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**ABSOLUTE STANDARDIZATION
OF THE RADIOACTIVE PAIR $^{95}\text{Zr}/^{95}\text{Nb}$**

by

H.H. HANSEN, E. DE ROOST, W. VAN DER EIJK and R. VANINBROUKX

1973



Joint Nuclear Research Centre
Geel Establishment - Belgium

Central Bureau for Nuclear Measurements - CBNM

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ABSTRACT

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KEY WORDS

CALIBRATION STANDARDS
ZIRCONIUM 95
NIOBIUM 95
SOLID SOLUTIONS
AGE ESTIMATION
BETA-MINUS DECAY
HALF-LIFE
COINCIDENCE METHODS
GAMMA RADIATION
GAMMA DETECTION
GAMMA SPECTROMETERS
SCINTILLATION COUNTERS
LI-DRIFTED GE DETECTORS
IMPURITIES
ERRORS

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1. Introduction

The absolute standardization of the $^{95}\text{Zr}/^{95}\text{Nb}$ isotopes is rather difficult due to the comparable half-lives of parent and daughter nuclei and due to the presence of a small but not negligible fraction of decays passing through an isomeric state in ^{95}Nb . Some aspects of the problem are discussed by PARKER ¹⁾ and HISCOTT and ALLEN ²⁾. In the present report the different steps of the calibration procedure are described in some detail. The most essential parts are the determination of the age of the radioactive solution and the determination of the total activity at any time. Peripherically a discussion of the decay properties which enter the calculations is necessary as well as the definition of possible radioactive impurities in the solution and the consideration of error sources. If there are discrepancies between results on certain decay data obtained from earlier investigations, a redetermination of those doubtful data ought to be envisaged before starting any standardization.

2. The $^{95}\text{Zr}/^{95}\text{Nb}$ Decay Scheme

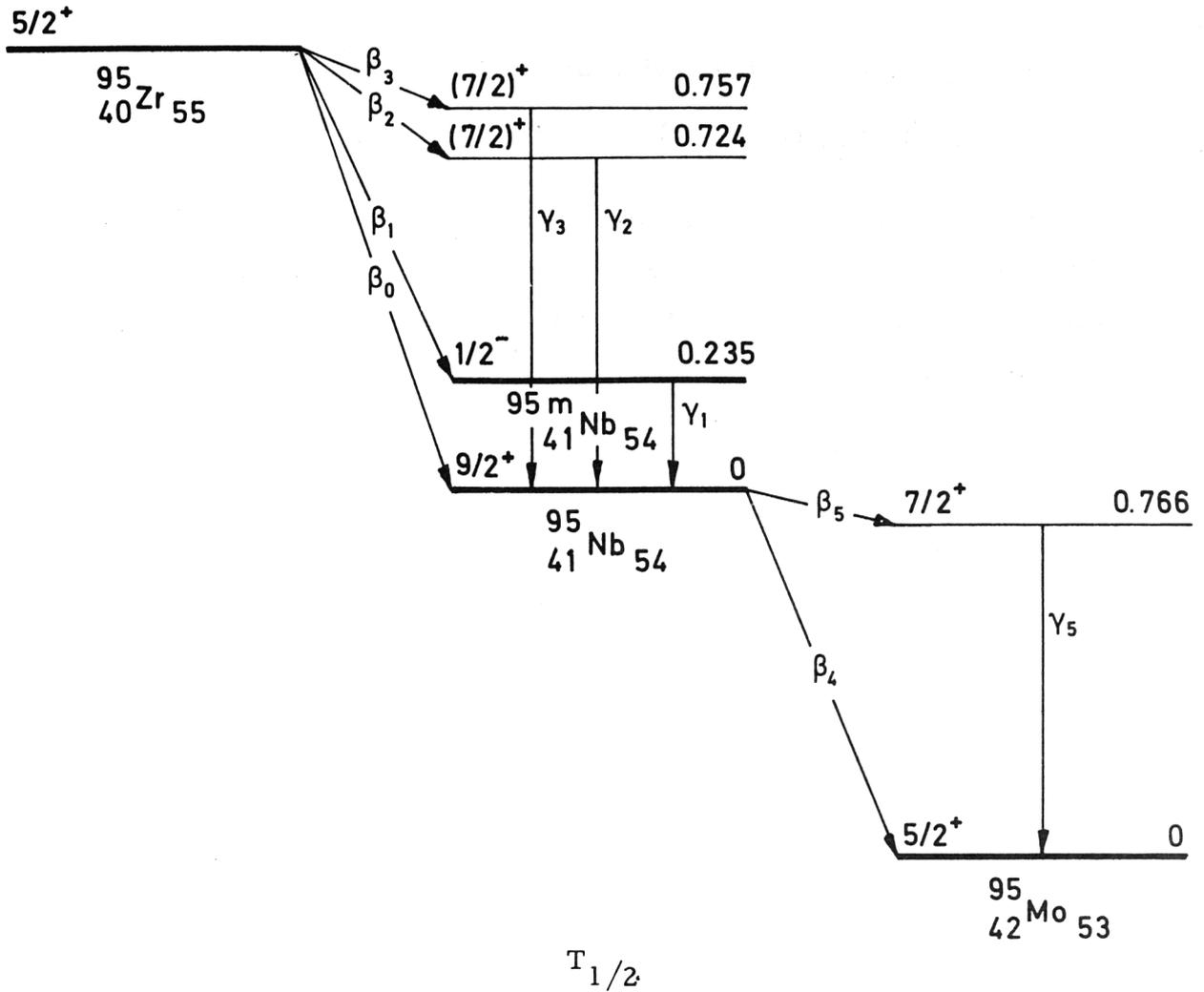
The decay properties of the $^{95}\text{Zr}/^{95}\text{Nb}$ pair have been investigated very often, indicating the importance of the nuclides in e.g. the study of reactor technology, fall-out and health physics. A rather complete listing of references on the decay properties may be found elsewhere ^{3, 4)}. The decay properties entering the calculations are represented in Fig. 1. The given values are extracted from the available experimental results. For the level feedings in ^{95}Nb by β^- -decay

only the most recent and accurate values ^{4, 6, 7)} have been considered. The β^- -transitions to the ground state of ⁹⁵Nb as well as ⁹⁵Mo seem to be not very well established, but are very weak ^{8, 9)} and have no remarkable influence on the accuracy of the standardization. The values for the most intense β^- -branchings have been verified by own measurements as described in section 6. Published values for the γ -ray energies are in very good agreement ^{4, 6, 10)}. Recent measurements on the internal conversion are rather consistent ^{4, 11, 12)}. For the K-shell internal conversion coefficient of the 234.7 keV γ -ray of ^{95m}Nb the result given by FOIN et al. ¹¹⁾ and for those of the other γ -rays the accurate values published by BRAHMAVAR and HAMILTON ⁴⁾ have been taken. It may be pointed to the fact that especially the values for the half-lives are different from those taken in earlier calibration work. In this paper the following half-lives are used: $T_{1/2}({}^{95}\text{Zr}) = (64.10 \pm 0.04)\text{d}$ ¹³⁾, $T_{1/2}({}^{95}\text{Nb}) = (35.15 \pm 0.06)\text{d}$ ¹⁴⁾ and $T_{1/2}({}^{95m}\text{Nb}) = (86.6 \pm 0.8)\text{h}$ ¹¹⁾. The error quoted by REYNOLDS et al. ¹⁴⁾ on the half-life of ⁹⁵Nb was 0.08%. Due to the rather short observation time it has been decided to enlarge the error as mentioned above. The half-lives of ⁹⁵Zr and ⁹⁵Nb also have been checked by own measurements (see section 6).

3. Growth and Decay Theory

At time t_0 (origin) no ^{95m}Nb (subscript C) and no ⁹⁵Nb (subscript B) shall be present and only the activity of ⁹⁵Zr (subscript A) may exist ($I_{\text{Zr}}(t_0) = I_{\text{A}}(0)$). Then let be at any time t

$$\begin{aligned} I_{\text{A}}(t) = I_{\text{A}} &= \text{activity of } {}^{95}\text{Zr} \\ I_{\text{C}}(t) = I_{\text{C}} &= \text{activity of } {}^{95m}\text{Nb} \\ I_{\text{B1}}(t) = I_{\text{B1}} &= \text{activity of } {}^{95}\text{Nb from } {}^{95}\text{Zr directly} \end{aligned}$$



^{95}Zr (64.10±0.04)d
 ^{95}Nb (35.15±0.06)d
 $^{95\text{m}}\text{Nb}$ (86.6 ±0.8)h

β^- -transition	$E_{\text{max}}(\beta)$ [keV]	$p(\beta)$ [%]
β_0	1122.3±3.9	0.4
β_1	887.6±4.0	1.4±0.2
β_2	398.1±3.9	44.3±0.5
β_3	365.6±3.9	53.9±0.6
β_4	924.8±0.7	0.08
β_5	159.0±0.7	99.92

γ -rays	E_γ [keV]	α_K [10^{-3}]	α [10^{-3}] ⁵⁾
γ_1	234.70±0.14	(2.35±0.20)· 10^3	2.84· 10^3
γ_2	724.23±0.04	1.56±0.14	1.61
γ_3	756.74±0.04	1.45±0.15	1.45
γ_5	765.83±0.04	1.32±0.13	1.43

Fig. 1: Decay scheme and some evaluated decay data in the decay of ^{95}Zr - ^{95}Nb - ^{95}Mo . $T_{1/2}$ =half life; $E_{\text{max}}(\beta)$ =maximum β^- energy; $p(\beta)$ = β^- transition probability; E_γ = γ -ray energy; α_K , α =K-shell and total internal conversion coefficient, respectively.

$$I_{B2}(t) = I_{B2} = \text{activity of } ^{95}\text{Nb from } ^{95}\text{Zr via } ^{95m}\text{Nb}$$

$$I_{B1}(t) + I_{B2}(t) = I_B(t) = I_B = \text{activity of } ^{95}\text{Nb.}$$

λ_A , λ_B , λ_C are the decay constants ($T_{1/2} = \ln 2 / \lambda$) of ^{95}Zr , ^{95}Nb and ^{95m}Nb , respectively. Using this terminology the following expressions for the activities and their ratios can be obtained. The ^{95}Zr activity is

$$I_A = I_A(0) e^{-\lambda_A t} . \quad (1)$$

When p ($=p(\beta_1)$ of Fig. 1) is the frequency of disintegrations of ^{95}Zr through the isomeric state at 0.235 MeV in ^{95}Nb , the activity of ^{95m}Nb is given by

$$I_C = I_A(0) \frac{p\lambda_C}{\lambda_C - \lambda_A} \left\{ e^{-\lambda_A t} - e^{-\lambda_C t} \right\} \quad (2)$$

$$I_C = I_A(0) e^{-\lambda_A t} \frac{p\lambda_C}{\lambda_C - \lambda_A} \left\{ 1 - e^{-(\lambda_C - \lambda_A) t} \right\} , \quad (3)$$

and the ratio of the ^{95m}Nb and ^{95}Zr activities is

$$S = \frac{I_C}{I_A} = \frac{p\lambda_C}{\lambda_C - \lambda_A} \left\{ 1 - e^{-(\lambda_C - \lambda_A) t} \right\} . \quad (4)$$

The activity of ^{95}Nb produced by the decay of the isomeric state ^{95m}Nb is given by

$$I_{B2} = I_A(0) \frac{p\lambda_C \lambda_B}{\lambda_C - \lambda_A} \left\{ \frac{1}{\lambda_B - \lambda_A} (e^{-\lambda_A t} - e^{-\lambda_B t}) - \frac{1}{\lambda_B - \lambda_C} (e^{-\lambda_C t} - e^{-\lambda_B t}) \right\} . \quad (5)$$

In all other cases, (1-p), ^{95}Zr decays directly into ^{95}Nb .
Its corresponding activity is given by

$$I_{B1} = I_A(0) \frac{(1-p)\lambda_B}{\lambda_B - \lambda_A} \left\{ e^{-\lambda_A t} - e^{-\lambda_B t} \right\} \quad (6)$$

$$I_{B1} = I_A(0) e^{-\lambda_A t} \frac{(1-p)\lambda_B}{\lambda_B - \lambda_A} \left\{ 1 - e^{-(\lambda_B - \lambda_A)t} \right\} \quad (7)$$

The total ^{95}Nb activity is then

$$I_B = I_{B1} + I_{B2}$$

$$I_B = I_A(0) \left[\frac{(1-p)\lambda_B}{\lambda_B - \lambda_A} (e^{-\lambda_A t} - e^{-\lambda_B t}) + \frac{p\lambda_B \lambda_C}{(\lambda_B - \lambda_A)(\lambda_C - \lambda_A)} (e^{-\lambda_A t} - e^{-\lambda_B t}) \right. \\ \left. - \frac{p\lambda_B \lambda_C}{(\lambda_B - \lambda_C)(\lambda_C - \lambda_A)} (e^{-\lambda_C t} - e^{-\lambda_B t}) \right] \quad (8)$$

$$I_B = I_A(0) \left[\frac{\lambda_B}{\lambda_B - \lambda_A} \left\{ (1-p) + \frac{p\lambda_C}{\lambda_C - \lambda_A} \right\} (e^{-\lambda_A t} - e^{-\lambda_B t}) \right. \\ \left. - \frac{p\lambda_B \lambda_C}{(\lambda_B - \lambda_C)(\lambda_C - \lambda_A)} (e^{-\lambda_C t} - e^{-\lambda_B t}) \right] \quad (9)$$

Combining eqs. (1), (3), (4) and (9) the total activity, I_T , is obtained as

$$I_T = I_A + I_B + I_C = I_A(1+s) + I_B$$

$$I_T = I_A(0) \left[(1+s)e^{-\lambda_A t} + \frac{\lambda_B}{\lambda_B - \lambda_A} \left\{ (1-p) + \frac{p\lambda_C}{\lambda_C - \lambda_A} \right\} (e^{-\lambda_A t} - e^{-\lambda_B t}) \right. \\ \left. - \frac{p\lambda_B \lambda_C}{(\lambda_B - \lambda_C)(\lambda_C - \lambda_A)} (e^{-\lambda_C t} - e^{-\lambda_B t}) \right] \quad (10)$$

Using the following substitutes: $F = p\lambda_C / (\lambda_C - \lambda_A)$,
 $G = \lambda_B \{(1-p)+F\} / (\lambda_B - \lambda_A)$ and $H = \lambda_B \cdot F / (\lambda_B - \lambda_C)$ eq. (10)
 can be simplified to

$$I_T = I_A(0) \left[(1+F+G) e^{-\lambda_A t} - (G-H) e^{-\lambda_B t} - (F+H) e^{-\lambda_C t} \right]. \quad (11)$$

By combination of the adequate equations the following suitable activity ratios can be obtained

$$R = \frac{I_B}{I_A} = \frac{1}{e^{-\lambda_A t}} \left[G e^{-\lambda_A t} - (G-H) e^{-\lambda_B t} - H e^{-\lambda_C t} \right] \quad (12)$$

$$S = \frac{I_C}{I_A} = \frac{F}{e^{-\lambda_A t}} \left[e^{-\lambda_A t} - e^{-\lambda_C t} \right] \quad (13)$$

$$T = \frac{I_A}{I_T} = \frac{e^{-\lambda_A t}}{(1+F+G) e^{-\lambda_A t} - (G-H) e^{-\lambda_B t} - (F+H) e^{-\lambda_C t}} \quad (14)$$

$$U = \frac{I_B}{I_T} = \frac{G e^{-\lambda_A t} - (G-H) e^{-\lambda_B t} - H e^{-\lambda_C t}}{(1+F+G) e^{-\lambda_A t} - (G-H) e^{-\lambda_B t} - (F+H) e^{-\lambda_C t}} \quad (15)$$

$$V = \frac{I_C}{I_T} = \frac{F (e^{-\lambda_A t} - e^{-\lambda_C t})}{(1+F+G) e^{-\lambda_A t} - (G-H) e^{-\lambda_B t} - (F+H) e^{-\lambda_C t}} \quad (16)$$

The eqs. (1), (3), (9), (11), (12), (13), (14), (15) and (16) have been calculated as a function of t using the constants as mentioned in Fig. 1 and normalizing to $I_A(0) = 1$. The results are shown in Fig. 2. The numbers indicated at the curves correspond to those of the equations in the text.

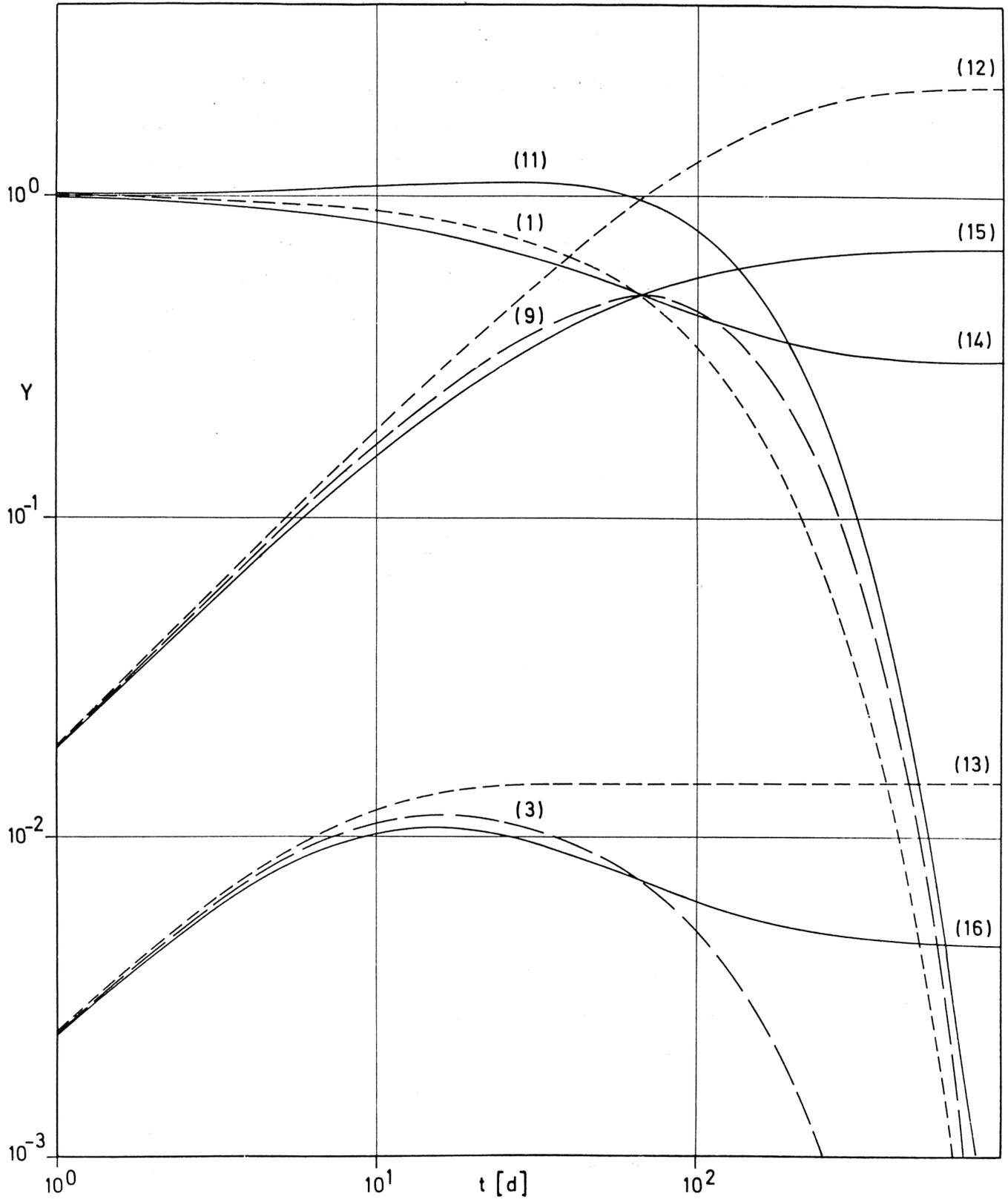


Fig. 2: Activities I and their ratios in the decay of ^{95}Zr as function of time t . Subscripts: $A=^{95}\text{Zr}$, $B=^{95}\text{Nb}$, $C=^{95\text{m}}\text{Nb}$, $T=\text{total}$. Original ^{95}Zr activity at $t=0$ has been normalized: $I_A(0)=1$.

Ordinate Y : I_A (1) I_T (11) $T=I_A/I_T$ (14)
 I_C (3) $R=I_B/I_T$ (12) $U=I_A/I_T$ (15)
 I_B (9) $S=I_B/I_A$ (13) $V=I_B/I_T$ (16)

4. Theoretical Formalism for Standardization

On the basis of the decay scheme (Fig. 1) and the equations derived in the preceding section a general formalism for the procedure of calibration can be deduced. It comprehends the description of the age determination for any $^{95}\text{Zr}/^{95}\text{Nb}$ mixture resulting in a date of origin (t_0 , the apparent date of ^{95}Zr isolation) and the description of the determination of the ^{95}Zr activity at this initial date. All other activities of ^{95}Zr and ^{95}Nb and their mixtures at any time t can then be calculated by applying the growth and decay theory.

4.1. Age Determination

For any time $t > 20$ d it can be assumed ¹⁾ that ^{95m}Nb is in a transient equilibrium with ^{95}Zr . Then eq. (12) may be simplified to

$$R = G \left[1 - m e^{-(\lambda_B - \lambda_A)t} \right] \quad (17)$$

where

$$m = \frac{(\lambda_C - \lambda_A) (\lambda_C - (1-p) \lambda_B)}{(\lambda_C - \lambda_B) (\lambda_C - (1-p) \lambda_A)}$$

There are different procedures for the age determination of a $^{95}\text{Zr}/^{95}\text{Nb}$ solution. Two of them are suitable when the ^{95}Zr and ^{95}Nb activities can not be treated separately. Then the ratio of a pair of total activities measured at two different times t_1 and t_2 will be used. The third way of proceeding presumes the separation of the ^{95}Zr and ^{95}Nb activities. It is based on the knowledge of the ratio R (see eq. (12)). However, by using such

activity ratios it can be achieved that the unknown initial activity of ^{95}Zr , $I_A(0)$, will be eliminated. Furthermore the experimental results can directly be fitted to an appropriate explicit expression from the preceding section.

4.1.1. Total Activity Ratio

The first rather simple procedure is to assume a time t_R as reference time for any calibration. For any time $t = t_R + \tau$, where τ may be positive or negative eq. (17) can be rewritten

$$R = G \left\{ 1 - m e^{-(\lambda_B - \lambda_A)(t_R + \tau)} \right\}, \text{ or} \quad (18)$$

$$R = G \left\{ 1 - m e^{-(\lambda_B - \lambda_A)t_R} e^{-(\lambda_B - \lambda_A)\tau} \right\}. \quad (18a)$$

For any standardization referring to the same reference time, t_R , follows

$$R = G \left\{ 1 - K e^{-(\lambda_B - \lambda_A)\tau} \right\}, \quad (19)$$

with the constant expression

$$K = m e^{-(\lambda_B - \lambda_A)t_R}. \quad (20)$$

When t_R is taken as initial date for τ , the activity ratio can be written $R(\tau) = I_B(\tau) / I_A(\tau)$. Using this relation in eq. (19) gives

$$I_B(\tau) = I_A(\tau) G \left\{ 1 - K e^{-(\lambda_B - \lambda_A)\tau} \right\}. \quad (21)$$

Assuming that the ^{95}Nb and ^{95}Zr events can not be separated, then always $I_T(\tau) = I_A(\tau) + I_B(\tau)$ will be measured. The total activity at τ is (with eq. (21))

$$I_T(\tau) = I_A(\tau) + I_A(\tau) G \left\{ 1 - K e^{-(\lambda_B - \lambda_A)\tau} \right\}. \quad (22)$$

Writing $I_A(\tau) = I_A(t_R) e^{-\lambda_A \tau}$, where $I_A(t_R)$ is the ^{95}Zr activity at reference time t_R , gives

$$I_T(\tau) = I_A(t_R) \left\{ (1+G) e^{-\lambda_A \tau} - G K e^{-\lambda_B \tau} \right\}. \quad (23)$$

In order to eliminate the unknown ^{95}Zr activity, $I_A(t_R)$, the measurements have to be performed at two different times (τ_1 and τ_2):

$$I_T(\tau_1) = I_1 = I_A(t_R) \left\{ (1+G) e^{-\lambda_A \tau_1} - G K e^{-\lambda_B \tau_1} \right\} \quad (24)$$

$$I_T(\tau_2) = I_2 = I_A(t_R) \left\{ (1+G) e^{-\lambda_A \tau_2} - G K e^{-\lambda_B \tau_2} \right\}; \quad (25)$$

from the combination of eqs. (24) and (25) follows

$$\frac{I_1}{I_2} = E_{12} = \frac{(1+G) e^{-\lambda_A \tau_1} - G K e^{-\lambda_B \tau_1}}{(1+G) e^{-\lambda_A \tau_2} - G K e^{-\lambda_B \tau_2}}. \quad (26)$$

The $I_A(t_R)$ which is unknown, but unequal zero, cancels, τ_1, τ_2 , I_1 and I_2 are experimental data and G, λ_A, λ_B are constant values determined by decay properties. Thus the unknown quantity K can be determined as

$$K = \frac{(1+G) \left\{ e^{-\lambda_A \tau_1} - E_{12} e^{-\lambda_A \tau_2} \right\}}{G \left\{ e^{-\lambda_B \tau_1} - E_{12} e^{-\lambda_B \tau_2} \right\}}. \quad (27)$$

The constant K contains the reference time t_R , the time elapsed since the origin date t_0 . From eq. (20) follows

$$t_R = \frac{1}{\lambda_B - \lambda_A} \ln \frac{m}{K} \quad (28)$$

The second more complicated method departs from the total activity at a time t (see eq. (11)). In addition the total activity at a later time $t+\Delta t$ is used:

$$I_T(t+\Delta t) = I_A(0) \left[(1+F+G)e^{-\lambda_A(t+\Delta t)} - (G-H)e^{-\lambda_B(t+\Delta t)} - (F+H)e^{-\lambda_C(t+\Delta t)} \right] \quad (29)$$

Eq. (29) will be combined with eq. (11) in order to form the ratio $D = I_T(t) / I_T(t+\Delta t)$. With a transformation of $I_T(t)$ into $[I_T(t+\Delta t)]^x$ the ratio D becomes

$$D = \frac{[I_T(t+\Delta t)]^x}{I_T(t+\Delta t)} \quad (30)$$

with

$$[I_T(t+\Delta t)]^x = I_A(0) \left[a(1+F+G)e^{-\lambda_A(t+\Delta t)} - b(G-H)e^{-\lambda_B(t+\Delta t)} - c(F+H)e^{-\lambda_C(t+\Delta t)} \right] \quad (31)$$

where $a = e^{-\lambda_A \Delta t}$, $b = e^{\lambda_B \Delta t}$ and $c = e^{\lambda_C \Delta t}$. Arranging eq. (30) under consideration of eqs. (29) and (31) the following expression for D is obtained

$$D = \frac{a(1+F+G)e^{-\lambda_A(t+\Delta t)} - b(G-H)e^{-\lambda_B(t+\Delta t)} - c(F+H)e^{-\lambda_C(t+\Delta t)}}{(1+F+G)e^{-\lambda_A(t+\Delta t)} - (G-H)e^{-\lambda_B(t+\Delta t)} - (F+H)e^{-\lambda_C(t+\Delta t)}} \quad (32)$$

Two experiments must be performed: one at a time t yielding the total activity $I_T(t)$ and another at time $t+\Delta t$ yielding the total activity $I_T(t+\Delta t)$. When the first experiment is made the time t has passed since the origin date t_0 . The absolute value of t is unknown. On the other hand the Δt is well known as the time interval between two experiments. The function given by eq. (32) must be calculated in dependence of the time t for the known time interval Δt as parameter. This gives a graphical representation of $D = f(t)$ which is valid for only one parameter Δt . Entering with the experimental ratio $D_{\text{exp}} = [I_T(t) / I_T(t+\Delta t)]_{\text{exp}}$ into this curve yields a certain value for the time t . Thus the origin date t_0 is defined again.

4.1.2. Separated Activity Ratio

From eq. (17) a rather simple relation for the age determination is obtained

$$t = \frac{1}{\lambda_A - \lambda_B} \ln \left[\frac{1}{m} \frac{G-R}{G} \right], \quad (33)$$

where t is the time passed since the origin date t_0 and $R = R(t)$ is the experimental ratio of the ^{95}Nb and ^{95}Zr activities measured at time t . In such a manner again a value for the initial date t_0 can be obtained.

4.1.3. Total and Separated Activities

The most straightforward procedure can be applied if a computer is available. A set of at least two experimental data pairs (time t and e.g. the total activity I_T) will be necessary. The date of origin t_0 will then be obtained from the calculation of the best fit through the available experimental points. Such a method can

be applied to most of the expressions mentioned in section 3 using immediately the measured total or separated activities.

4.2. Activity Determination

The activity determination can be performed with any suitable device for absolute or relative but calibrated counting procedure. Most convenient methods are the $4\pi\beta\text{-}\gamma$ coincidence counting (e.g. proportional counter together with two NaI(Tl) crystals) and the γ -ray counting with an efficiency calibrated detector (e.g. NaI(Tl) crystal). The most reasonable procedure is to determine the ^{95}Zr disintegration rate at time t of the experiment, $N_o(\text{Zr})$, and to calculate then the ^{95}Zr disintegration rate or activity which was available at the origin date t_o .

4.2.1. $4\pi\beta\text{-}\gamma$ Coincidence Method

The formalism for the $4\pi\beta\text{-}\gamma$ coincidence method has been described elsewhere^{15, 16)}. Expressions for the counting rates in the two single and the coincidence channels can be deduced on the basis of the decay scheme shown in Fig. 1 under consideration of all possible interactions in the different detectors. In the electron channel, electrons from the various β^- -transitions and from the internal conversion processes of the different γ -rays from the decay of ^{95}Zr as well as ^{95}Nb will be detected. In addition to these events the interaction of γ -rays in the electron detector has to be considered. The number of events (corrected for background and dead time) in the electron detector at any time t is given by

$$N_R(t) = N_R = N_\beta(\text{Zr}) + N_\beta(\text{Nb}) \quad (34)$$

with

$$\begin{aligned}
 N_{\beta}(\text{Zr}) = N_o(\text{Zr}) & \left[p_o \epsilon_{\beta_o} + p_1 \epsilon_{\beta_1} + p_2 \epsilon_{\beta_2} + p_3 \epsilon_{\beta_3} \right. \\
 & + p_1 \frac{1}{1+\alpha_1} \left\{ (\epsilon_{\beta})_{\gamma_1} + \alpha_1 \epsilon_{e_1} \right\} \\
 & + p_2 (1-\epsilon_{\beta_2}) \frac{1}{1+\alpha_2} \left\{ (\epsilon_{\beta})_{\gamma_2} + \alpha_2 \epsilon_{e_2} \right\} \\
 & \left. + p_3 (1-\epsilon_{\beta_3}) \frac{1}{1+\alpha_3} \left\{ (\epsilon_{\beta})_{\gamma_3} + \alpha_3 \epsilon_{e_3} \right\} \right] \quad \text{and} \quad (35)
 \end{aligned}$$

$$\begin{aligned}
 N_{\beta}(\text{Nb}) = N_o(\text{Nb}) & \left[p_4 \epsilon_{\beta_4} + p_5 \epsilon_{\beta_5} \right. \\
 & \left. + p_5 (1-\epsilon_{\beta_5}) \frac{1}{1+\alpha_5} \left\{ (\epsilon_{\beta})_{\gamma_5} + \alpha_5 \epsilon_{e_5} \right\} \right]. \quad (36)
 \end{aligned}$$

Here $p_i = p(\beta_i)$ ($i=0, \dots, 5$) are the level feedings, α_i ($i=1, 2, 3, 5$) are the total internal conversion coefficients, and ϵ_{β_i} , ϵ_{e_i} (ϵ_{β}) $_{\gamma_i}$ ($i=1, \dots, 5$) are the β -detector efficiencies for β -particles, conversion electrons and γ -rays, respectively. $N_o(\text{Zr})$ and $N_o(\text{Nb})$ are the respective disintegration rates of ^{95}Zr and ^{95}Nb . The following assumptions can be made in order to simplify eqs. (35) and (36): $\langle \epsilon_{\beta_o}, \epsilon_{\beta_1}, \epsilon_{\beta_4} \rangle_{av} = \epsilon_{\beta_a}$; $\langle \epsilon_{\beta_2}, \epsilon_{\beta_3} \rangle_{av} = \epsilon_{\beta_b}$;

$\epsilon_{e_i} = 1$ ($i=1, 2, 3, 5$); $\langle \alpha_i \rangle_{av} = \alpha$, $\langle (\epsilon_{\beta})_{\gamma_i} \rangle_{av} = (\epsilon_{\beta})_{\gamma}$ ($i=2, 3, 5$). Taking into account that $N_o(\text{Nb}) = R N_o(\text{Zr})$, eq. (34) can be arranged

$$\begin{aligned}
 N_{\beta} = N_o(\text{Zr}) & \left[(p_o + p_1 + p_4 R) \epsilon_{\beta_a} + (p_2 + p_3) \epsilon_{\beta_b} + p_5 R \epsilon_{\beta_5} \right. \\
 & + \frac{1}{1+\alpha} \left\{ (\epsilon_{\beta})_{\gamma} + \alpha \right\} \left\{ (p_2 + p_3) (1-\epsilon_{\beta_b}) + p_5 R (1-\epsilon_{\beta_5}) \right\} \\
 & \left. + \frac{p_1}{1+\alpha_1} \left\{ (\epsilon_{\beta})_{\gamma_1} + \alpha_1 \right\} \right]. \quad (37)
 \end{aligned}$$

In the γ -ray channel the events are also coming both from ^{95}Zr and from ^{95}Nb decay. When setting windows of a discriminator only on the γ -ray peaks, events arising from bremsstrahlung and X-rays can be neglected. The total number of γ rays at any time t is then given by

$$N_{\gamma}(t) = N_{\gamma} = N_{\gamma}(\text{Zr}) + N_{\gamma}(\text{Nb}) \quad (38)$$

with

$$N_{\gamma}(\text{Zr}) = N_o(\text{Zr}) \left[\frac{P_1}{1+\alpha_1} \epsilon_{\gamma_1} + \frac{P_2}{1+\alpha_2} \epsilon_{\gamma_2} + \frac{P_3}{1+\alpha_3} \epsilon_{\gamma_3} \right] \quad (39)$$

and

$$N_{\gamma}(\text{Nb}) = N_o(\text{Nb}) \frac{P_5}{1+\alpha_5} \epsilon_{\gamma_5} \quad (40)$$

Here the same nomenclature has been used as before; in addition ϵ_{γ_i} are the γ -ray detector efficiencies. Assuming that $\langle \epsilon_{\gamma_i} \rangle_{\text{av}} = \epsilon_{\gamma}$ ($i=2, 3, 5$), and considering the same simplifications as mentioned above, eq. (38) can be rewritten

$$N_{\gamma} = N_o(\text{Zr}) \epsilon_{\gamma} \left[\frac{1}{1+\alpha} (p_2 + p_3 + p_5 R) + \frac{P_1}{1+\alpha_1} \cdot \frac{\epsilon_{\gamma_1}}{\epsilon_{\gamma}} \right] \quad (41)$$

In the coincidence channel again events from ^{95}Zr as well as ^{95}Nb decay are contributing to the total coincidence counting rate. It should be pointed to the fact that there is no coincident correlation in the β_1 -branch of the ^{95}Zr decay. At any time t the coincidence rate is

$$N_c(t) = N_c = N_c(\text{Zr}) + N_c(\text{Nb}) \quad (42)$$

with

$$N_c(\text{Zr}) = N_o(\text{Zr}) \left[\frac{P_2}{1+\alpha_2} \left\{ \epsilon_{\beta_2} \epsilon_{\gamma_2} + (1-\epsilon_{\beta_2}) (\epsilon_{\beta})_{\gamma_2} \tilde{\epsilon}_{\gamma_2} \right\} + \frac{P_3}{1+\alpha_3} \left\{ \epsilon_{\beta_3} \epsilon_{\gamma_3} + (1-\epsilon_{\beta_3}) (\epsilon_{\beta})_{\gamma_3} \tilde{\epsilon}_{\gamma_3} \right\} \right] \quad (43)$$

and

$$N_c(\text{Nb}) = N_o(\text{Nb}) \frac{P_5}{1+\alpha_5} \left\{ \epsilon_{\beta_5} \epsilon_{\gamma_5} + (1-\epsilon_{\beta_5}) (\epsilon_{\beta})_{\gamma_5} \tilde{\epsilon}_{\gamma_5} \right\} \quad (44)$$

With the same simplifications and notations as used above and also under the assumption that the efficiency for γ -rays making events both in the γ -ray detector and in the electron detector is for all γ -rays involved similar to the γ -ray detection efficiency, $\langle \tilde{\epsilon}_{\gamma_i} \rangle_{av} = \epsilon_{\gamma}$ ($i=2, 3, 5$), the expression for the total coincidence rate reduces to

$$N_c = N_o(Zr) \frac{\epsilon_{\gamma}}{1+\alpha} \left[(p_2+p_3) \epsilon_{\beta_b} + p_5 R \epsilon_{\beta_5} + (\epsilon_{\beta_{\gamma}})_{\gamma} \left\{ (p_2+p_3) (1-\epsilon_{\beta_b}) + p_5 R (1-\epsilon_{\beta_5}) \right\} \right] . \quad (45)$$

Introducing the ratio $\epsilon = N_c/N_{\gamma}$ which can experimentally be determined, it can be written

$$\frac{N_{\beta} N_{\gamma}}{N_c} = \frac{1}{\epsilon} N_{\beta} . \quad (46)$$

The ratio ϵ has been used in its explicitly written form in order to determine the efficiency ϵ_{β_5}

$$\epsilon = \frac{(\epsilon_{\beta_{\gamma}})_{\gamma} \left\{ p_2+p_3+p_5 R \right\} + (1-(\epsilon_{\beta_{\gamma}}))_{\gamma} \left\{ (p_2+p_3)\epsilon_{\beta_b} + p_5 R \epsilon_{\beta_5} \right\}}{p_2+p_3+p_5 R + \frac{1+\alpha}{1+\alpha_1} \cdot p_1 \frac{\epsilon_{\gamma 1}}{\epsilon_{\gamma}}} \quad (47)$$

or

$$(1-(\epsilon_{\beta_{\gamma}}))_{\gamma} p_5 R \epsilon_{\beta_5} = \epsilon \left\{ p_2+p_3+p_5 R + \frac{1+\alpha}{1+\alpha_1} p_1 \frac{\epsilon_{\gamma 1}}{\epsilon_{\gamma}} \right\} - (\epsilon_{\beta_{\gamma}})_{\gamma} \left\{ p_2+p_3+p_5 R \right\} - (1-(\epsilon_{\beta_{\gamma}}))_{\gamma} (p_2+p_3)\epsilon_{\beta_b} . \quad (48)$$

Inserting eq. (48) into eq. (37) shows that the part containing ϵ_{β_b} cancels. It remains an expression without contributions

related to ϵ_{β_b} as well as ϵ_{β_5} . Furthermore all parts with $(\epsilon_{\beta})_{\gamma}$ vanish and eq. (37) becomes

$$N_{\beta} = N_o(Zr) \left[(p_o + p_1) \epsilon_{\beta_a} + \frac{p_1}{1 + \alpha_1} \left\{ (\epsilon_{\beta})_{\gamma_1} + \alpha_1 \right\} + \frac{\alpha}{1 + \alpha} (p_2 + p_3) \right. \\ \left. + \frac{1}{1 + \alpha} \left\{ p_2 + p_3 + p_5 R + \frac{1 + \alpha}{1 + \alpha_1} \cdot p_1 \cdot \frac{\epsilon_{\gamma_1}}{\epsilon_{\gamma}} \right\} \epsilon + \left\{ p_4 \epsilon_{\beta_a} + \frac{\alpha}{1 + \alpha} p_5 \right\} R \right] . \quad (49)$$

Combining eqs. (46) and (49) an expression for $N_o(Zr)$ is obtained

$$N_o(Zr) = \frac{N_{\beta} N_{\gamma}}{N_c} P \quad (50)$$

with

$$\frac{1}{P} = \frac{1}{\epsilon} \left[\frac{1}{1 + \alpha} \left\{ p_2 + p_3 + \frac{1 + \alpha}{1 + \alpha_1} p_1 \frac{\epsilon_{\gamma_1}}{\epsilon_{\gamma}} \right\} \epsilon + \frac{p_5}{1 + \alpha} R \epsilon + (p_o + p_1) \epsilon_{\beta_a} \right. \\ \left. + \frac{\alpha}{1 + \alpha} (p_2 + p_3) + \frac{p_1}{1 + \alpha_1} \left\{ (\epsilon_{\beta})_{\gamma_1} + \alpha_1 \right\} + \left\{ p_4 \epsilon_{\beta_a} + \frac{\alpha}{1 + \alpha} p_5 \right\} R \right]$$

or

$$\frac{1}{P} = \frac{1}{\epsilon} \left[A \epsilon + B R \epsilon + C + D R \right] . \quad (51)$$

The constants A, B, C, and D contain only the decay properties (see Fig. 1) and the quantities ϵ_{β_a} , $\epsilon_{\gamma_1}/\epsilon_{\gamma}$, and $(\epsilon_{\beta})_{\gamma_1}$ which depend on the experimental conditions and which have to be measured or estimated. The $\epsilon = N_c/N_{\gamma}$ is an experimental result which can be determined rather accurate by long term counting. On the other hand it is evident that the ^{95}Zr activity can not

be taken immediately from the ratio $N_{\beta}N_{\gamma}/N_c$, due to its dependence on $R = R(t)$. Thus it is necessary to know first the origin date t_o in order to be able to calculate $R(t)$ for the date of the measurement. Only then the $N_o(Zr)$ can be determined according to eq. (50).

4.2.2. γ -Ray Spectrometer Method

The use of a γ -ray detection device allows a treatment which is simpler than that described in the preceding section for the $4\pi\beta$ - γ coincidence counting. However it presumes that its detection efficiency as a function of the photon energy is known from former calibrations. But then it offers a second independent method for the activity determination. The total photon spectrum is composed of X-rays, γ -rays and bremsstrahlung quanta. When using an integral counting mode with a NaI(Tl) γ -ray spectrometer¹⁷⁾ at any time t the total rate of ^{95}Zr and ^{95}Nb photons is given by

$$N_{\text{ph}}(t) = N_{\text{ph}}(\text{Zr}) + N_{\text{ph}}(\text{Nb}) \quad (52)$$

with

$$N_{\text{ph}}(\text{Zr}) = N_{\text{X}}(\text{Zr}) + N_{\gamma}(\text{Zr}) + N_{\text{BS}}(\text{Zr}) \quad (53)$$

and

$$N_{\text{ph}}(\text{Nb}) = N_{\text{X}}(\text{Nb}) + N_{\gamma}(\text{Nb}) + N_{\text{BS}}(\text{Nb}) \quad (54)$$

Assuming that only K X-rays have to be considered in the experiment, due to the complete absorption of the X-rays from L and higher shells in a suitably chosen absorber, then eqs.(53) and (54) become

$$N_{\text{ph}}(\text{Zr}) = N_o(\text{Zr}) \left[\frac{P_1}{1+\alpha_1} \epsilon_{\gamma_1} + \frac{P_2+P_3}{1+\alpha} \epsilon_{\gamma} + \left\{ \frac{P_1}{1+\alpha_1} \alpha_{K_1} + \frac{P_2+P_3}{1+\alpha} \alpha_K \right\} \omega_K \epsilon_{X_K} \right. \\ \left. + \frac{P_1}{1+\alpha_1} \left\{ (1-\epsilon_{\gamma_1}) + \alpha_{K_1} \omega_K (1-\epsilon_{X_K}) \right\} \epsilon_{\text{BS}_1} + \frac{P_2+P_3}{1+\alpha} \left\{ (1-\epsilon_{\gamma}) + \alpha_K \omega_K (1-\epsilon_{X_K}) \right\} \epsilon_{\text{BS}} \right] \quad (53a)$$

and

$$N_{ph}(Nb) = N_o(Nb) \left[\frac{P_5}{1+\alpha} \epsilon_\gamma + \frac{P_5}{1+\alpha} \alpha_K \omega_K \epsilon_{X_K} + \frac{P_5}{1+\alpha} \left\{ (1-\epsilon_\gamma) + \alpha_K \omega_K (1-\epsilon_{X_K}) \right\} \epsilon_{BS_5} \right]. \quad (54a)$$

Here the same nomenclature has been used as in the preceding section. In order to obtain these equations the following assumptions have been used for simplification:

$$\langle \alpha_i \rangle_{av} = \alpha, \quad \langle \alpha_{K_i} \rangle_{av} = \alpha_K \quad \text{and} \quad \langle \epsilon_{\gamma_i} \rangle_{av} = \epsilon_\gamma \quad \text{for } i = 2, 3, 5,$$

$$\langle \epsilon_{X_K}^{(1)} \rangle_{av} = \epsilon_{X_K}, \quad \langle \omega_K^{(1)} \rangle_{av} = \omega_K \quad \text{for } l = Nb, Mo. \quad \omega_K \text{ is the}$$

K-shell fluorescence yield, ϵ_{BS_i} are the bremsstrahlung efficiency for the i-th transition, $\langle \epsilon_{BS_i} \rangle_{av} = \epsilon_{BS}$ for $i = 2, 3$. All events where a bremsstrahlung quantum will be followed by an Auger electron or an X-ray from the L or higher shells can be neglected. Their contribution to the total counting rate has been estimated to be lower than 10^{-4} . Using the activity ratio R for ^{95}Nb and ^{95}Zr eq. (52) can be rewritten as

$$N_o(Zr) = Q \cdot N_{ph}(t) \quad (55)$$

with

$$\begin{aligned} \frac{1}{Q} = & \frac{P_2+P_3}{1+\alpha} \left[\epsilon_\gamma + \left\{ (1-\epsilon_\gamma) + \alpha_K \omega_K (1-\epsilon_{X_K}) \right\} \epsilon_{BS} \right] + \omega_K \left[\frac{P_1}{1+\alpha_1} \alpha_{K_1} + \frac{P_2+P_3}{1+\alpha} \alpha_K \right] \\ & + \frac{P_1}{1+\alpha_1} \left[\epsilon_{\gamma_1} + \left\{ (1-\epsilon_{\gamma_1}) + \alpha_{K_1} \omega_K (1-\epsilon_{X_K}) \right\} \epsilon_{BS_1} \right] + R \frac{P_5}{1+\alpha} \alpha_K \omega_K \epsilon_{X_K} \\ & + R \frac{P_5}{1+\alpha} \left[\epsilon_\gamma + \left\{ (1-\epsilon_\gamma) + \alpha_K \omega_K (1-\epsilon_{X_K}) \right\} \epsilon_{BS_5} \right]. \end{aligned} \quad (56)$$

Besides the time dependent ratio $R = R(t)$ the factor Q contains only decay properties which can be taken from Fig. 1 and efficiencies which depend on the experimental conditions. In the case of using a calibrated detection device the efficiencies are known. The activity $N_0(\text{Zr})$ can then be determined as soon as the date of origin t_0 is known, because this is needed for the calculation of the ratio R .

5. Experimental Procedure of Calibration

As an example the treatment of a $^{95}\text{Zr}/^{95}\text{Nb}$ solution will be described which has been standardized on request of the CEN/SCK, Mol, Belgium. The measurements have been performed with an efficiency calibrated NaI(Tl) γ -ray spectrometer, a $4\pi\beta$ - γ coincidence arrangement and a Ge(Li) γ -ray detector. The aim was the preparation of a set of ampoules filled with solutions containing amounts of ^{95}Zr of known activities between 2 and 50 μCi . From γ -ray measurements performed during several days it could be estimated that on 1st February 1972 the age of the radioactive material was about 25 days and its total activity about 425 $\mu\text{Ci/g}$.

5.1. Sources and Solutions

The preparation of sources and solutions has been carried out according to the procedures described elsewhere¹⁸⁾. The special scheme for the preparation of dilutions and sources for this calibration is given in Fig. 3. From a primary solution of 2.7 ml two qualitative sources have been prepared by pipetting a known amount on thin polyethylene foils, which were put (after drying) into small Al containers. In addition three secondary solutions of different dilution have been made by adding a solvent of 0.01M oxalic acid in 2M nitric acid. One of them (B1) has been taken as reserve whereas the two others (B2, B3) have been further diluted by adding different amounts of solvent. The amounts of solution and solvent used for the preparation

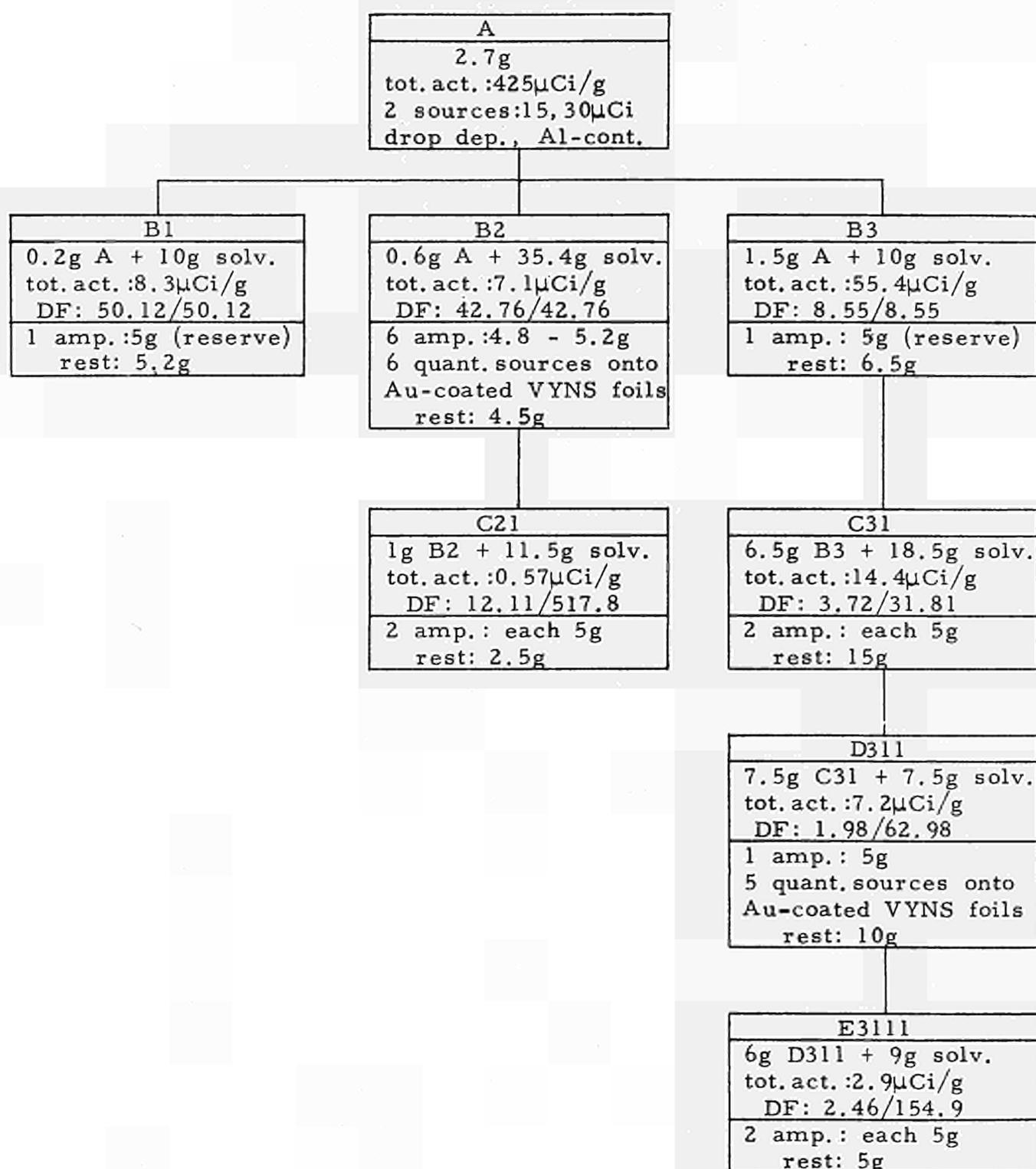


Fig. 3: Dilution scheme for the calibration of $^{95}\text{Zr}/^{95}\text{Nb}$.

A: original solution; B, C, D, E: consecutive dilution steps; solvent: 0.01 M oxalic acid in 2 M nitric acid; DF: dilution factor defined as the ratio of weights of active solution plus solvent and active solution alone (first figure refers to preceding solution, the second one to the master solution A).

of the dilutions were determined by weighing. The dilution factors are defined as the ratio of weights of the active solution plus solvent and the active solution alone. They are chosen in such a manner that firstly all solutions of requested activities could be obtained and that secondly in both branches at different dilution steps (e.g. B2 and D311) sources of similar strength could be prepared for the standardization by $4\pi\beta\text{-}\gamma$ coincidence and γ -ray counting. Thus, from the different sets of standardization results the specific activity of the master solution can be deduced by applying the different well known dilution factors.

5.2. Determination of Impurities

From the beginning of the investigation during a period of 4 months the γ -ray spectrum has been measured regularly with a Ge(Li) detector. In total 12 measurements have been made. In the spectra a series of γ -rays could be identified arising from the decays of ^{181}Hf ($T_{1/2} = 44.5\text{d}$; $E_{\gamma} = 0.133, 0.346, 0.482\text{ MeV}$ ¹⁹), ^{175}Hf ($T_{1/2} = 70\text{d}$; $E_{\gamma} = 0.343\text{ MeV}$ ¹⁹) and ^{60}Co ($T_{1/2} = 5.28\text{ y}$; $E_{\gamma} = 1.173, 1.332\text{ MeV}$ ¹⁹). The intensities of these impurities have been determined relative to the ^{95}Zr activity at each date of experiment. Referring them to the date of origin t_0 there were relative to the ^{95}Zr activity: $(1.0 \pm 0.1)\%$ ^{181}Hf , $(1.5 \pm 0.3)\%$ ^{175}Hf and $(0.008 \pm 0.001)\%$ ^{60}Co . The given errors are one-standard deviations (1σ).

In addition to these impurities due to foreign isotopes the possible presence of an "intrinsic impurity" has to be considered. Depending on the origin of the radioactive material and on the chemical processing it can happen that at time t_0 a certain amount of genuine ^{95}Nb exists beside the ^{95}Zr activity. The radiation from these ^{95}Nb isotopes can not be distinguished from that emitted by ^{95}Nb nuclei originating in the ^{95}Zr decay. An identification of such

a possible original ^{95}Nb admixture can only be made by measuring the total activity as a function of time and by comparing it with theoretical functions calculated under the assumption of different amounts of genuine ^{95}Nb . Total activity measurements performed with the NaI(Tl) γ -ray spectrometer during a time period of 3 months showed that an eventual ^{95}Nb admixture at the origin had to be smaller than $(0.1 \begin{smallmatrix} +0.2 \\ -0.1 \end{smallmatrix})\%$, and can be taken to be zero for this study.

5.3. Age Determination

In the case of using the NaI(Tl) γ -ray spectrometer, the integral number of events counted and corrected for impurities, background and dead time, is proportional to the total $^{95}\text{Zr}/^{95}\text{Nb}$ activity. Two qualitatively prepared sources have been measured both under two different geometrical conditions. Within four months a series of 17 measurements have been performed for each of the mentioned experimental sets. The procedures described in section 4.1.1. have been applied to combinations of activities $I(t_i)$ measured at time t_i and $I(t_k)$ measured at time t_k under consideration of the condition $|t_i - t_k| \geq 20$ d. Most of the corrections applied are dependent on the time when the experiment was executed. A typical value for the correction of dead time losses was about 0.4% with an error of 5% and that of background was 1% with an error of 3%. A factor of 0.985 allowed for the impurities and had an error of 0.3%. The reproducibility of the system caused an error of 0.2%. In total an experimental systematic error of $(\sum \Delta_i^2)^{1/2} = \pm 0.36\%$ (Δ_i being the individual errors) could be attributed to the corrected counting rates.

In a similar manner the experimental results of the $4\pi\beta$ - γ coincidence counting have been treated. The experimentally determined ratio $N_{\beta}N_{\gamma}/N_c$, corrected for impurities, background, accidental coincidences and dead time is proportional to the total $^{95}\text{Zr}/^{95}\text{Nb}$ activity. The factor of proportionality is constant within 0.1% for all measurements which have been performed between 40 and 80d from t_0 . Seven sources have been measured at 4 different dates. The combinations of the total activities again have been treated following the procedure of section 4.1.1. considering the condition $|t_i - t_k| \geq 10\text{d}$. The following characteristic values could be assumed for the calculation of errors: the correction for dead time was about $(0.5 \pm 0.03)\%$. The background in the γ -ray channel is 1%, that in the electron channel 0.01% and that in the coincidence channel 0.02%, each with a relative error of 10%. Impurity corrections contributed 0.16% and accidental coincidences $(0.6 \pm 0.03)\%$. The reproducibility of the system introduced an error of 0.1%. Thus, a typical value for the experimental systematic error on the ratio $N_{\beta}N_{\gamma}/N_c$ is $(\sum \Delta_i^2)^{1/2} = \pm 0.2\%$ (Δ_i as above).

Using the Ge(Li) detector of known relative detection efficiency in total 18 measurements with two sources yielded a corresponding number of activity ratios $R = R(t)$ (see eq. (12)). As described in section 4.1.2. immediately from eq. (33) the age of the radioactive material could be determined. The determination of the relative peak areas corrected for background and impurity contributions has been performed with an IBM 1800 computer. The error introduced by this procedure is adopted to be 0.5%. A typical dead time correction was 2% with an error of 10%. The error due to the influence of the relative efficiencies has been estimated to be 0.4%. Finally a systematic error of $(\sum \Delta_i^2)^{1/2} = \pm 0.67\%$ could be given on the activity ratio R (Δ_i see above).

The straightforward method mentioned in section 4.1.3. has been applied to the experimental data measured with all three devices (NaI(Tl) and Ge(Li) detectors and $4\pi\beta\text{-}\gamma$ coincidence apparatus). These results are proportional to the total $^{95}\text{Zr}/^{95}\text{Nb}$ activity (eq. (11)). Furthermore the ratio of the ^{95}Nb and ^{95}Zr activities (eq. (12)) and that of ^{95}Zr and total activities (eq. (14)) as measured with the Ge(Li) detector have been used. The calculations have been executed with an IBM-1800 computer using a fitting program (ORGLS) given by BUSING and LEVY ²⁰). The systematic experimental errors are the same as discussed above in connection with the different counting devices.

In addition to the mentioned experimental sources of error, the uncertainties of the decay properties entering the calculations will also contribute to the final error. It has been calculated that for the two methods described in section 4.1.1. an error of respective 0.14% and 0.34% has to be considered. For the procedure mentioned in section 4.1.2. the error contribution will be 0.08%. When using the computer fitting method (see section 4.1.3.) the corresponding error contributions are 0.54%, 0.89%, and 0.54% when using the eqs. (11), (12), and (14), respectively. The final total error on the date of origin will be composed of the standard error (s) and the systematic errors (δ) of the individual results. In Table I the experimental results for the age determination and their errors have been collected. The mean value for the date of origin t_0 is the January 10, 1972 at 18h \pm 12h. It has been calculated using the reciprocals of the squared total errors on the individual results as weights. The given error corresponds to the mean of the individual total errors.

Table I : Experimental results for the age determination

Detector	Text Reference	n ^{a)}	t[d] ^{b)}	s[d] ^{c)}	δ[d] ^{d)}	Δt[d] ^{e)}	origin date	t _o
NaI(Tl)	section 4.1.1. 1. method	115	50.100	0.040	0.266	0.305	10-01-72,	21h36'
4πβγ		41	50.642	0.090	0.160	0.250	10-01-72,	08h36'
NaI(Tl)	section 4.1.1. 2. method	120	49.651	0.049	0.362	0.411	11-01-72,	08h23'
4πβγ		41	50.123	0.093	0.257	0.350	10-01-72,	21h03'
Ge(Li)	section 4.1.2.	16	50.707	0.151	0.422	0.573	10-01-72,	07h02'
NaI(Tl)	section 4.1.3.	4	49.690	0.115	0.462	0.577	11-01-72,	07h26'
4πβγ		7	50.212	0.103	0.361	0.464	10-01-72,	18h55'
Ge(Li)		8	49.755	0.217	0.665	0.882	11-01-72,	05h53'

a) number of results (combinations, measurements)

b) $t = t_1 - t_0$; $t_1 \equiv 01-03-72, 00h00'$; $t_0 \equiv$ date of origin

c) standard error $s = [\sum_1 |t_i - \bar{t}|^2 / n(n-1)]^{1/2}$

d) sum of systematic errors due to the experimental conditions and the uncertainties of the decay properties

e) total error on t : $\Delta t = s + \delta$

5.4. Activity Determination

For the measurements with the 4πβ-γ coincidence arrangement seven quantitatively prepared sources have been used each at four different times t (see Table II). The masses of the radioactive material deposited onto VYNS foils coated with Au on both sides, with a total thickness of about 50μg/cm², were between 0.24499 and 0.46323mg of the primary solution (see Fig. 3). The rates in the different counting channels have

been corrected for background, dead time, impurities and accidental coincidences. With the knowledge of the origin date t_0 the ratios $R(t)$ have been calculated according to eq. (12) for each measuring time. Using these calculated R values and the experimental ratios for $\epsilon = N_c/N_\gamma$ the factor P could be obtained from eq. (51). The variation of R and P with the measuring time t is shown in Table II. The product $(1+R) \cdot P$ is a measure of the

Table II : Experimental conditions for the activity determination by $4\pi\beta\text{-}\gamma$ coincidence counting (example for 1 source)

t [d]	R	P	$(1+R) P$
43.889	0.716094	0.574909	0.986598
51.891	0.819277	0.542598	0.987136
62.887	0.949581	0.506638	0.987732
77.853	1.107569	0.468975	0.988397

radioactive equilibrium between the ^{95}Zr and ^{95}Nb activities and tends to be unity in the limit of very great time t . As $(1+R) P$ determines directly as factor the total $^{95}\text{Zr}/^{95}\text{Nb}$ activity it must be calculated carefully for all measurements with $t \leq 400\text{d}$. From eq. (50) the ^{95}Zr activity at the measuring time is obtained. By applying the decay time correction the original ^{95}Zr activity at time t_0 will be

$$\begin{aligned}
 I_0 (4\pi\beta\text{-}\gamma \text{ } ^{95}\text{Zr}, t_0) &= (13353 \pm 76) \text{ dps/mg} \\
 &= (0.3609 \pm 0.0021) \mu\text{Ci/mg} .
 \end{aligned}$$

The error is the square root of the sum of the squared individual

errors on $N_p N_\gamma / N_c$ (0.18%), P (0.5%) weight W (0.08%), impurity (0.16%) and decay correction (0.1%).

The measurements with the efficiency calibrated NaI(Tl) γ -ray spectrometer have been made with eleven quantitatively prepared sources including those used for the $4\pi\beta$ - γ coincidence counting. The radioactive material (between 0.24498 and 0.46323 mg of the primary solution, see Fig. 3, dilution B2 and D311) has been deposited onto Au coated VYNS foils with a total thickness of about $50\mu\text{g}/\text{cm}^2$. In total 14 measurements were performed at two dates and under three different geometrical conditions. The total counting rates have been corrected for background, dead time and impurities. After calculation of the ratio $R(t)$ according to eq. (12), the factor Q (eq. (56)) could be determined using the decay properties and the known detection efficiencies of the NaI(Tl) crystal. From eq. (55) follows then the ^{95}Zr activity at the measuring time t . At the origin date t_0 the ^{95}Zr activity is

$$\begin{aligned} I_0(\text{NaI(Tl)}, ^{95}\text{Zr}, t_0) &= (13308 \pm 83) \text{ dps/mg} \\ &= (0.3597 \pm 0.0022) \mu\text{Ci/mg} . \end{aligned}$$

The error is composed as in the preceding case by the individual errors on N_{ph} (0.2%), Q including the efficiency (0.5%), weight W (0.08%), impurity (0.3%) and decay correction (0.03%).

Both results for the original ^{95}Zr activity obtained from two independent experiments agree within 0.35%. As both methods are of similar accuracy no preference should be given to one of them. As the final result for the specific activity of ^{95}Zr at the origin date t_0 a mean value can be given:

$$I_{\text{Zr}}(t_0) = (13331 \pm 56) \text{ dps/mg} = (0.3603 \pm 0.0015) \mu\text{Ci/mg} .$$

The requested standardized solutions have been prepared by filling an amount of 5ml with a pipette into glass ampoules. It is clear that the filling of the ampoules by such a volumetric methods leads to small differences of the liquid-level. Using a NaI(Tl) γ -ray spectrometer this effect causes differences in geometry and consequently in the final detection efficiency and hence in the total activity. In order to correct for such a volume influence a series of ampoules has been filled with variable amounts of solution (4.8 to 5.2 ml, see Fig. 3, B2) of the same dilution allowing to normalize the results on one fixed volume (e.g. 5.0 ml). On the other hand the activities of the solutions are determined gravimetrically. From the exact weights of the amount of liquid, the specific activity of the primary solution (^{95}Zr activity/mg at t_0) and the dilution factors, the total activity contained in each of the ampoules can be deduced. In such a manner ^{95}Zr activities between 3.6 and 58.8 μCi (at t_0) have been obtained. The errors on these activities are composed of those on the primary activity (0.42%), on the weighing (0.08%) and on the dilution factors (0.01%).

6. Determination of $^{95}\text{Zr}/^{95}\text{Nb}$ Decay Properties

The values of the decay properties entering the standardization calculation could be taken unambiguously from the literature. No serious discrepancies exist between different publications. Consequently there was no need to initiate a complete measuring program for the redetermination of any of them. However from the experimental work for the present calibration a series of measurements could be used in order to obtain some information on the properties of the $^{95}\text{Zr}/^{95}\text{Nb}$ decay. The half lives of the nuclides involved as well as the β^- -branching intensities have been deduced.

6.1. Half-lives of ^{95}Zr and ^{95}Nb

The half-life of ^{95}Zr has been determined from measurements with the Ge(Li) detector. The number of pulses summed up over the peaks within always the same limits have been defined as a measure of the intensities. Thus, the peaks of the γ_2 - and γ_3 -rays (see Fig. 1) were followed during a period of 135 days. The relative geometry (distance and position) between the sources and the detector and the electronic conditions have been kept well defined and stable for all runs performed at different times. After consideration of pulses due to background, higher energetic γ -rays and impurities all calculations have been executed with an IBM-1800 computer. The reproducibility was better than 0.3% as checked with the peak intensities of the ^{60}Co γ -rays. The statistical counting errors were always better than 0.2%. The results of 19 runs yielded a half-life of 64.10d for the γ_2 -ray and 64.28d for the γ_3 -ray. The mean value is 64.2d with an error of 0.6%. The error is composed of the standard error (0.25%) and the systematic ones (0.35%). The result obtained as a by-product is not very accurate, but points to an agreement with the ^{95}Zr half-life used in the course of this standardization.

The half-life of ^{95}Nb has been measured with sources which originally were used for the efficiency calibration of the NaI(Tl) crystal. An extended study on 4 sources and different experimental conditions has been performed during a period of 95 days. Results obtained by 4 π R- γ coincidence counting as well as γ -ray spectrometer counting are available. A mean value of 35.0d has been calculated, to which an estimated error of 0.3% should be attributed. The final evaluation of the measured data is yet in progress. Especially the influence of a genuine ^{95}Zr admixture and its consequent production of an additional ^{95}Nb amount has to be considered carefully. A rough estimation

indicates the tendency to lower slightly the above mentioned result. This fact emphasizes that the agreement between the half-life of ^{95}Nb determined actually and that one used in the present standardization is just at a tolerable limit.

6.2. β^- -Branchings of ^{95}Zr

The intensity of three β^- -transitions (β_1 , β_2 and β_3) have been deduced from the corresponding γ -rays measured with the Ge(Li) detector and the theoretical internal conversion coefficients ⁵⁾. For that purpose the following relations have been used

$$p(\beta_0) + p(\beta_1) + p(\beta_2) + p(\beta_3) = 1$$

$$N_{\gamma_i} = N_0 p(\beta_i) (1 - \kappa_i) \epsilon_{\gamma_i} \quad \text{with } (i = 1, 2, 3) .$$

N_{γ_i} are the counting rates summed over the i -th γ -ray peak corrected for dead time, background and impurity; N_0 is the disintegration rate; $p(\beta_i)$ are the β^- -branchings; κ_i and ϵ_{γ_i} are the internal conversion probability and the photopeak efficiency (including the solid angle) for the i -th γ -ray, respectively. When using ratios of the different γ -ray counting rates it can be shown that the disintegration rate, N_0 , cancels and that only the relative efficiencies of the Ge(Li) detector have to be known. Under the assumption that $p(\beta_0) = 0.4\%$ the following mean results have been obtained from 11 different runs: $p(\beta_1) = (1.4 \pm 0.2)\%$, $p(\beta_2) = (44.5 \pm 0.5)\%$ and $p(\beta_3) = (53.7 \pm 0.6)\%$. The given errors are the standard errors plus the systematic ones ($4.1\% + 10\%$, $0.4\% + 0.7\%$ and $0.4\% + 0.7\%$, respectively). The systematic errors are composed as $(\sum \Delta_i^2)^{1/2}$ with partial errors Δ_i due to dead time (0.2%), peak evaluation ($0.5 - 5\%$) and relative efficiencies ($0.4 - 5\%$). The agreement of these results with the β^- -transition intensities adopted for the standardization is very satisfactory.

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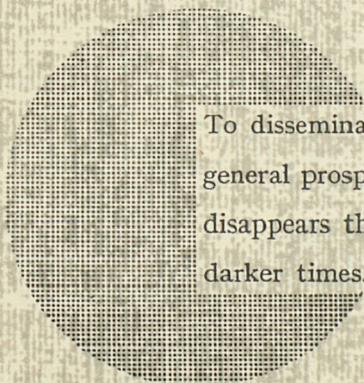
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