

Decay corrections and radioactive equilibrium – a practical summary

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Introduction

The measurement of radionuclide activities presents a rather unique challenge in that the quantity being measured is constantly changing. This means that in order to have a useful measurement, the result needs to be specified at a certain reference time. The correction from the time of measurement to the reference time is made by use of equations which describe the radioactive decay of the radionuclide of interest over time. While in many cases this correction is straightforward, there are situations where the situation is complicated by ingrowth from a parent radionuclide or certain equilibrium conditions.

Several “tricky” decay corrections were encountered in the proficiency tests organized by IAEA NAEL-TEL in 2017, 2018 and 2019. It was therefore decided that a short guide would be developed to help laboratories to apply appropriate decay corrections to their measurements. This document will hopefully be a useful tool for the laboratories to carry out their analytical work in an accurate way, by assessing and identifying potentially complicating decay situations.

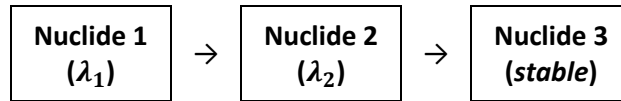
Note that for all uncertainty calculations, it is assumed that the contributions to the overall uncertainty of the elapsed time (since the reference date and during measurement) as well as from decay constants are negligible compared to the uncertainty contributions coming from the activity determination.

Mathematical symbols used in this document

A_i	activity of nuclide i at the time of measurement
$A_{i,0}$	activity of nuclide i at the reference time
a_i	activity concentration (e.g. Bq/kg) of nuclide i at the time of measurement
$a_{i,0}$	activity concentration (e.g. Bq/kg) of nuclide i at the reference time
λ_i	decay constant of nuclide i , given by the formula $\lambda_i = \ln(2) / t_{1/2,i}$ where $t_{1/2,i}$ is the half-life of nuclide i
t	time elapsed since a set “reference time”
t_m	real time of the measurement/spectrum acquisition
$u(y)$	standard uncertainty (k=1) of quantity y
$u_c(y)$	combined standard uncertainty (k=1) of quantity y

Corrections for decay to a reference time

Consider the following decay chain:



Assume that the activity and associated uncertainty of nuclide 1 (“mother”) and nuclide 2 (“daughter”) at the time of measurement is known, while activities at the reference time need to be determined.

Furthermore, we assume that the elapsed time t and the half-lives $t_{1/2,i}$ (and thus also the decay constants λ_i) are well-known and thus do not contribute significantly to the uncertainty.

Activity of nuclide 1 decay corrected to the reference time

The basic decay equation should be applied:

$$A_{1,0} = A_1 \cdot e^{\lambda_1 \cdot t}$$

$$u(A_{1,0}) = u(A_1) \cdot e^{\lambda_1 \cdot t}$$

Activity of nuclide 2 decay corrected to the reference time

For nuclide 2 the second-order Bateman [1] equation needs to be applied:

$$A_{2,0} = A_2 \cdot e^{\lambda_2 \cdot t} - \frac{\lambda_2}{\lambda_2 - \lambda_1} A_1 [e^{\lambda_2 \cdot t} - e^{\lambda_1 \cdot t}]$$

$$u_c(A_{2,0}) = \sqrt{(e^{\lambda_2 \cdot t})^2 \cdot u^2(A_2) + \left(\frac{\lambda_2}{\lambda_2 - \lambda_1} [e^{\lambda_2 \cdot t} - e^{\lambda_1 \cdot t}] \right)^2 \cdot u^2(A_1)}$$

Radioactive equilibrium

The general second-order Bateman equation for the activity of nuclide 2 as a function of time may be written as:

$$A_2 = A_{2,0} \cdot e^{-\lambda_2 \cdot t} + \frac{\lambda_2}{\lambda_2 - \lambda_1} A_{1,0} [e^{-\lambda_1 \cdot t} - e^{-\lambda_2 \cdot t}]$$

Depending on how nuclide 1 and nuclide 2 decay in relation to each other, there is the possibility to reach certain equilibrium states as described below.

Transient equilibrium

Transient equilibrium occurs in cases where $\lambda_2 > \lambda_1$ (nuclide 1 has a longer half-life than nuclide 2).

We assume that a long enough time has elapsed so that $A_{2,0} \cdot e^{-\lambda_2 \cdot t} \approx 0$, and $[e^{-\lambda_1 \cdot t} - e^{-\lambda_2 \cdot t}] \approx e^{-\lambda_1 \cdot t}$. In this case the activity of nuclide 2 is given by:

$$A_2 = \frac{\lambda_2}{\lambda_2 - \lambda_1} A_{1,0} \cdot e^{-\lambda_1 \cdot t}$$

This equation has the following implications:

- The activity of nuclide 2 is equal to the activity of nuclide 1 multiplied by the ratio $\left(\frac{\lambda_2}{\lambda_2 - \lambda_1}\right)$
- Nuclide 2 decays by the half-life of nuclide 1

Secular equilibrium

Secular equilibrium occurs in cases where $\lambda_2 \gg \lambda_1$ (nuclide 1 has a much longer half-life than nuclide 2).

In addition to the assumptions made for transient equilibrium, we additionally have that $\frac{\lambda_2}{\lambda_2 - \lambda_1} \approx 1$. This means that the activity of nuclide 2 is given by:

$$A_2 = A_{1,0} \cdot e^{-\lambda_1 \cdot t}$$

This equation has the following implications:

- The activity of nuclide 2 is approximately equal to the activity of nuclide 1
- Nuclide 2 decays by the half-life of nuclide 1

No equilibrium

No equilibrium will exist in the case where $\lambda_1 > \lambda_2$ (half-life of nuclide 2 is longer than that of nuclide 1).

In these cases the complete Bateman equation has to be applied for decay corrections.

Calculating the time since separation

Assuming that there exists a point in time where the activity of nuclide 2 was zero (i.e. only nuclide 1 was present), we can rearrange the Bateman equation to calculate the time elapsed since then. We call this the “time since separation”, t_{sep} , given by:

$$t_{sep} = \frac{\ln \left(1 - \frac{A_2}{A_1} \cdot \frac{\lambda_2 - \lambda_1}{\lambda_2} \right)}{\lambda_1 - \lambda_2}$$

with uncertainty

$$u_c(t_{sep}) = \frac{\frac{A_2}{A_1} \sqrt{\left(\frac{u(A_2)}{A_2} \right)^2 + \left(\frac{u(A_1)}{A_1} \right)^2}}{\lambda_2 - (\lambda_2 - \lambda_1) \cdot \frac{A_2}{A_1}}$$

Note that it is only possible to perform this calculation while nuclide 1 and nuclide 2 are not yet in equilibrium, i.e. $\frac{A_2}{A_1}$ must be significantly lower than the “equilibrium ratio” $\frac{\lambda_2 - \lambda_1}{\lambda_2}$ for it to work.

This kind of calculation can be useful to perform *nuclear chronometry*, for example to determine when a nuclear explosion [2] or radiochemical separation event took place.

Decay during the acquisition period

For nuclides which have half-lives on the same order of magnitude as the measurement time of the sample it is necessary to perform a correction for decay during the acquisition period itself.

This correction becomes significant in cases where the half-life of the nuclide is around 20 times longer than the measurement time, i.e. when $t_{1/2} < 20 \cdot t_m$.

For nuclide 1, this correction can be expressed mathematically as:

$$A_{1,m} = A_1 \cdot \frac{\lambda_1 \cdot t_m}{1 - e^{-\lambda_1 \cdot t_m}}$$
$$u(A_{1,m}) = \frac{\lambda_1 \cdot t_m}{1 - e^{-\lambda_1 \cdot t_m}} \cdot u(A_1)$$

Note that in this equation A_1 is the non-decay corrected calculated activity of nuclide 1, while $A_{1,m}$ represents the activity of nuclide 1 at the starting time of the measurement.

For nuclide 2, the correction for decay during the acquisition period becomes more complex due to the simultaneous ingrowth of nuclide 1. However; as such cases are not frequently encountered for typical sample analyses this will not be covered in detail in this document and reference is instead made to Harms and Jerome (2004) [3].

Total decay correction for an unsupported radionuclide

The complete picture of the decay of an unsupported radionuclide (i.e. it is decaying by its own half-life without any ingrowth from a parent radionuclide) is shown in Figure 1 below.

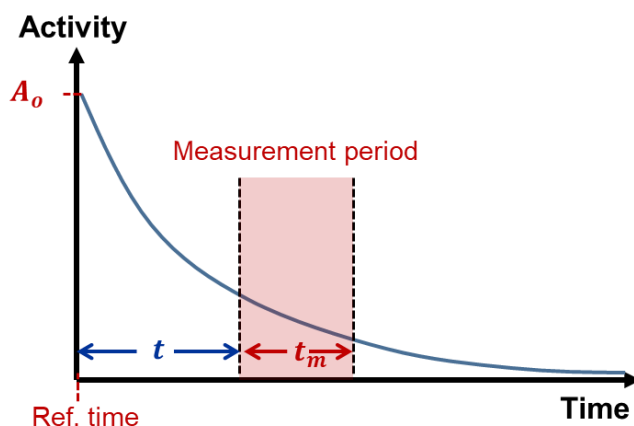


Figure 1 The total decay picture for an unsupported radionuclide.

In this case the total decay correction will be the product of two decay corrections:

1. The correction from the reference time to the start of the measurement period
2. The correction for decay during the measurement period.

The total activity of this radionuclide, at the reference time, is therefore expressed as:

$$A_{1,0} = A_1 \cdot e^{\lambda_1 \cdot t} \cdot \frac{\lambda_1 \cdot t_m}{1 - e^{-\lambda_1 \cdot t_m}}$$

Assuming again that only the activity contributes significantly, the uncertainty will be given by:

$$u_c(A_{1,0}) = u_c(A_1) \cdot e^{\lambda_1 \cdot t} \cdot \frac{\lambda_1 \cdot t_m}{1 - e^{-\lambda_1 \cdot t_m}}$$

Practical hints for performing appropriate decay corrections

This section outlines some practical hints which may be considered during the analysis process when trying to determine the reference date activity of a radionuclide of interest which may be affected by a non-trivial decay correction.

Use correct nuclide library data

The data in the nuclide library is used by the analysis software to, among other things, perform simple decay corrections. In this case the corrections of a specific nuclide are made using the half-life which is associated to that nuclide in the library file. It is recommended to ensure that the library data used for activity calculations accurately reflects the decay situation of the sample you are measuring, especially in the case where you may have a radionuclide in secular or transient equilibrium with a longer-lived parent nuclide. This is, for example, frequently the case for many of the natural series radionuclides.

Know the possibilities and limitations of your software

Some commercial software can do all types of decay corrections given the correct input from the user, while other software has more limited functionality and the corrections must be done manually. Knowing what your software can and cannot do will be very useful to help decide whether any of the corrections need to be carried out and applied separately.

Look at the non-decay corrected activities of mother- and daughter nuclides

Non-decay corrected activities of radionuclides in the same decay chain which are widely disparaging may be an indication of a possible disequilibrium. Particularly if the ratio of a daughter nuclide activity to the mother nuclide activity is significantly different from the “equilibrium ratio”, i.e. $\frac{A_2}{A_1} \neq \frac{\lambda_2}{\lambda_2 - \lambda_1}$.

In cases without equilibrium, the full Bateman equation must be applied for decay correction of the daughter nuclide.

Measure the sample again after some time to see how the activity has changed

Performing one or more measurements of the same sample after the initial one will allow you to “track” the decay of the nuclide(s) of interest to see how it behaves by plotting the calculated activity of each measurement as a function of time. This may give an indication of whether equilibrium is present.

Check that everything “makes sense”!

The most powerful tools when performing radionuclide analyses are human logic and reasoning. If the results don’t make sense, there is probably an unresolved issue. Never just blindly trust your software!

References

- [1] Bateman, H., 1910. The solution of a system of differential equations, occurring in the theory of radioactive decay, Proc. Camb. Philos. Soc. 15, 423-427.
- [2] Pomme, S., Collins, S.M., 2014. Unbiased equations for ⁹⁵Zr–⁹⁵Nb chronometry, Appl. Radiat. Isot 90, 234-240.
- [3] Harms, A.V., Jerome, S.M., 2004. On the integrated decay and ingrowth equations used in the measurement of radioactive decay families: the general solution, Appl. Radiat. Isot 61(2-3), 367-372.

Calculation examples

Example 1 – $^{228}\text{Ra}/^{228}\text{Th}$ disequilibrium in TEL PT 2019 water sample 01

Background information

This section is included to give a bit of background information to the production and decay behavior of the water samples. It is not required for performing the corrections.

In the 2019 proficiency test of the IAEA Terrestrial Environment Laboratory (TEL), participants were asked to calculate the activity of a water sample in which there was disequilibrium in the thorium series. This disequilibrium was caused by chemical separation of radium isotopes from natural thorium, so that the only nuclides present directly after the separation were ^{228}Ra and ^{224}Ra . Directly after separation the two radium isotopes continue decaying, repopulating the daughter radionuclides.

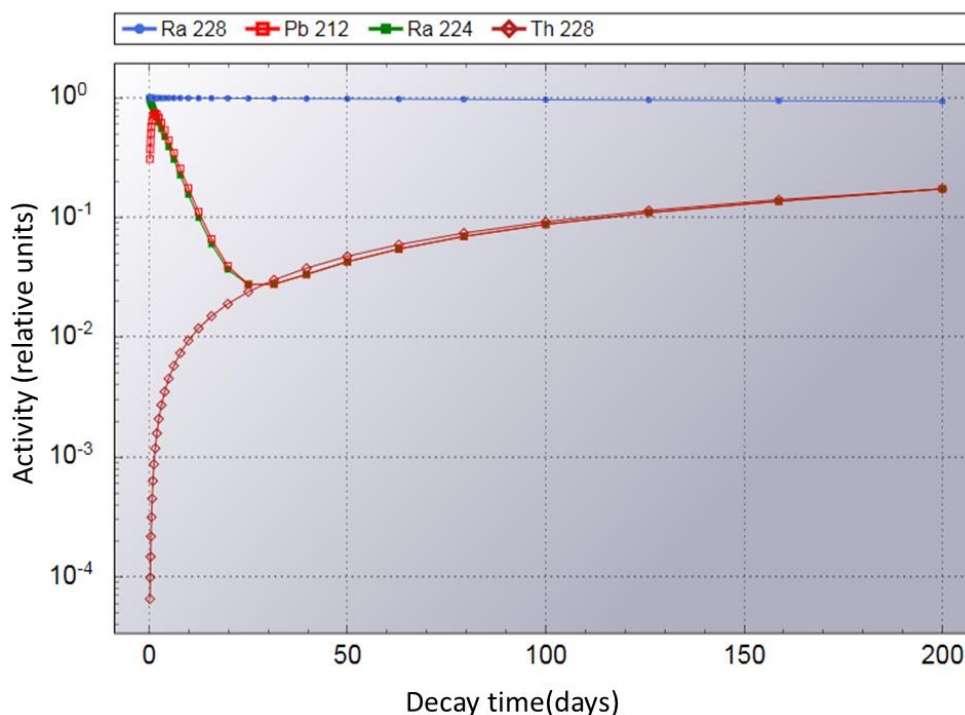


Figure 2 Decay of separated Ra-solution which was used to spike the water sample, as calculated by Nucleonica DelNUS+++.

Since ^{228}Ra is at this time unsupported, it will undergo simple decay according to its own half-life. Its daughter ^{228}Ac , with approximately 6 hour half-life, will quickly in-grow and reach secular equilibrium.

^{228}Th is not present directly after the separation, and will only be produced by further decay of ^{228}Ac which as mentioned is in secular equilibrium with ^{228}Ra and thus decaying by the 5.75 year half-life. The ^{228}Th will therefore in-grow consistently until transient equilibrium is reached between ^{228}Ra and ^{228}Th around 20 years after separation.

^{224}Ra will also be present right after the separation; however, the unsupported ^{224}Ra will decay faster than it is being produced and virtually all of the “original” activity will be gone after around one month at which time it will be approaching secular equilibrium with ^{228}Th . It takes some time to reach full equilibrium, however after around 90 days the activity of the progenies is approximately 95 % and the two are completely equal after around 195 days. Eventually a semi-secular equilibrium situation where the ratio of ^{228}Th -progeny activity to the activity of ^{228}Th itself approaches 1.02.

The further daughters of ^{224}Ra will quickly in-grow following the chemical separation and will in practice reach equilibrium with their mother after around 22 days.

The reference date was set a suitable amount of time after the separation date so that the original ^{224}Ra activity content was virtually completely gone. Furthermore the dates at which the participants received the samples was at a time where ^{228}Th was approximately in equilibrium with its progeny.

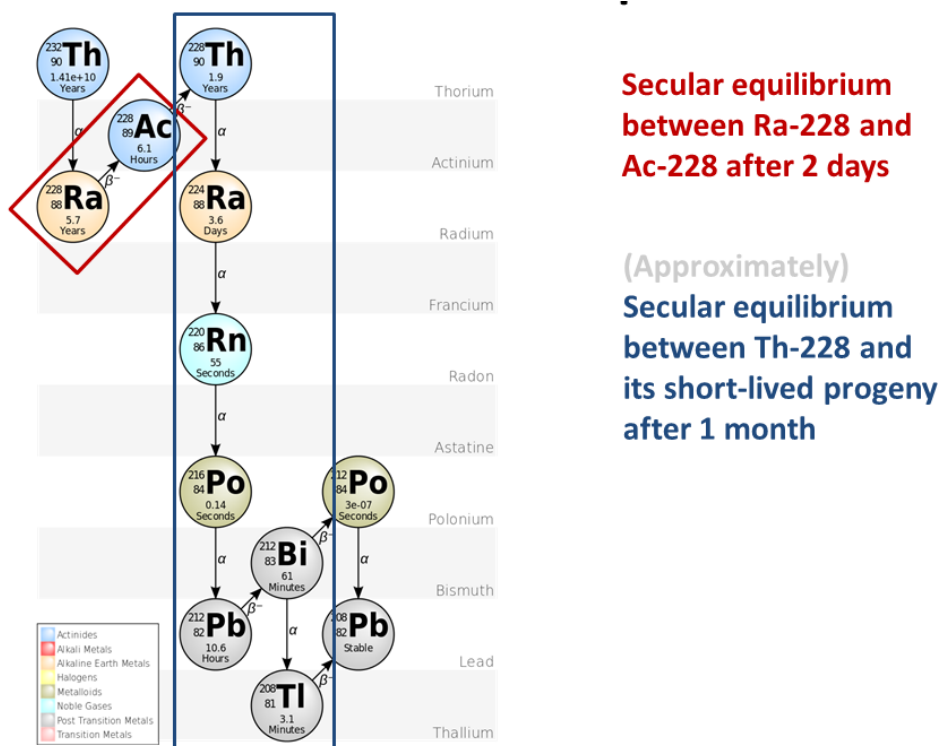


Figure 3 Simplified decay model for the thorium series, assuming the prevalence of two main sub-series starting with ^{228}Ra and ^{228}Th , respectively, which will reach equilibrium with shorter-lived progeny after approximately one month.

This allows us to define a simplified decay model for this situation, with two main components:

- $^{228}\text{Ra} + ^{228}\text{Ac}$ – decaying normally according to the half-life of ^{228}Ra
- ^{228}Th + all its shorter-lived progeny – in-growing according the decay relationship between ^{228}Th and ^{228}Ra .

This simplified decay model is illustrated in Figure 4.

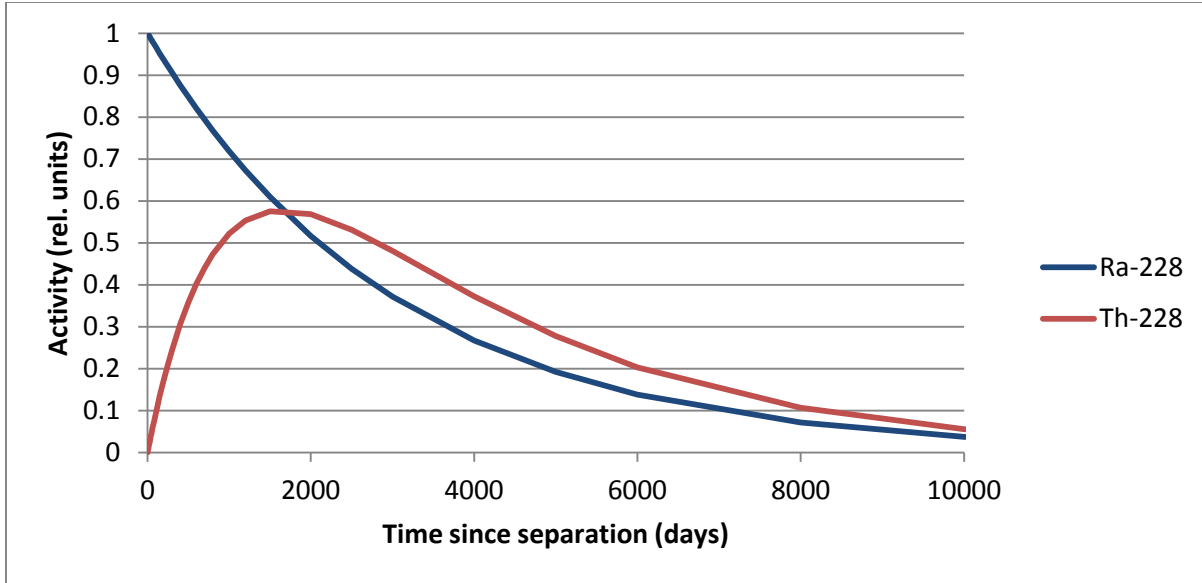


Figure 4 Simplified model for decay of ^{228}Ra and ingrowth of ^{228}Th after chemical separation of Ra-isotopes.

Measurement and activity calculation

A sample of Water 01 was measured on a HPGe system for a period of 240,000 seconds live time, and results were calculated to the measurement date (2019-10-07) giving the following activity values:

Nuclide	Activity $\pm 1\sigma$ (Bq/kg)
Pb-212	4.41 $\pm$ 0.13
Ac-228	20.9 $\pm$ 1.1

Based on the assumptions described in the previous section, we can assume that ^{212}Pb is in secular equilibrium with ^{228}Th and ^{228}Ac is in secular equilibrium with ^{228}Ra . Therefore the approximation can be made that the activities of the two nuclides reported in the table represent the activity of the parts of the decay chain. I.e.

$$a_{\text{Th-228}} \cong 4.41 \pm 0.13 \text{ Bq/kg}$$

$$a_{\text{Ra-228}} \cong 20.9 \pm 1.1 \text{ Bq/kg}$$

The ratio of the two activities is:

$$\frac{a_{\text{Th-228}}}{a_{\text{Ra-228}}} \approx 0.21$$

which is noticeably different from the theoretical equilibrium ratio given by:

$$\frac{\lambda_{\text{Th-228}}}{\lambda_{\text{Th-228}} - \lambda_{\text{Ra-228}}} \approx 1.5$$

This shows that transient equilibrium does not exist yet between ^{228}Ra and ^{228}Th at the time of measurement, which means that ^{228}Th is currently in-growing.

The activity for ^{228}Ra at the reference date is given by the simple exponential decay equation, considering that the time elapsed between the reference time and the measurement was 189 days:

$$\begin{aligned} a_{Ra-228,0} &= a_{Ra-228} \cdot e^{\lambda_{Ra-228} \cdot t} \\ &= 20.9 \cdot e^{0.000330 \cdot 190} \\ &\cong 22.3 \text{ Bq/kg} \end{aligned}$$

The uncertainty of the calculated ^{228}Ra -activity is given by

$$\begin{aligned} u(a) &= u(a_{Ra-228}) \cdot e^{\lambda_{Ra-228} \cdot t} \\ &= 1.1 \cdot e^{0.000330 \cdot 190} \\ &\cong 1.2 \text{ Bq/kg} \end{aligned}$$

The activity of ^{228}Th (and daughters) at the reference time is given by the rearranged Bateman equation:

$$\begin{aligned} a_{Th-228,0} &= a_{Th-228} \cdot e^{\lambda_{Th-228} \cdot t} - \frac{\lambda_2}{\lambda_2 - \lambda_1} a_{Ra-228} [e^{\lambda_{Th-228} \cdot t} - e^{\lambda_{Ra-228} \cdot t}] \\ &= 4.41 \cdot e^{0.000992 \cdot 190} - \frac{0.000992}{0.000992 - 0.000330} \cdot 20.9 \cdot [e^{0.000992 \cdot 190} - e^{0.000330 \cdot 190}] \\ &\cong 0.85 \text{ Bq/kg} \end{aligned}$$

The uncertainty of this activity is calculated from:

$$\begin{aligned} u_c(a_{Th-228,0}) &= \sqrt{(e^{\lambda_{Th-228} \cdot t})^2 \cdot u^2(a_{Th-228}) + \left(\frac{\lambda_2}{\lambda_2 - \lambda_1} [e^{\lambda_{Th-228} \cdot t} - e^{\lambda_{Ra-228} \cdot t}] \right)^2 \cdot u^2(a_{Ra-228})} \\ &= \sqrt{(e^{0.000992 \cdot 190})^2 \cdot (0.13)^2 + \left(\frac{0.000992}{0.000992 - 0.000330} [e^{0.000992 \cdot 190} - e^{0.000330 \cdot 190}] \right)^2 \cdot (1.1)^2} \\ &\cong 0.28 \text{ Bq/kg} \end{aligned}$$

The results (including uncertainties with coverage factor k=1) can therefore be expressed as:

$$A_{Ra-228,0} = 22.3 \pm 1.2 \text{ Bq/kg}$$

and

$$A_{Th-228,0} = 0.85 \pm 0.28 \text{ Bq/kg}$$

These results are in very good agreement with the reference values of $22.08 \pm 0.92 \text{ Bq/kg}$ for ^{228}Ra and $0.80 \pm 0.06 \text{ Bq/kg}$ for ^{228}Th , both in equilibrium with their respective short-lived progeny.

Note that the possible error encountered by using this simplified decay model, caused by using a shorter-lived daughter to calculate the activity concentration of ^{228}Th , is maximum 5 % after 95 days following separation and maximum 2 % after 170 days since the separation.

Example 2 – ⁹⁵Zr/⁹⁵Nb chronometry

A sample was measured on a HPGe system for a period of 7200 seconds live time, and results were calculated to the measurement date (2019-05-12) giving the following activity values:

Nuclide	Activity $\pm 1\sigma$ (Bq)

Nb-95	283 $\pm$ 12
Zr-95	342 $\pm$ 17

Questions:

1. What is the equilibrium ratio for the two nuclides? Are ⁹⁵Zr and ⁹⁵Nb in radioactive equilibrium?
2. What were the activities of ⁹⁵Zr and ⁹⁵Nb on the reference date 1st April 2019?
3. Assuming all ⁹⁵Nb was produced by ingrowth of separated ⁹⁵Zr, what was the date of separation?

Answer to question 1:

Table 1 Half-lives and decay constants of ⁹⁵Zr and ⁹⁵Nb

Nuclide	Half-life $t_{1/2}$ (d)	Decay const. λ (d ⁻¹)
⁹⁵ Zr	64.032	0.01083
⁹⁵ Nb	34.991	0.01981

Table 1 shows the half-lives of ⁹⁵Zr and ⁹⁵Nb as well as the decay constants. Based on this the equilibrium ratio for the two radionuclides is calculated as:

$$\frac{\lambda_{Nb-95}}{\lambda_{Nb-95} - \lambda_{Zr-95}} \cong 2.21$$

The activity ratio of the two radionuclides is given by:

$$\frac{A_{Nb-95}}{A_{Zr-95}} = \frac{283 \text{ Bq}}{342 \text{ Bq}} \cong 0.83$$

Since $\frac{\lambda_{Nb-95}}{\lambda_{Nb-95} - \lambda_{Zr-95}} \neq \frac{A_{Nb-95}}{A_{Zr-95}}$ radioactive equilibrium does not exist between the two nuclides.

Answer to question 2:

A total of 41 days has passed between the reference date and the date of the measurement. Since the measurement time is much shorter than the respective half-lives, there is no need to perform any correction for decay during the measurement period itself.

The activity of ⁹⁵Zr on the reference date is calculated by the standard decay equation:

$$A_{Zr-95,0} = A_{Zr-95} \cdot e^{\lambda_{Zr-95} \cdot t} \cong 533 \text{ Bq}$$

The uncertainty is given by:

$$u(A_{Zr-95,0}) = u(A_{Zr-95}) \cdot e^{\lambda_{Zr-95} \cdot t} \cong 27 \text{ Bq}$$

For ^{95}Nb , since it is not in equilibrium with ^{95}Zr which means it is currently ingrowing, the activity concentration is calculated from the rearranged Bateman equation:

$$A_{Nb-95,0} = A_{Nb-95} \cdot e^{\lambda_{Nb-95} \cdot t} - \frac{\lambda_2}{\lambda_2 - \lambda_1} A_{Zr-95} [e^{\lambda_{Nb-95} \cdot t} - e^{\lambda_{Zr-95} \cdot t}] \cong 114 \text{ Bq}$$

The uncertainty is given by:

$$u_c(A_{Nb-95,0}) = \sqrt{(e^{\lambda_{Nb-95} \cdot t})^2 \cdot u^2(A_{Nb-95}) + \left(\frac{\lambda_2}{\lambda_2 - \lambda_1} [e^{\lambda_{Nb-95} \cdot t} - e^{\lambda_{Zr-95} \cdot t}]\right)^2 \cdot u^2(A_{Zr-95})} \cong 38 \text{ Bq}$$

The results (including uncertainties with coverage factor $k=1$) for the activities on the reference date can therefore be expressed as:

$$A_{Zr-95,0} = 533 \pm 27 \text{ Bq}$$

and

$$A_{Nb-95,0} = 114 \pm 38 \text{ Bq}$$

Answer to question 3:

The date of separation (where the activity of ^{95}Nb was 0) is calculated from:

$$t_{sep} = \frac{\ln\left(1 - \frac{A_{Nb-95}}{A_{Zr-95}} \cdot \frac{\lambda_{Nb-95} - \lambda_{Zr-95}}{\lambda_2}\right)}{\lambda_{Zr-95} - \lambda_{Nb-95}} = 52.35 \dots \cong 52 \text{ days}$$

The uncertainty of this value is:

$$u_c(t_{sep}) = \frac{\sqrt{\left(\frac{u(A_{Nb-95})}{A_{Nb-95}}\right)^2 + \left(\frac{u(A_{Zr-95})}{A_{Zr-95}}\right)^2}}{\lambda_{Nb-95} \cdot \frac{A_{Zr-95}}{A_{Nb-95}} - (\lambda_{Nb-95} - \lambda_{Zr-95})} = 4.36 \dots \cong 5 \text{ days}$$

Considering the dates mentioned at the start of this example, the above results correspond to the date of separation being:

$$21^{\text{st}} \text{ March 2019 } (\pm 5 \text{ days})$$