 | 0.55 | 0.051 | 0.028 | $1.t_{1/2}$ | $2.t_{1/2}$ | 0.125 |
| Np-238 | 2.12d | 984 | 0.04 | 0.24 | 0.0096 | $t_{1/2}/2$ | $1.t_{1/2}$ | 0.146 |
| Pa-232 | 1.31d | 969 | 0.04 | 0.45 | 0.018 | 1d | $2.t_{1/2}$ | 0.103 |

* assuming $\theta_{th} = 10^{13}$, $\theta_{epi} = 5 \times 10^{11}$n cm$^{-2}$ s$^{-1}$
+ values for 5 mL volume in well-type Ge detector

Table 2. Values of advantage factor AF for NAA of some long-lived alpha emitters

| Nuclide pair | $\lambda_1$ | AF |
|---|---|---|
| $U^{238}/U^{239}$ | $4.93 \times 10^{-18}$ | $7.0 \times 10^6$ |
| $U^{238}/Np^{239}$ | $4.93 \times 10^{-18}$ | $8.0 \times 10^5$ |
| $Th^{232}/Pa^{233}$ | $1.57 \times 10^{-18}$ | $4.0 \times 10^5$ |
| $Th^{230}/Th^{231}$ | $2.91 \times 10^{-13}$ | 27 |
| $Np^{237}/Np^{238}$ | $1.027 \times 10^{-14}$ | 640 |
| $Pa^{231}/Pa^{232}$ | $6.72 \times 10^{-13}$ | 106 |

concentrations (activities) of these nuclides in real samples. The relative sensitivity by RNAA per unit mass for the nuclides will be proportional to the product $e_2f_2$ . NAP. BDF. (Absolute sensitivities will heavily depend on the assumptions made about neutron flux, irradiation conditions, cooling and counting times, type of detector, the presence of spectral interferences, and whether a preconcentration from a larger sample is made). Typical levels of the five radionuclides considered in some environmental samples are given in Table 3 along with their specific activities.

Returning to Table 2, it is apparent that RNAA of $^{237}$Np, $^{230}$Th and $^{231}$Pa should be favourable. In fact there is a considerable literature on RNAA of $^{237}$Np in radioecological studies [1, 9-11]; using preconcentration Kim et al. [10] were able to determine it at fallout levels in soil. The first report on $^{230}$Th seems to be that of Kathren et al. [12, 13], but their work involved spiking biological matrices with $^{230}$Th and attempting to determine it by INAA. The only other work seems to be RNAA of $^{230}$Th, without

Table 3. Specific activities and typical levels in the environment

| Nuclide | Specific activity | Concentration range |
|---|---|---|
| U-238 | 12.5 mBq $\mu g^{-1}$ or 80 $\mu g$ $Bq^{-1}$ | 1-10 $\mu g$ $g^{-1}$ soils, sediments (tens-hundreds mBq $g^{-1}$) |
| Th-232 | 4.08 mBq $\mu g^{-1}$ or 245 $\mu g$ $Bq^{-1}$ | 2-20 $\mu g$ $g^{-1}$ soils, sediments (tens of mBq $g^{-1}$) |
| Th-230 | 0.76 Bq $ng^{-1}$ or 1.31 ng $Bq^{-1}$ | 50-200 mBq $g^{-1}$ soils, sediments |
| Np-237 | 26.2 Bq $\mu g^{-1}$ or 38 ng $Bq^{-1}$ | 1-5 mBq $g^{-1}$ Sellafield area sediments<br>0.5 mBq g R. Ribble mud (ex Springfields)<br>mBq $kg^{-1}$ soil fallout levels |
| Pa-231 | 1.76 Bq $ng^{-1}$ or 0.57 ng $Bq^{-1}$ | 1-10 mBq $g^{-1}$ geological materials (equilibrium with U-235) |

a preseparation, in stream sediment by Byrne [2]. $^{234}$Th was added as a useful yield tracer. A limitation on further studies on $^{230}$Th at lower levels in our TRIGA reactor is the poorly thermalised neutron flux, which makes the correction necessary for $^{231}$Th produced by the fast neutron reaction $^{232}$Th (n, 2n) a considerable one at many natural $^{230}$Th/$^{232}$Th ratios.

Since no work on NAA of $^{231}$Pa seems to have been reported, in this study we explored possibilities for its determination via $^{232}$Pa. $^{233}$Pa offers a convenient tracer for both pre- and post-irradiation separations, as well as preliminary method development.

## 4 Experimental

Samples: So-called »red mud« is a waste product of uranium mining, produced by liming the spent liquors after U extraction. This material from the former Žirovski vrh uranium mine, Slovenia, contains ca. 25 and 50 mg $kg^{-1}$ Th and U, respectively, as well as about $6x10^4$ Bq $kg^{-1}$ $^{230}$Th.

Irradiation, standards: About 0.5 g sample in the direct method or some mL of solution containing preconcentrated $^{231}$Pa were irradiated in sealed polythene ampoules with a $^{231}$Pa standard (AEA Technology, Harwell, U. K., diluted to 10 Bq $g^{-1}$) for about 20 hours at a flux of $1.5x10^{12}$ n $cm^{-2}$ $s^{-1}$ in the rotating rack of the Institute's TRIGA Mk II reactor.

*Radiochemical separation:*

(i) Preseparation (optional): A few grams of red mud were dissolved in conc. HCl in a beaker containing $^{233}$Pa yield tracer, adjusted to 9M and passed down an anion exchange column (Dowex-1, Cl-form, 100-200 mesh, 100x10 mm diameter) at 1 mL $min^{-1}$. The column was washed with 100 mL 9M HCl, 100 mL 8M $HNO_3$ and Pa selectively eluted with 50 mL 9M HCl/0.005 M HF. This was evaporated to near dryness, taken up in a few mL of 8M $HNO_3$/0.1 M HF and sealed into the irradiation ampoule.

(ii) Post-irradiation separation:

If a preseparation (as above) had been applied, the irradiated solution was transferred to a 50 mL separatory funnel with 5M $HNO_3$, 0.2 g boric acid added to complex $F^-$, and Pa extracted with 6 mL 5 % TOPO in toluene. The organic phase was washed once with 5 M $HNO_3$ and 5 mL of organic phase pipetted into a measuring vial for $\gamma$–spectrometry in a well- type Ge detector.

If no preseparation had been applied, the irradiated sample was divided so that a small aliquot was retained to count $^{233}$Pa (from $^{232}$Th in the sample) for determining the recovery, while the bulk was dissolved and Pa separated as above by anion exchange for $\gamma$ – spectrometry.

## 5 Results and Discussion

The $\gamma$-spectrum of $^{232}$Pa with $^{233}$ Pa tracer separated from neutron irradiated red mud is shown in Fig. 1. The peak at 969 keV offers the best signal/noise ratio; note that tracer $^{233}$Pa has no higher energy peaks, and that $^{239}$Np is very effectively removed by the separation procedure. The separation, though a very simple one step procedure, is adequate for measurement of these levels of $^{231}$Pa (via $^{232}$Pa).

Table 4 shows results by both the direct and preseparation procedures for two red mud samples. Since this material has a high $^{231}$Pa content, independent radiometric analysis by $\gamma$ - spectrometry was possible on one hundred gram aliquots by counting for several days, quantifying the weak 299.9, 302.5 and 329.9 keV $^{231}$Pa gamma peaks. As shown in Table 4 these results are in good agreement with the RNAA values.

By performing RNAA in the preseparation mode on larger samples, using a higher neutron flux and optimising irradiation, decay and counting times, it may be estimated that sensitivity could be increased by a factor $10^2$ – $10^3$ to allow analysis at the Bq kg$^{-1}$ level. This would enable RNAA of $^{231}$Pa in environmental materials such as fly ash, soil and sediments at real levels.

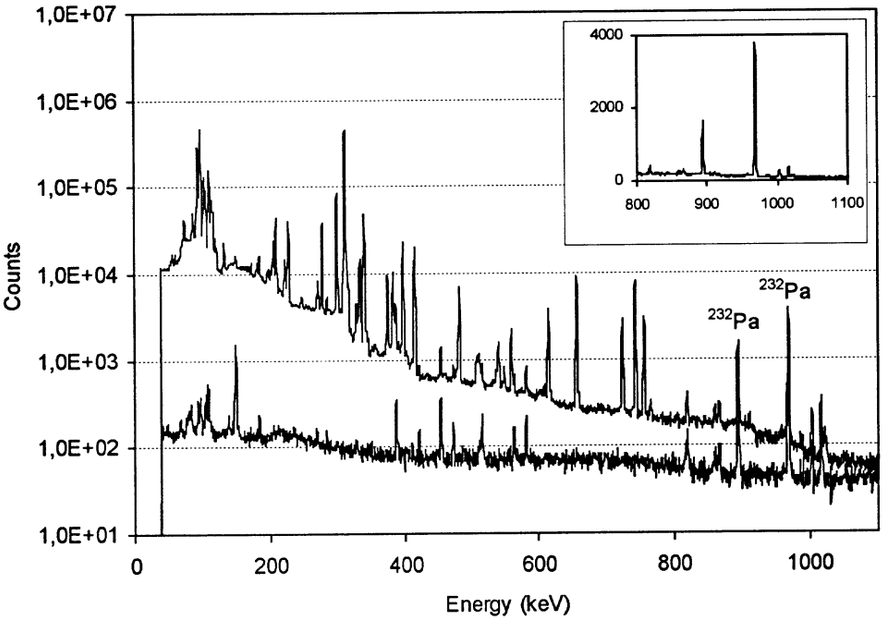


Fig. 1. $\gamma$-spectra of $^{232}$Pa separated from red mud by post-irradiation RNAA (upper) and $^{232}$Pa standard (lower). Inset is the partial RNAA sample spectrum on a linear scale

Table 4. Determination of Pa-231 in red mud samples

| Sample | Pa-231 (Bq $kg^{-1}$) | | |
|---|---|---|---|
| | Gamma spectrometry | RNAA | |
| | | Post-irradiation separation | Preseparation before irradiation |
| 1 | 1120<br>1150<br>1240<br>1170±60(3) | 1350 | 1170 |
| 2 | 1910<br>2050<br>2160<br>2040±125(3) | 2110<br>2210 | 2080<br>1980 |

## 6 Other Nuclides by NAA

**$^{129}$I:** There is an extensive literature on NAA of $^{129}$I and unfortunately we have no space to consider it here. For a good discussion of some of the problems and features of the technique, consult [14]. One weakness in many procedures for $^{129}$I seems to be determination of the preseparation yield, often accomplished from tens to hundreds of grams of sample in a combustion train by inhomogeneous addition of $^{125}$I tracer. It appears inherently unlikely that this added liquid tracer which is not in radiochemical equilibrium with iodine isotopes in the sample, can truly represent the chemical recovery. A better method could be to activate part of the sample by neutron irradiation so that it becomes labelled internally with $^{131}$I from fission of $^{235}$U present in the sample and then mix with the remainder. The actual $^{131}$I content can be relatively simply determined in an aliquot by radiochemical separation following closed oxygen combustion or alkaline fusion [15], and compared to the $^{131}$I found in the preconcentrated iodine to obtain the preseparation yield. Alternatively, NAA of stable iodine ($^{127}$I) in the sample and comparison with the amount of iodine recovered in the preseparation (by INAA) would give the chemical yield.

**$^{99}$Tc:** As early as the fifties attempts to measure $^{99}$Tc by NAA using 16 second $^{100}$Tc were undertaken (see references in Houdek et al [16]). This group studied the determination of $^{99}$ Tc in $^{99m}$ Tc labelled pharmaceuticals and generator eluates. Due non-ideal conditions, sensitivity was poor. Using more modern cyclic activation analysis, sensitivities at ng $g^{-1}$ level should be attainable. (Nuclear parameters are similar to those for Se via 17 second $^{77m}$Se which has nanogram sensitivity in cyclic activation analysis). An interference - free detection limit of 4ng for $^{99}$Tc for cyclic activation analysis via $^{100}$Tc was recently obtained (Bode-[17]). Similar limits of detection were claimed by Sekine et al. [18] using bremsstrahlung excitation of $^{99}$Tc via the reaction $^{99}$Tc( $\gamma$, $\gamma'$)$^{99m}$Tc.

Levels of $^{99}$Tc in the seaweed Fucus vesiculosus, which strongly accumulates Tc, have been reported [19] to be at the Bq $g^{-1}$ (dry weight) level along the shores of the Irish Sea (influence of the Sellafield discharge). It would be greatly advantageous to monitor those levels by the rapid non- destructive technique of cyclic activation

analysis or by bremstrahlung excitation analysis instead of slow and expensive radiometric methods.

## 7 Analysis of U and Th Radioisotopes Using Internal Standards via NAA

A new approach [19],[20] to radioisotopic analysis of U ($^{235}$U, $^{234}$U, $^{235}$U) and Th ($^{228}$Th, $^{230}$Th, $^{232}$Th) using alpha spectrometry is offered by its combination with prior NAA of $^{238}$U and $^{232}$Th in the sample. In environmental materials this can be accomplished routinely by INAA, using $\gamma$-spectrometry of the induced $^{239}$Np and $^{233}$Pa radionuclides. From the mass concentrations of $^{238}$U and $^{232}$Th their activity concentrations are derived, and these values are then used as internal standards in the alpha spectrometric analysis. This is performed on separate sample aliquots by the usual dissolution, separation, thin source preparation and $\alpha$-spectrometric procedures. However, since the activity concentrations of $^{238}$U and $^{232}$Th are already known, only the relative peak heights of the U and Th radioistopes in the respective alpha spectra are needed to obtain the absolute concentrations of $^{234}$U and $^{235}$U, and of $^{228}$Th and $^{230}$Th.

Thus the advantages of this procedure are that neither the chemical yield (recovery) of the radiochemical separations, nor the counting efficiency of the detectors need be known. Hence the use of expensive, calibrated, external radioisotopic tracers (such as $^{232}$U, $^{229}$Th) is eliminated. The use of such tracers also involves some other drawbacks such as ingrowth of undesirable daughter products (e.g. $^{228}$Th from $^{232}$U), or deterioration of limits of detection of a peak in the alpha spectrum due to the presence of another adjacent, higher energy alpha peak from the tracer e.g. $^{229}$Th at 4.82 MeV and $^{230}$Th at 4.69, especially if »tailing« occurs due to sub- optimum resolution or source thickness.

As well as the fact that in the new approach even the sample mass is not required in the alpha spectrometric analysis, the use of an internal standard should be intrinsically more reliable than an external, added tracer, especially when samples are difficult to dissolve or there may be a question about achieving full radiochemical exchange, e.g. several valency states. Of course the disadvantage is that prior INAA is needed, but this can be done at a cost which is very small compared to alpha spectrometric analysis. Probably the best feature of the new method is that if INAA is performed in conjunction with classical $\alpha$-spectrometry using added tracers, a set of independent results of great value in quality control can be obtained.

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