PAPER

On the Decay Corrections for Mixed ^{95}Zr-^{95}Nb Sources

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Decay corrections for mixed sources of genetically related ^{95}Zr and ^{95}Nb may appear to be more complex than those usually required for routine radionuclidic assays. The complexity arises because of the existence of a sufficiently long-lived ^{95m}Nb metastable state in the decay series, and because both ^{95}Zr and ^{95m}Nb exhibit multi-branched decay. The necessary corrections are presented here in straightforward algebraic expressions. For sources in which ^{95m}Nb is in secular equilibrium with ^{95}Zr, the decay correction for ^{95}Nb reduces to the simple form for a parent-to-child genetic relation, in which the presence of the intermediate ^{95m}Nb state in the decay sequence can be ignored.

Introduction

This note has been written and is intended to assist users of mixed ^{95}Zr-^{95}Nb sources in performing decay corrections for these two genetically related radionuclides. It has been observed that the necessary calculations seem to be outside the experience and daily practices of laboratory workers who perform routine radioactivity measurements. The decay corrections may initially appear to be somewhat more complex than usual in the sense that ^{95}Zr decays not only to ^{95}Nb in a simple parent-to-child relation, but also decays to ^{95}Nb as a parent-to-grandchild through an intermediate, appreciably-long, ^{95m}Nb metastable state — both of which occur by well-established β^- transitions. In addition to the multi-branched decay of ^{95}Zr to both ^{95m}Nb and ^{95}Nb, the ^{95m}Nb also branches its decay to both ^{95}Nb (through internal transitions with γ-ray and conversion electron emissions) and to ^{95}Mo (the stable state of the decay sequence) by β^- decay.

The results presented here are hardly original. They date back to the seminal work of Bateman[1] in 1910 who provided solutions for the linked differential equations that relate the temporally dependent decay of genetically related radionuclides. Regrettably few of the standard texts and reference works on radioactivity measurements ever present the Bateman equation solutions (except for the simplest parent-child relation) in completely written-out algebraic expressions, that exclude the use of sum ($\Sigma_{i=j \text{ to } k} x_i = x_j + x_{j+1} + \cdots + x_k$) and product ($\Pi_{i=j \text{ to } k} x_i = x_j \cdot x_{j+1} \cdots x_k$) series notation. The presented treatments might easily be less than transparent to everyday practitioners of radionuclidic metrology. For example, a generalized presentation could be something like:

> For a series of descendant radionuclides $i = 1$ to n, each having an initial ($t = 0$) activity of $A_{i(0)}$ and a decay constant λ_i, the n_{th} generation activity A_n at any time t is

$$\begin{aligned} A_n = {} & A_{1(0)}[\Sigma_{i=1 \text{ to } n} C_i \exp(-\lambda_i t)] \\ & + A_{2(0)}[\Sigma_{i=2 \text{ to } n} C_i \exp(-\lambda_i t)] + \ldots \\ & + A_{n-1(0)}[\Sigma_{i=n-1 \text{ to } n} C_i \exp(-\lambda_i t)] \\ & + A_{n(0)} \exp(-\lambda_n t) \end{aligned} \qquad (1)$$

> where the coefficients C_i for each term are:

$$C_i = [\Pi_{k=i+1 \text{ to } n} \lambda_k] / [\Pi_{j=i \text{ to } n} (\lambda_j - \lambda_i)] \quad (\text{with } j \neq i).$$

None of these texts or references, to my knowledge, treat the decay of a genetic series with its members having multi-

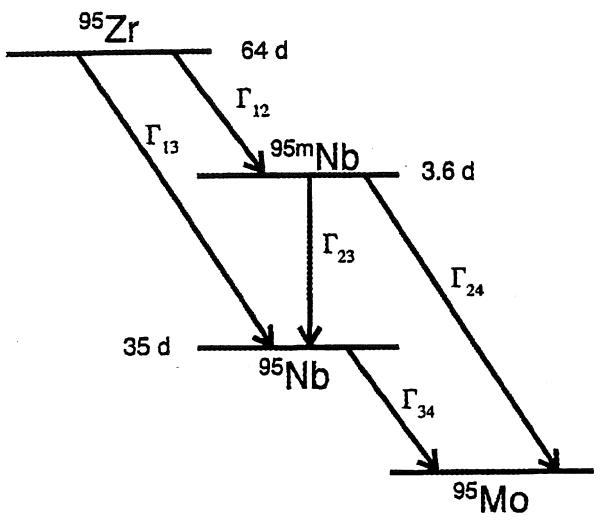

Figure 1 The ^{95}Zr-^{95m}Nb-^{95}Nb decay series. The scheme is representational and omits other gamma-ray transitional states within ^{95}Nb and ^{95}Mo.

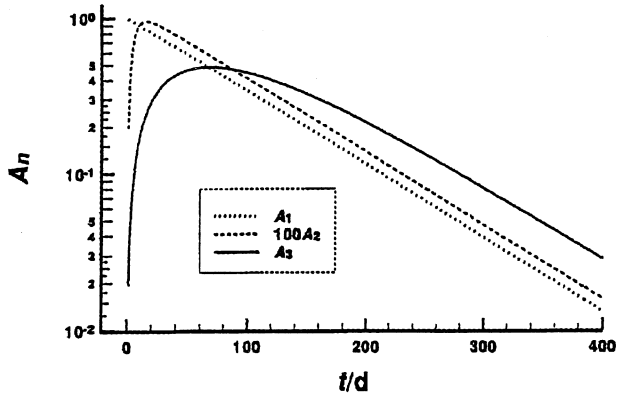

Figure 2 Activities of ^{95}Zr (A_1), ^{95m}Nb (A_2), and ^{95}Nb (A_3) as a function of time t (in units of days) for a pure ^{95}Zr source with unit activity ($A_{1(0)} = 1$) at $t = 0$ and no initially present ^{95m}Nb and ^{95}Nb ($A_2 = A_3 = 0$).

branched decay. Nor do they present decay equations for cases when some of the intermediate members of a descendant series are in radioactive equilibrium. The generic Equation (1) governs all of the decay expressions that follow.

The ^{95}Zr-^{95m}Nb-^{95}Nb Decay Sequence

The radionuclide ^{95}Zr never occurs without the presence of either ^{95m}Nb or ^{95}Nb. In the first place, the ^{95m}Nb child (except at very short times after a Zr separation) is usually in secular equilibrium with ^{95}Zr. In the second place, the ^{95}Nb child and grandchild grows in with the decay of ^{95}Zr, and can also be present in excess amounts in some mixed ^{95}Zr-^{95}Nb sources. The National Institute of Standards and Technology (NIST), for example, as part of a recent measurement proficiency test of nuclear-power-industry laboratories who participate in the Nuclear Energy Institute (NEI) measurement assurance program,[2,3] recently distributed a "blind" test sample (i.e., one of known, but undisclosed radionuclidic content) that was essentially a ^{95}Nb source, but having a substantial ^{95}Zr fraction.

A representational scheme for the ^{95}Zr-^{95m}Nb-^{95}Nb decay sequence is illustrated in Figure 1. For convenience, the indices j = 1,2,3,4 are used to designate, respectively: ^{95}Zr, ^{95m}Nb, ^{95}Nb, and ^{95}Mo. The decay constants (λ) and branching ratios (Γ) used in the illustrated calculations that follow, as taken from ENSDF,[4] are:

$\lambda_1 = (0.010827 \pm 0.000008)$ d^{-1} [$T_{½(1)} = 64.02$ d]
$\lambda_2 = (0.1921 \pm 0.0018)$ d^{-1} [$T_{½(2)} = 86.6$ h]
$\lambda_3 = (0.019818 \pm 0.000004)$ d^{-1} [$T_{½(3)} = 34.975$ d]

and

$\Gamma_{12} = 0.0113 \pm 0.0012$
$\Gamma_{13} = 0.9887 \pm 0.0012$
$\Gamma_{23} = 0.944 \pm 0.006$
$\Gamma_{24} = 0.056 \pm 0.006$

where Γ_{12} and Γ_{13} are the respective branching ratios for decay of ^{95}Zr to ^{95m}Nb and to ^{95}Nb, and where Γ_{23} and Γ_{24} are those for decay of ^{95m}Nb to ^{95}Nb and to ^{95}Mo. The branch from ^{95}Nb to ^{95}Mo is assumed to be $\Gamma_{34} = 1$.

Decay Equations

For any given mixed source of ^{95}Zr-^{95m}Nb-^{95}Nb with initial activities (at any arbitrary $t = 0$ reference time) of $A_{1(0)}$, $A_{2(0)}$, and $A_{3(0)}$, their activities at any other time t are given by:

$$A_1 = A_{1(0)}\exp(-\lambda_1 t) \qquad (2)$$

$$A_2 = A_{2(0)}\exp(-\lambda_2 t) + A_{21}$$
$$= A_{2(0)}\exp(-\lambda_2 t) + A_{1(0)}\Gamma_{12}[\lambda_2/(\lambda_2-\lambda_1)]\,[\exp(-\lambda_1 t) - \exp(-\lambda_2 t)] \quad (3)$$

$$A_3 = A_{3(0)}\exp(-\lambda_3 t) + A_{32} + A_{31} + A_{321}$$
$$= A_{3(0)}\exp(-\lambda_3 t) + A_{2(0)}\Gamma_{23}[\lambda_3/(\lambda_3-\lambda_2)]\,[\exp(-\lambda_2 t) - \exp(-\lambda_3 t)] + A_{1(0)}\Gamma_{13}[\lambda_3/(\lambda_3-\lambda_1)]\,[\exp(-\lambda_1 t) - \exp(-\lambda_3 t)] + A_{1(0)}\Gamma_{12}\Gamma_{23}\{[\lambda_2\lambda_3/\{(\lambda_2-\lambda_1)(\lambda_3-\lambda_1)\}]\exp(-\lambda_1 t) + [\lambda_2\lambda_3/\{(\lambda_1-\lambda_2)(\lambda_3-\lambda_2)\}]\exp(-\lambda_2 t) + [\lambda_2\lambda_3/\{(\lambda_1-\lambda_3)(\lambda_2-\lambda_3)\}]\exp(-\lambda_3 t) \quad (4)$$

Equation (2) is, of course, just the usual expression for the exponential decay of the ^{95}Zr parent. The first terms of Equations (3) and (4) correspond to those parts of the ^{95m}Nb and ^{95}Nb activities that were originally present at time $t = 0$ that are still present at time t; while the second terms of Equations (3) and (4) correspond, respectively, to the ingrowth of ^{95m}Nb as a child of ^{95}Zr (call it A_{21}) and the ingrowth of ^{95}Nb as a child of ^{95m}Nb (A_{32}); and while the third and fourth terms of Equation (4) correspond to the ingrowth of ^{95}Nb as a child (A_{31}) and as a grandchild of ^{95}Zr (A_{321}), respectively. Figure 2 illustrates the temporal dependence of A_1, A_2, and A_3 for an initially pure source of ^{95}Zr with conditions $A_{1(0)} = 1$ and $A_{2(0)} = A_{3(0)} = 0$. The three curves represent A_1, A_{21}, and $(A_{31} + A_{321})$, respectively.

In practice the activities on the left-hand sides of Equations (2) through (4) might be expressed in terms of experimental counting rates at times t, such as a background-corrected counting rate R_γ for some γ ray:

$A = R_\gamma/\Gamma_\gamma\varepsilon_\gamma$, where Γ_γ is the probability per decay for the γ ray (appropriately normalized to its decay branch) and where ε_γ is the γ-ray's photopeak detection efficiency. For a somewhat different situation, Collé,[5] for example, presented an expression for the total liquid scintillation counting rate as a function of experimentally observed-times for all of the decay branches in the ^{95}Zr-^{95m}Nb-^{95}Nb decay sequence.

Equations (2) through (4) are appropriate expressions that can be used to decay correct the results of any measurements of A_j (or R_j) at some time t to any reference time $t = 0$ (or conversely for correcting results at some $t = 0$ reference time to time t). In most mixed ^{95}Zr-^{95}Nb sources, ^{95m}Nb will be in secular equilibrium with ^{95}Zr. For any time $t > 30$ d or so, both radionuclides will decay with the half-life of the ^{95}Zr parent such that the ratio of the two activities at any subsequent time $t = $ e is a constant equal to $A_{2e}/A_{1e} = \Gamma_{12}[\lambda_2/(\lambda_2-\lambda_1)] = 0.0120$. Rarely does ^{95}Nb reach a comparable state of radioactive equilibrium with ^{95}Zr, except for very aged sources that would be almost beyond their useful lifetime. Nevertheless, the A_3/A_1 activity ratio asymptotically approaches an equilibrium value of about 2.2, which is achieved only after the passage of at least 600 days. Simple data-linearization techniques to graphically assess the degree of equilibrium in such genetic relationships have also been presented by Collé.[5]

^{95}Nb Decay with ^{95m}Nb in Equilibrium with ^{95}Zr

Decay corrections with Equation (4) are difficult to effect unless the ^{95m}Nb is in equilibrium with ^{95}Zr, or unless there is an independent assessment of the initial activity of ^{95m}Nb [because of the $A_{2(0)}$-containing second term in Equation (4)]. For the usual case where ^{95m}Nb and ^{95}Zr are in equilibrium at both the measurement time t and at the reference time $t = 0$, $A_{2e(0)}$ assumes the value $A_{1e(0)}\Gamma_{12}[\lambda_2/(\lambda_2-\lambda_1)]$ and Equation (4) becomes independent of $A_{2(0)}$:

$$A_{3e} = A_{3(0)}\exp(-\lambda_3 t) + A_{1(0)}\Gamma_{13}[\lambda_3/(\lambda_3-\lambda_1)]\,[\exp(-\lambda_1 t) - \exp(-\lambda_3 t)] + A_{1(0)}\Gamma_{12}\Gamma_{23}[\lambda_3/(\lambda_3-\lambda_1)]\{[\exp(-\lambda_1 t)]\,[\lambda_2/(\lambda_2-\lambda_1)] - [\exp(-\lambda_3 t)]\,[\lambda_2/(\lambda_2-\lambda_3)]\} + A_{1(0)}\Gamma_{12}\Gamma_{23}[\lambda_2\lambda_3/\{(\lambda_2-\lambda_1)(\lambda_2-\lambda_3)\}]\exp(-\lambda_3 t) \quad (5)$$

Equation (5) is a general expression that is applicable for any multi-branched parent-child-grandchild decay sequence (i.e., one comparable to that shown in Figure 1) in which the child is in radioactive equilibrium with the parent.

Because of the small branching of ^{95}Zr to ^{95m}Nb (Γ_{12}) and of ^{95m}Nb to ^{95}Mo (Γ_{24}), whose product $\Gamma_{12}\Gamma_{24}$ is the fractional ^{95m}Nb activity (from ^{95}Zr) that does not decay to ^{95}Nb, Equation (5) can be adequately approximated by the expression:

$$A_{3ae} = A_{3(0)}\exp(-\lambda_3 t) + A_{1(0)}[\lambda_3/(\lambda_3-\lambda_1)]\,[\exp(-\lambda_1 t) - \exp(-\lambda_3 t)] \quad (6)$$

whose second term has the form of just that for a parent-child relation since the intermediate ^{95m}Nb (in equilibrium) is also decaying with the ^{95}Zr half-life. Use of the Equation (6) approximation results in a calculational error of -0.0004% or less depending upon the magnitude of $A_{3(0)}$; e.g., for large t with $A_{3(0)}$ approaching zero, the ratio of A_{3ae}/A_{3e} approaches a minimum $A_{3ae}/A_{3e} = 0.999996$ (i.e., -0.0004%).

Additional Considerations

The ^{95}Nb-to-^{95}Zr activity ratio is often of interest. From Equation (5) and (2), and for conditions in which A_2 is in secular equilibrium with A_1, one can express the ratio for the generalized case as:

$$A_{3e}/A_{1e} = [A_{3e(0)}/A_{1e(0)}]\exp[-(\lambda_3-\lambda_1)t] + G_t \quad (7)$$

where G_t is a temporal function of only the decay constants and branching ratios (and not any activities):

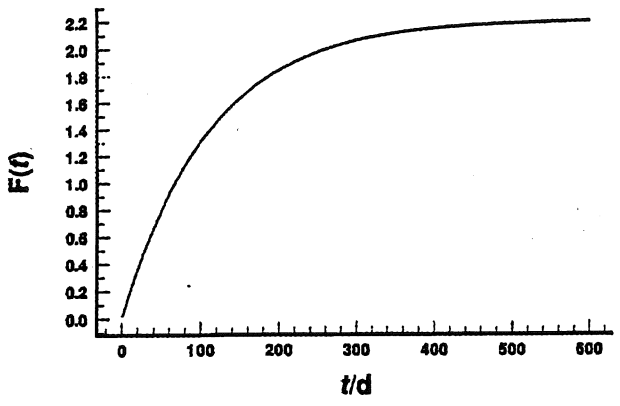

Figure 3 The function F_t over the time interval $0 \le t \le 600$ d. Refer to text.

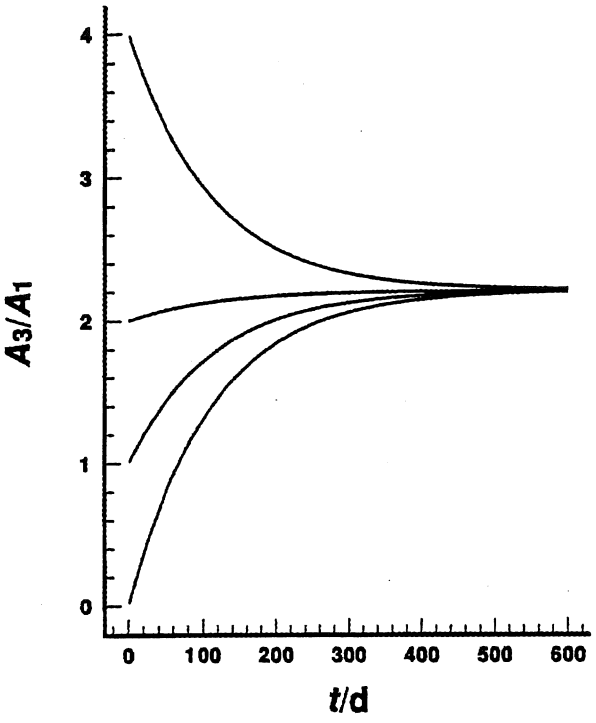

Figure 4 ^{95}Nb to ^{95}Zr activity ratios A_3/A_1 as a function of time t (in units of days) for initial activity ratios of $A_{3(0)}/A_{1(0)}$ = 0, 1, 2, and 4. The A_3/A_1 values for the initial conditional $A_{3(0)}/A_{1(0)}$ = 0 are obtained from the ratio of the full-formed Equations (2) and (4); whereas those for the latter cases with ^{95m}Nb in secular equilibrium with ^{95}Zr {i.e., with $A_2 = A_{1(0)}\Gamma_{12}[\lambda_2/(\lambda_2-\lambda_1)]\exp(-\lambda_1 t)$} are obtained from Equation (7).

$$G_t = \Gamma_{13}[\lambda_3/(\lambda_3-\lambda_1)]\{1 - \exp[-(\lambda_3-\lambda_1)t]\} + \Gamma_{12}\Gamma_{23}[\lambda_2\lambda_3/\{(\lambda_3-\lambda_1)(\lambda_2-\lambda_1)\}]\{1 - \exp[-(\lambda_3-\lambda 1)t]\} + \Gamma_{12}\Gamma_{23}[\lambda_2\lambda_3/\{(\lambda_2-\lambda_1)(\lambda_2-\lambda_3)\}]\,[\exp[-(\lambda_3-\lambda_1)t] \quad (8)$$

For the ^{95}Zr-^{95m}Nb-^{95}Nb decay sequence, G_t reduces to

$$F_t = [\lambda_3/(\lambda_3-\lambda_1)]\{1 - \exp[-(\lambda_3-\lambda_1)t]\} \quad (9)$$

just as Equation (5) reduced to Equation (6). Figure 3 illustrates the Equation (9) dependence of F_t as a function of t over the time interval $0 \le t \le 600$ d. Results for the A_3/A_1 ratio as a function of time t for various initial $A_{3(0)}/A_{1(0)}$ ratios as would be reflected in typical Equation (7) decay corrections are illustrated in Figure 4.

The Equation (8) and (9) expressions have direct applicability and illustrate how these complex decay equations can be drastically simplified for the very useful linear-transform techniques that are described elsewhere.[5,6]

A curious, perhaps common, decay-correction mistake may be made if one incorrectly assumes that the second term of Equation (6) should be modified by the quantity $(\Gamma_{13} + \Gamma_{12}\Gamma_{23})$ which corresponds to the total branching for both direct ^{95}Zr decay to ^{95}Nb (Γ_{13}) and the ^{95}Zr decay to ^{95}Nb through ^{95m}Nb ($\Gamma_{12}\Gamma_{23}$); i.e.,

$$A_{3xe} = A_{3(0)}\exp(-\lambda_3 t) + A_{1(0)}(\Gamma_{13} + \Gamma_{12}\Gamma_{23})[\lambda_3/(\lambda_3-\lambda_1)]\,[\exp(-\lambda_1 t) - \exp(-\lambda_3 t)] \quad (10)$$

This quantity has an identity of $(\Gamma_{13} + \Gamma_{12}\Gamma_{23}) = (1 - \Gamma_{12}\Gamma_{24})$ where $\Gamma_{12}\Gamma_{24}$ represents the fractional ^{95}Zr activity that does *not* decay through ^{95}Nb. Equation (10) in contradistinction to Equation (6) may seem on first appearance to be a more intuitively correct approximation for Equation (5), but it is not. It is rather easy to numerically demonstrate, by comparisons of the ratios A_{3ae}/A_{3e} and A_{3xe}/A_{3e}, that use of Equation (10) will result in metrologically-significant calculational errors* that approach -0.064% at a maximum for large t.

It must be emphasized that the Equations' (6) and (10) equilibrium approximations may not be valid for any other similar-type, multi-branched parent-child-grandchild series (with differing decay constants and branching ratios). Whereas the more general equilibrium expression of Equation (5) is valid for any other comparable decay sequence (irrespective of the decay constants and branching ratios so long as A_2 is in radioactive equilibrium with A_1).

* These are "errors" in the true sense in that they could be avoided or accounted for by correction. They are considered to be "metrologically significant" since their magnitudes rival those for typical uncertainty components in radionuclidic assays by metrological laboratories like NIST. For example, the routine gravimetric, source-preparation procedures used in our laboratory as they apply to the preparation of counting sources have relative standard uncertainties of about ±0.05%. In general, any error or uncertainty component is considered "significant" if it has a relative magnitude of order of about 0.01%.

Summary Thoughts

Users of mixed ^{95}Zr-^{95}Nb sources may find the equations and discussion presented herein to be helpful. The decay correction for the ^{95}Zr parent [as given in Equation (2)] is as trivial as usual. Equation (4) is a full-formed expression for the ^{95}Nb activity's temporal dependence. It is generally applicable for decay corrections over any time intervals and for any initial non-equilibrium condition. Its use requires knowledge of both the initial ^{95}Zr and ^{95m}Nb activities, as well as that for the ^{95}Nb. For the more common situation when ^{95m}Nb is already in secular equilibrium with ^{95}Zr, the necessary correction for ^{95}Nb can be adequately approximated by the use of the simple expression of Equation (6). The decay correction in this case still requires knowledge of the initial ^{95}Zr activity in addition to the ^{95}Nb activity. The more generalized treatment for the equilibrium case as given by Equation (5) [or Equation (7) for the activity ratio] may also be instructive for application to other similar kinds of genetically related decay series.

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Biography

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