

PAPER

A Simple Transform to Linearize and Resolve Two-Component Decay Data: Illustration of its Use and Efficacy in Assaying $^{32}\text{P}/^{33}\text{P}$ Mixtures by Liquid Scintillation Counting

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A simple mathematical transformation to convert two-component exponential decay data into a linear function to resolve the two components has considerable utility. The approach offers a straightforward graphical means of judging the quality of the available measurement data and of critically evaluating how well the components are resolved. The use and advantages of this transform are illustrated for the case of assaying ^{32}P in the presence of a ^{33}P impurity by $4\pi\beta$ liquid scintillation spectrometry.

The transform

Experimentally-determined, background-corrected massic counting rates R for the summed decay of two independently-decaying radioactive species as a function of experimentally-observed times t can be given by

$$R = A_{1(t)}\epsilon_1\exp(-\lambda_1 t) + A_{2(t)}\epsilon_2\exp(-\lambda_2 t) \quad (1)$$

where $A_{1(t)}$ and $A_{2(t)}$ are the massic activities of the two species at some $t = 0$ reference time, respectively; where ϵ_1 and ϵ_2 are their respective detection efficiencies at time t ; and where λ_1 and λ_2 are their respective decay constants. Thus, any set of (R, t) data can be simply converted into linear form

$$Y = A_{1(t)} + A_{2(t)}X \quad (2)$$

with $Y = R/\epsilon_1\exp(-\lambda_1 t)$ and $X = \epsilon_2\exp(-\lambda_2 t)/\epsilon_1\exp(-\lambda_1 t) = (\epsilon_2/\epsilon_1)\exp[(\lambda_1 - \lambda_2)t]$. As indicated, the intercept of Y at $X = 0$ is just the derived massic activity $A_{1(t)}$, and the slope dY/dX is the massic activity $A_{2(t)}$.

This very simple linear transformation^{*1*} has considerable utility for many situations where the λ_1 and λ_2 decay constants for the two components are well known and when the ϵ_1 and ϵ_2 efficiencies are determinable. Its efficacy shall be demonstrated below, in the examples given, for the liquid scintillation (LS) assay of ^{32}P in the presence of substantial ^{33}P impurity.

Introductory comments on the assay of $^{33}\text{P}/^{32}\text{P}$ mixtures

The radionuclide ^{32}P is a commonly used high-energy β -emitting calibration standard, and has importance in many applications including those within the industrial processing, nuclear power, radiopharmaceutical, medical therapy, nuclear physics, and biomedical research communities. Most commercial supplies of ^{32}P , however, invariably contain an impurity of ^{33}P . The impurity ratio I , for the ^{33}P -to- ^{32}P activities, is typically of the order of $I \cong 0.01$ for relatively fresh supplies that have not undergone substantial decay.^{*2} As a result, assays of ^{32}P normally require an independent or corollary determination of this usually attendant impurity.

* All notes, sequentially numbered, are given as supplementary endnotes.

This is somewhat difficult in that both ^{32}P and ^{33}P are pure β emitters having no other radiative signatures (e.g., γ rays), and because their two decay constants (or half-lives) differ by less than a factor of two. Furthermore, the usually less abundant ^{33}P impurity has a substantially lower maximum β endpoint energy [$E_{\beta(\text{max})} = 249$ keV] compared to that for ^{32}P [$E_{\beta(\text{max})} = 1710$ keV] so that its β -spectrum is largely buried underneath the dominant ^{32}P spectrum. In common practice, the two components are resolved by following the counting rate of a source as a function of time and fitting the background-corrected net rate to a function consisting of the sum of the two ^{32}P and ^{33}P exponentially decaying terms to extract (as fitted parameters) the ^{32}P and ^{33}P activities [as in equation (1)]. Stevenson,¹ amongst many other authors, illustrated the difficulty in trying to resolve two such components when they have very comparable half-lives. It becomes an even more difficult task when the impurity ratio I is less than a few percent. In this case, one must perform the measurements over relatively long decay time t intervals to effect an adequate resolution of the two components.³³ An additional complication may arise if the respective detection efficiencies of the two components vary with time.

LS assay of $^{33}\text{P}/^{32}\text{P}$ mixtures

This laboratory, for example, routinely performs $4\pi\beta$ LS spectrometric assays of ^{32}P and ^{33}P mixtures by fitting time-dependent count rate data to resolve the two components. For a given LS cocktail formed with an aliquant of mass m of a $^{33}\text{P}/^{32}\text{P}$ solution in some suitable scintillant, the total number of counts C_i detected in a counting interval T can be given by

$$C_i/mT = A_{32(t)}\epsilon_{32}\exp(-\lambda_{32}t_i) + A_{33(t)}\epsilon_{33}\exp(-\lambda_{33}t_i) + B_i/T \quad (3)$$

where $A_{32(t)}$ and $A_{33(t)}$ are the massic activities of ^{32}P and ^{33}P in the solution at some $t_i = 0$ reference time, respectively; where ϵ_{32} and ϵ_{33} are the respective $4\pi\beta$ LS detection efficiencies (at time t_i if they are temporally dependent); where λ_{32} and λ_{33} are decay constants of ^{32}P and ^{33}P , respectively; and where B_i/T is the estimation of the background counting rate for a composition-matched blank cocktail at time t_i . The counting intervals are always $1/\lambda_{32} \gg T \ll 1/\lambda_{33}$. The ϵ_{32} and ϵ_{33} efficiencies are evaluated by efficiency tracing with composition-matched ^3H -standard cocktails using the well-known CIEMAT/NIST methodology.³⁴ Therefore, the background-corrected counting rate $R_i = (C_i - B_i)/mT$ at time t_i at the midpoint of the counting interval T is just

$$R_i = A_{32(t)}[\epsilon_{32}\exp(-\lambda_{32}t_i) + I_0\epsilon_{33}\exp(-\lambda_{33}t_i)] \quad (4)$$

where $I_0 = A_{33(t)}/A_{32(t)}$. With sufficient (R_i, t_i) counting data pairs, $A_{32(t)}$ and I_0 can be obtained as constant parameters by fitting the (R_i, t_i) data to the functional form of equation (4).

Let's now examine several realistic cases, and in doing so ask two very relevant questions: viz., (i) Can I appreciate (e.g., by direct graphical observation) how well my (R_i, t_i) data set fit the functional form of equation (4)?; and (ii) Is the measurement time interval, over which my determinations of (R_i, t_i) were made, sufficiently long to evaluate $A_{32(t)}$ and I_0 to my required precision? Related to the second query is the important question: Can I a priori predict (and thereby plan) what t_i interval is required to determine $A_{32(t)}$ and I_0 to the precision that I might require for my assay?

Illustrated applications of the transform

The three examples that follow are based on data obtained from this laboratory within the past two years using our well-established procedures for the LS spectrometry of gravimetrically-determined aliquants of solutions containing β -emitting radionuclides.^{12-15,17,21-25} The routine gravimetric, source-preparation procedures used in our laboratory as they apply to the preparation of LS counting sources, as well as estimations of their associated uncertainties, have been treated at length previously.²⁸⁻³⁰ Mass determinations for the aliquants have relative standard uncertainties³¹⁻³² of about $\pm 0.05\%$. The measurements for these examples were performed with one of our two LS spectrometer systems.^{17,25,30} Its principal operating characteristics are outlined in Table 1. Descriptions of these operating characteristics, the instrument's respective performance, and use within this laboratory for various radionuclidic calibrations are available.^{12-15,17,26-30} The LS counting sources were prepared with aliquants of the $^{33}\text{P}/^{32}\text{P}$ solutions in either one of two "ready-to-use," commercially-prepared scintillants: "Ultima-Gold AB" (Packard Instrument Co., Meriden, CT) or "Ready Safe" (Beckman Instruments, Inc., Fullerton, CA) [Table 2]; and were contained in either conventional 22-mL, low-potassium, borosilicate glass LS vials having plastic screw caps with polyethylene vee-cone liners or in 22-mL high-density polyethylene vials with polymerized-urea screw caps. The ^3H -standard cocktails used for the ^{32}P and ^{33}P efficiency tracing were prepared with aliquants of careful gravimetric dilutions of a NIST ^3H (tritiated-water) standard.³³ Efficiency variations for the tracing was achieved by either using varying aliquant sizes (and hence varying aqueous mass fraction f_w) or by the use of a 10% solution of CH_3NO_2 in ethanol as an imposed quenching agent. The quench indicating parameter (QIP) used to account for small quenching differences between the ^3H and $^{33}\text{P}/^{32}\text{P}$ cocktails was an instrument-derived Horrocks number H .³⁴ The calculated QIP-adjusted ^{32}P and ^{33}P efficiencies ϵ_{32} and ϵ_{33} , as obtained from tracing with the experimentally-determined ^3H efficiencies, were obtained with the EFFY4 code.¹⁸ Table 3 summarizes the nuclear data³⁵ that was used as input for the EFFY4-code calculations; to determine the $\exp(-\lambda_{32}t_i)$ and $\exp(-\lambda_{33}t_i)$ decay terms; and to calculate the decay corrections for the ^3H -standard cocktails.

Characteristic	"System B"
LS spectrometer model	Beckman LS7800
operating mode	sum-coincidence
photomultiplier tubes	Hamamatsu R331-05
operating temperature	ambient
coincidence resolving time	22 ns
sum-coincident pulse amplification	logarithmic
pulse resolving time	5 μs to 33 μs (variable with pulse height)
spectral analog-to-digital converter (ADC) capacity	1000 channels
nominal conversion gain (energy per channel)	variable (with logarithmic energy)
detection threshold (nominal)	≤ 1 keV
live-time determination method (and uncertainty)	gated oscillator (scaled) (± 0.1 %)
quench indicating parameter (QIP)	Horrocks number (H)
external γ -ray source for QIP determination (and location)	^{137}Cs (side)

Table 1 Characteristics of the "system B" LS spectrometer used for the $^{32}\text{P}/^{32}\text{P}$ assays given in the three examples.

Commercial scintillant	Acronym descriptor	Manufacturer	Density (g·mL ⁻¹)	Composition
Ultima-Gold AB	UG	Packard	0.96	di-isopropyl naphthalene (DIPN); with unspecified emulsifiers; 2,5-diphenyloxazole (PPO) and bis(2-methylstyryl)benzene (bis-MSB) fluors
Ready Safe	RS	Beckman	0.97	phenylxyl ethane (PXE), 50-80 %; non-ionic surfactant, 20-50 %; PPO, < 1 %

Table 2 Scintillants (commercially-prepared) used for the $^{32}\text{P}/^{32}\text{P}$ assays given in the three examples.

Radionuclide	^{32}P	^{33}P	^3H
half-life, $\ln(2)/\lambda$	14.262 ± 0.014 d	25.34 ± 0.12 d	12.33 ± 0.06 a
$E_{\beta(\text{max})}$	1710.3 ± 0.6 keV	248.5 ± 1.5 keV	18.619 ± 0.011 keV
$E_{\beta(\text{mean})}^{[a]}$	694.9 ± 0.3 keV	76.4 ± 0.5 keV	5.69 ± 0.04 keV
β transition	allowed	allowed	allowed
β spectrum shape factor	1	1	1

Table 3 Relevant nuclear data used for the $^{32}\text{P}/^{32}\text{P}$ assays and as obtained from ENSDF(reference 35).

^[a] The values of $E_{\beta(\text{mean})}$ are not required as input into the EFFY code, but rather are calculated by EFFY from input values of $E_{\beta(\text{max})}$. The $E_{\beta(\text{mean})}$ values tabulated here are those obtained from the ENSDF compilation.³⁵ For comparison, those obtained from the EFFY4¹⁸ code (using the tabulated $E_{\beta(\text{max})}$ values) are $E_{\beta(\text{mean})} = 694.6$ keV for ^{32}P , $E_{\beta(\text{mean})} = 76.3$ keV for ^{33}P , and $E_{\beta(\text{mean})} = 5.70$ keV for ^3H .

Example 1

Figure 1 displays a typical set of (R_i, t_i) data that was obtained for a determination of $A_{32(\text{C})}$ and I_2 for a particular $^{33}\text{P}/^{32}\text{P}$ solution. This example is a relatively easy two-component resolution situation (and is thereby a somewhat optimistically extreme case) because of the large I_2 . The plotted points, obtained over three separate measurement trials, represent actual experimental data whereas the solid curve is that obtained by fitting the (R_i, t_i) data pairs to equation. (4). The individual ϵ_{32} and ϵ_{33} values for equation. (4) were evaluated from the ^3H -standard efficiency tracing at each datum. The resolved parameters are $A_{32(\text{C})} = (1906.0 \pm 1.9) \text{ Bq}\cdot\text{g}^{-1}$ and $I_2 = 0.172 \pm 0.001$ [with $A_{33(\text{C})} = (327.7 \pm 1.7) \text{ Bq}\cdot\text{g}^{-1}$] where the cited uncertainty intervals are only fitting uncertainties (as derived from the residuals on the fit). The experimental conditions for the three trials are summarized in Table 4. As indicated, an initial set of four cocktails, ^{35}S labeled H2 through H5, (along with composition-matched blanks and ^3H -standard cocktails) were measured 10 times (for trial 1) over a time interval of about 4 d, and were remeasured 5 times approximately 2 weeks later (for trial 2) over a period of about 2 d. To verify that the $^{33}\text{P}/^{32}\text{P}$ cocktails were indeed

"tractable"²³ to the ^3H -standard cocktails over the ≈ 15 -d interval, a second series of $^{33}\text{P}/^{32}\text{P}$ cocktails (labeled H6-H10) and new blanks and ^3H -standard cocktails were prepared and measured for trial 3.

On inspection of Figure 1, one might reasonably ask: Is this a good fit (i.e., am I truly comfortable with these results, irrespective of the apparently good fitting uncertainties)? Clearly the plot of R_i versus t_i data of Figure 1 is not sufficiently sensitive to give one much confidence in the quality of the fit or that the ^{33}P impurity was well resolved. Plotting the R_i data on a logarithmic axis is equally uninformative. One can, of course, plot the fitted residuals (a highly recommended procedure), as in Figure 2, to ascertain if there are any unusual structural or glitch-like features in the fitted data. The residual plot, however, similarly does not provide a very transparent way of observing how well the ^{33}P impurity was resolved.

In contradistinction, Figure 3 exhibits the identical data contained in Figure 1 after invoking the data transformation of equation (2). In this case, the well-defined and delineated slope $dY/dX = A_{33(\text{C})}$ clearly establishes that the impurity was resolved very adequately. One can go one step further and

	Trial 1	Trial 2	Trial 3
cocktail identity	H2 - H5	H2 - H5	H6 - H10
number of $^{33}\text{P}/^{32}\text{P}$ cocktails	4	4	5
number of ^3H cocktails	5	5	6
range of solution aliquant in cocktails (g)	$0.20 \leq m \leq 0.57$	$0.20 \leq m \leq 0.57$	$m \approx 0.24$
aqueous mass fraction in cocktails	$0.020 \leq f_w \leq 0.055$	$0.020 \leq f_w \leq 0.055$	$f_w \approx 0.024$
cocktail mass (g)	$9.98 \leq m_c \leq 10.14$	$9.98 \leq m_c \leq 10.14$	$m_c \approx 10.06$
imposed quench agent to vary efficiencies	aliquant m sizes	aliquant m sizes	10 % solution of CH_3NO_2 in ethanol
range of ^3H -standard detection efficiencies	$0.4502 \leq \epsilon_3 \leq 0.4919$	$0.4500 \leq \epsilon_3 \leq 0.4867$	$0.4652 \leq \epsilon_3 \leq 0.4908$
range of ^{32}P efficiencies	$0.9982 \leq \epsilon_{32} \leq 0.9983$	$0.9981 \leq \epsilon_{32} \leq 0.9983$	$0.9982 \leq \epsilon_{32} \leq 0.9984$
range of ^{33}P efficiencies	$0.9509 \leq \epsilon_{33} \leq 0.9543$	$0.9458 \leq \epsilon_{33} \leq 0.9524$	$0.9533 \leq \epsilon_{33} \leq 0.9558$
number of measurements on each cocktail	10	5	5
cocktail "age" at measurement times (days)	$1 < t_{\text{age}} < 6$	$14 < t_{\text{age}} < 17$	$0 < t_{\text{age}} < 3$
counting time interval	$T = 50 \text{ min}$	$T = 50 \text{ min}$	$T = 50 \text{ min}$
range of measurement times (d)	$1.05 \leq t_i \leq 5.16$	$13.93 \leq t_i \leq 15.98$	$16.12 \leq t_i \leq 18.18$

Table 4 Experimental conditions for the LS assay of a $^{33}\text{P}/^{32}\text{P}$ solution as employed for the three trials of Example 1.

look at the data obtained from just the trial 1 measurements. This result is given in Figure 4 which has fitted parameters of $A_{32(0)} = (1933 \pm 12) \text{ Bq}\cdot\text{g}^{-1}$ and $A_{33(0)} = (302 \pm 11) \text{ Bq}\cdot\text{g}^{-1}$. Again, it is apparent that the ^{33}P impurity was resolved even over the short ≈ 4 -d measurement interval (because of the large I_0). Figure 5 contains comparable results for trials 2 and 3, and manifests poorer precision in determining $A_{33(0)}$ over these shorter ≈ 2 -d measurement intervals.

It should be noted that for all four of the above fits (i.e., that for the aggregate data of the trials and those for the individual three trials) the fitted $A_{32(0)}$ and $A_{33(0)}$ parameters were wholly invariant (to a minimum of 4 or 5 significant figures) of whether one did non-linear χ^2 -minimization regressions with equation (4) or whether one did linear regressions on the transformed data as with equation (2). Small insignificant differences in the assigned fitting uncertainties on the parameters were just dependent on the calculational algorithms used for the two types of regressions. In general, I would tend to recommend that one use the equation (2) linear transformation approach to graphically examine the data and the quality of the ^{33}P impurity resolution; and that one use a proven-to-be-reliable, non-linear χ^2 -minimization procedure to fit the measurement data to equation (1) [or equation (4)] to extract "final" $A_{32(0)}$ and $A_{33(0)}$ parameters and their fitted uncertainties.

A last point using this data set can be made to vividly illustrate (possibly with some belaboring and exaggeration) the advantage in using the transformation approach. Imagine if you will, perhaps as a result of a careless mistake on the part of some over-worked researcher, that all of the t_i values for the trial 1 measurements had incorporated an initially undetected

calculational timing offset of exactly 0.5000 d (with respect to t_0 and to the t_i values for the later two trial measurements). Imagine further, in the absence of some independent data-analysis audit, that this error (i.e., mistake) was not detected; and one had proceeded through the usual analysis approach. The fitted-parameter results would have relative fitting uncertainties of 0.3 % for $A_{32(0)}$ and 0.8 % for $A_{33(0)}$. These uncertainties are not much worse than that obtained for the "true" fits without the mistake (given previously); yet, the fitted values for $A_{32(0)}$ and $A_{33(0)}$, respectively, would now be over 10 % and 40 % different! What if the mistake hadn't been caught in the audit? A plot of R_i versus t_i for the data and for the functional curve obtained with the fitted parameters, as in Figure 1, would likely have been too insensitive to detect the mistake. A plot of the residuals to the fit, as in Figure 2, would have displaced some of the early and late datum in the two groups (i.e., those of trial 1 and those of trials 2 and 3) of measurements, but not enough to cause serious suspicion on the quality of the input data. Use of other statistical estimators, e.g., the fit's adjusted correlation coefficient r^2 , would give results that would similarly appear to be quite reasonable, and probably would not arouse doubts to the determination and resolution of the ^{33}P and ^{32}P components since any difference in an estimator like r^2 would be quite small. Now, let's look at this miscalculated data in terms of the linearizing transformation. As seen in Figure 6, it is clear that there is something drastically "wrong" in that the regression line bisects the two groups such that all the early points have positive residuals and that all the later points have negative residuals, and that the two groups have decidedly different dY/dX slopes. Surely, any respectable researcher, on

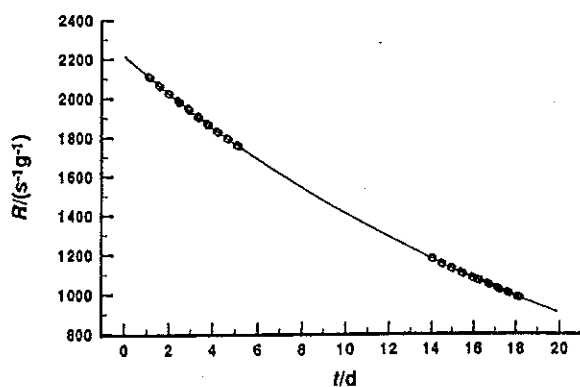


Figure 1 LS counting data (Example 1) for the composite decay of ^{33}P and ^{32}P , as given by equation (1), for a solution with an impurity ratio $I_0 = A_{33(0)}/A_{32(0)} = 0.17$. The plotted datum points represent experimentally-determined (R_i, t_i) pairs (with corresponding ^{33}H -standard efficiency-traced ϵ_{32} and ϵ_{33} determinations). The solid curve is the χ^2 -minimized regression result for fitted parameters $A_{32(0)} = (1906 \pm 2) \text{ Bq}\cdot\text{g}^{-1}$ and $A_{33(0)} = (328 \pm 2) \text{ Bq}\cdot\text{g}^{-1}$.

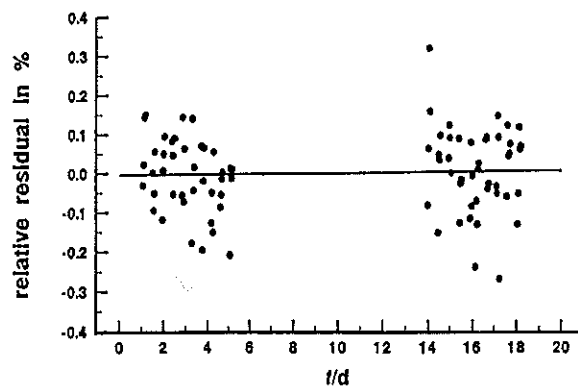


Figure 2 Relative residuals, expressed in %, for the regression given in Figure 1.

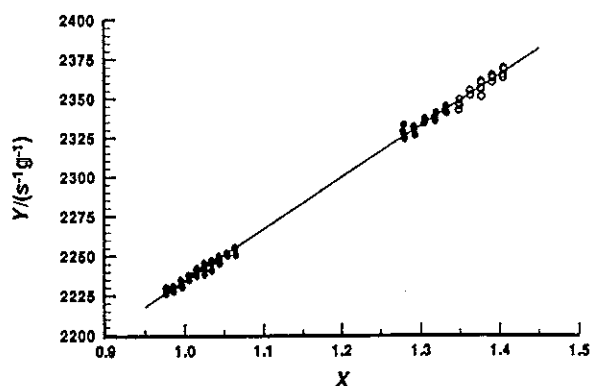


Figure 3 Linearized data transform, using equation (2), for the LS counting data given in Figure 1 for Example 1. The line is that obtained for a regression of the data to a linear function. The slope dY/dX corresponds to $A_{32(3)}$, while the intercept of Y at $X = 0$ is $A_{32(2)}$. The results include those obtained with two sets of cocktails (Table 4), denoted by closed and open circles.

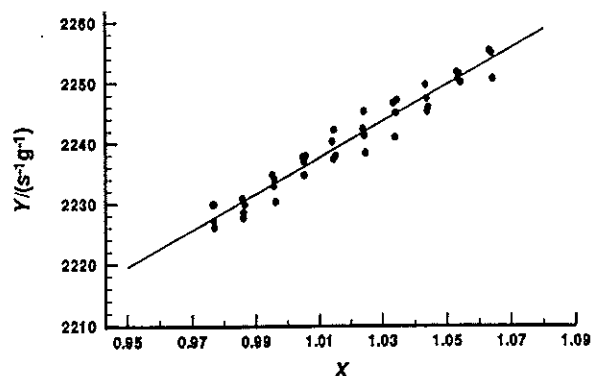


Figure 4 Linearized data transform for a subset of the Example 1 data. It contains only the trial 1 (Table 4) measurement results obtained over about a 4-d counting interval.

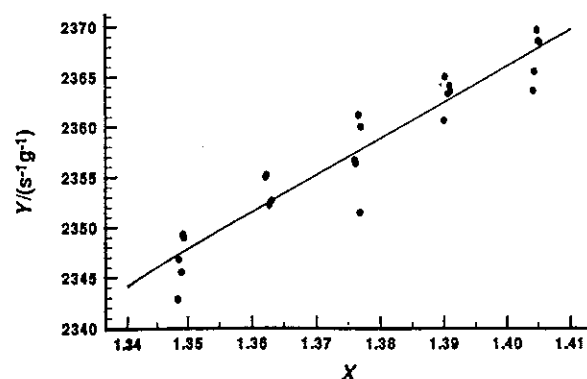
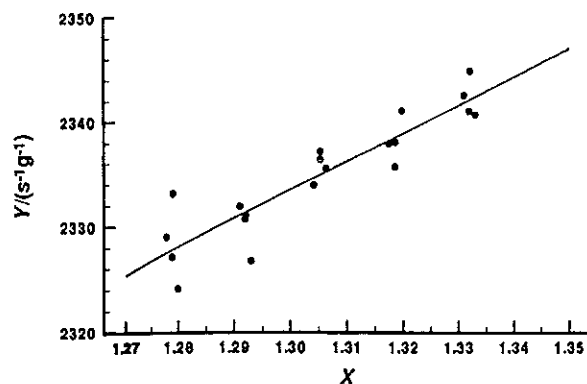


Figure 5 Linearized data transforms for the other two subsets of the Example 1 data. The upper trace is that for the re-measurement of the initial cocktails over a period of about 2 d which was performed about two weeks after preparation (trial 2). The lower trace is that for a new set of freshly-prepared cocktails (trial 3) which were also counted over about a 2-d interval.

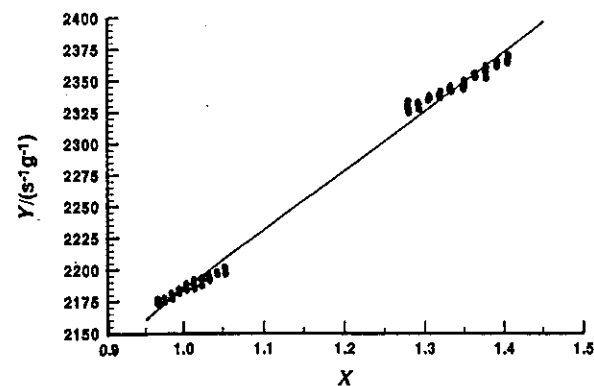


Figure 6 Illustration of the use of the transform for detecting possible problems with the quality of measurement data. The illustration assumes that the data of Figure 1 had mistakenly incorporated a 0.5000 d timing offset in calculations for one of the three trials of measurements. Refer to text for discussion.

having this graphical display in hand, would begin to question either the input data or the data-analysis model. I further contend that this type of mistake would probably not have been caught without the use of the graphically-displayed transform.

Example 2

Figure 7 gives the (R_i, t_i) measurement results (with companion ϵ_{32} and ϵ_{33} efficiency determinations at each datum) which were used for a ^{33}P impurity evaluation on a standardized ^{32}P solution. These results comprise part of the I_0 determination that was obtained for the certification of NIST Standard Reference Materials SRM 4406H-N and 4406L-N.³⁶ This is a much more difficult case to resolve since $I_0 < 0.01$ at $t = 0$. The determination was based on two sets of about 150 measurements that were separated in time by about 70 d. Initially, 30 gravimetrically-related $^{33}\text{P}/^{32}\text{P}$ cocktails (and corresponding blanks and ^3H -standard cocktails) were prepared, and multiple measurements on each were made over a period of about 6 days. Another set of 20 similar $^{33}\text{P}/^{32}\text{P}$ cocktails (again with newly-prepared blanks and ^3H -standard cocktails) were subsequently prepared, and each of these was measured several times over another roughly 6-d period. The second set of new cocktails was used because the initial cocktails, based on our experience, would have undergone deleterious degradations and could not be expected to be sufficiently stable or "tractable"²³ over such a long >70-d interval.

Fitted parameters obtained from a regression of the two combined data sets are $A_{32(0)} = (3.354 \pm 0.004) \text{ MBq}\cdot\text{g}^{-1}$ and $A_{33(0)} = (26.6 \pm 4.4) \text{ kBq}\cdot\text{g}^{-1}$ which corresponds to impurity ratios of $I_0 = 0.0079$ at $t = 0$ and $I = 0.037$ at $t = 72 \text{ d}$. As before, it is difficult (from just looking at Figure 7 or at the magnitudes of the fitted uncertainties) to judge the quality of the resolution. It becomes readily apparent, however, after use of the data transformation of equation (2). Figure 8 shows these transformed results. The distinctly defined slope $dY/dX = A_{33(0)}$ is visually dramatic.

Again, going one step further, we can look at the two parts of the data separately. This is done in Figure 9, and displays that neither set alone would have adequately resolved the ^{33}P impurity.

Example 3

For completeness in demonstrating the efficacy of this linearizing data transformation approach, we can consider a case for a very aged (low-activity level) special solid source which actually contained more ^{33}P activity than ^{32}P activity. The low-volume solution used for the assay was obtained from chemically digesting the source. The case was also unusual in that the solution had a substantial HNO_3 concentration (with traces of HF) and high PO_4^{3-} and metal ion content.³⁷ The LS counting data for such a case is given in Figure 10. Four cocktails (with a set of composition-matched

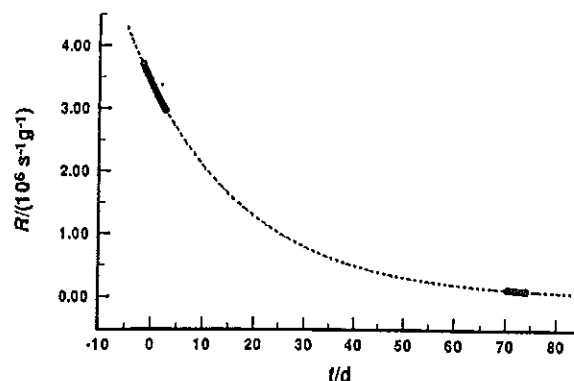


Figure 7 LS counting data (Example 2) for the composite decay of ^{32}P and ^{33}P , as given by equation (1), for a solution with an impurity ratio $I_0 = A_{33(0)}/A_{32(0)} \cong 0.008$. The plotted datum points represent experimentally-determined (R_i, t_i) pairs (with corresponding ^3H -standard efficiency-traced ϵ_{32} and ϵ_{33} determinations) that were obtained from measurements on two sets of LS cocktails made about 70 d apart. The solid curve is the χ^2 -minimized regression result for fitted parameters $A_{32(0)} = (3.354 \pm 0.004) \text{ MBq}\cdot\text{g}^{-1}$ and $A_{33(0)} = (26.6 \pm 4.4) \text{ kBq}\cdot\text{g}^{-1}$.

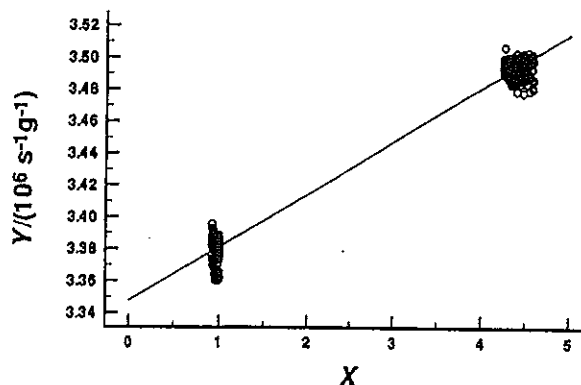


Figure 8 Linearized data transform, using equation (2), for the LS counting data given in Figure 7 for Example 2. The well-defined and delineated slope $dY/dX = A_{33(0)}$ indicates the good resolution of the ^{33}P component.

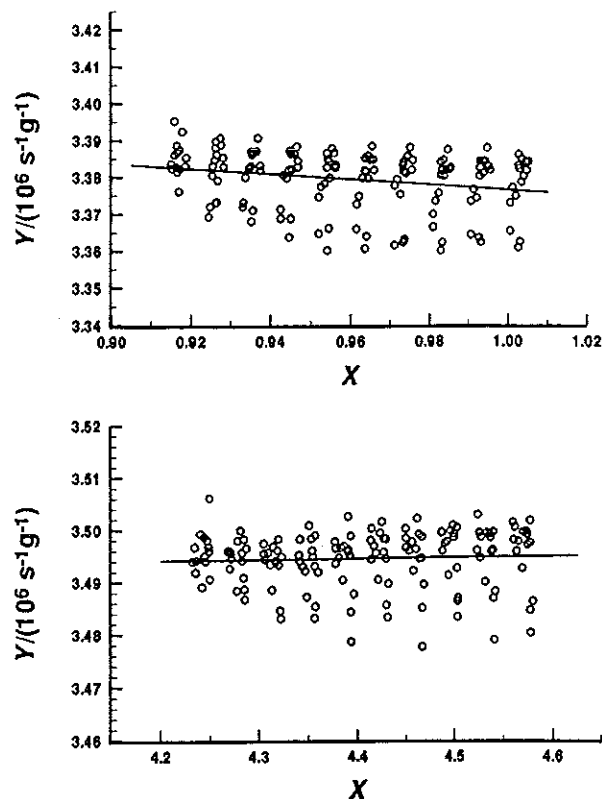


Figure 9 Linearized data transforms for the two sets of counting results given in Figure 7 for Example 2. Neither the first set of measurements with an impurity ratio of $I < 0.01$ (upper trace) nor the second set with $I \approx 0.04$ (lower trace) could adequately resolve the ^{33}P component over their short measurement-time intervals

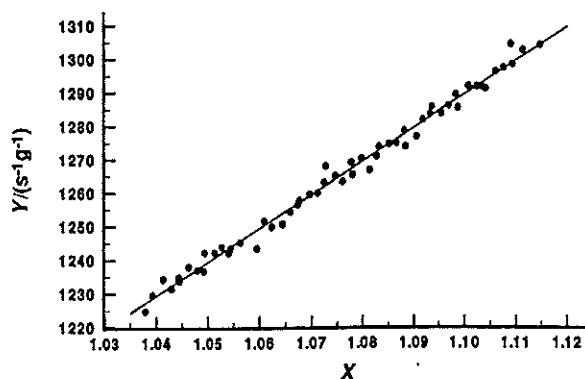


Figure 11 Linearized data transform, using equation (2), for the LS counting data given in Figure 10 for Example 3. The slope dY/dX corresponds to $A_{33(g)}$, while the intercept of Y at $X = 0$ is $A_{32(g)}$.

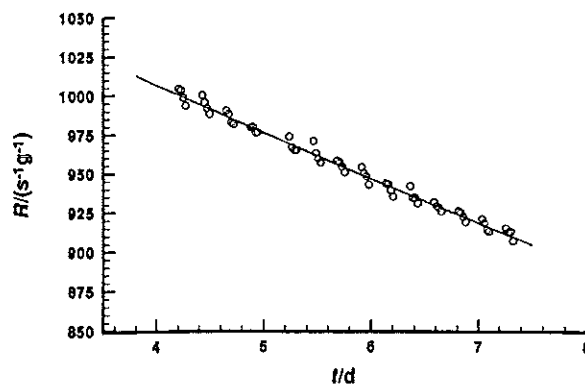


Figure 10 LS counting data (Example 3) for the composite decay of ^{32}P and ^{33}P , as given by equation (1), for a solution with an impurity ratio $I_0 = A_{33(g)}/A_{32(g)} > 5$ (i.e., substantially more ^{33}P than ^{32}P). The plotted datum points represent experimentally-determined (R, t) pairs (with corresponding ^3H -standard efficiency-traced ϵ_{32} and ϵ_{33} determinations) that were obtained from measurements on 4 LS cocktails over a period of about 3 d. The solid curve is the χ^2 -minimized regression result for fitted parameters $A_{32(g)} = (189 \pm 14) \text{ Bq}\cdot\text{g}^{-1}$ and $A_{33(g)} = (1000 \pm 13) \text{ Bq}\cdot\text{g}^{-1}$.

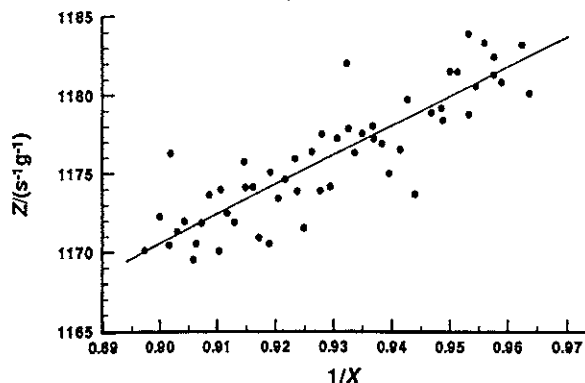


Figure 12 An alternative linearized data transform, using equation (5), for the LS counting data given in Figure 10 for Example 3. In this case, the slope $dZ/d(1/X)$ corresponds to $A_{33(g)}$, while the intercept of Z at $1/X = 0$ is $A_{32(g)}$.

blanks and ^3H -standard cocktails) were each measured, over the course of about 3 d, 14 times. The relatively large dispersion in the R_i versus t_i data arises because of statistical "counting error" imprecision and background subtraction variations at low counting rates, and because of cocktail instabilities due to their unusual compositions (high acidity and ionic content in the aqueous portion).

The regression results are $A_{32(t)} = (189 \pm 14) \text{ Bq}\cdot\text{g}^{-1}$ and $A_{33(t)} = (1000 \pm 13) \text{ Bq}\cdot\text{g}^{-1}$, and the results for the equation (2) data transformation is shown in Figure 11.

Inasmuch as $A_{32(t)} < A_{33(t)}$, one could alternatively perform the linearizing transformation in terms of

$$Z = A_{32(t)}/X + A_{33(t)} \quad (5)$$

with $Z = R/\epsilon_{33}\exp(-\lambda_{33}t)$ and $1/X = \epsilon_{32}\exp(-\lambda_{32}t)/\epsilon_{33}\exp(-\lambda_{33}t) = (\epsilon_{32}/\epsilon_{33})\exp[(\lambda_{33}-\lambda_{32})t]$ such that $A_{33(t)}$ is now the intercept of Z at $1/X = 0$ and where the slope $dZ/d(1/X) = A_{32(t)}$. This transform is illustrated in Figure 12 (for the same data as given in Figure 11). The larger imprecision in the $dZ/d(1/X)$ slope of Figure 12 (compared to dY/dX in Figure 11) merely reflects that $A_{32(t)} < A_{33(t)}$ and that $A_{32(t)}$ is determined with a larger relative uncertainty than $A_{33(t)}$.⁶

Measurement-time separation required to resolve two components

The transform of equation (2) [or of equation (5)] can also be used as a simple tool for estimating the measurement-time separation required to resolve two components. How well the resolution is effected depends, of course, on the activity ratio I of the two components, on the maximum time interval over which the measurements were obtained, and on the number and frequency of the measurements made over the time interval. The last factor (e.g., by performing many frequent measurements) will influence the precision in determining I if the components are resolved, but the factor alone may not be sufficient to resolve the components. Figure 9 demonstrated that even 150 measurements over a short t with low I was insufficient in resolving the components. A convenient way to identify the required time interval for a given I is to consider the fractional change $f_{\Delta Y}$ in Y . Examinations of Figures 3, 4, 5, 8, 11 and 12 demonstrate that an impurity can be resolved with changes as small as even 1% (Figure 12) and can be resolved very well (with even very low impurity ratios) with changes of less than 5% (Figure 8). With large changes in Y and attendant large I (as in Figures 4 and 5), the impurity can be resolved from measurements over very short time intervals.

The time interval t_{\min} needed to obtain a fractional change $f_{\Delta Y}$ in Y for a given impurity ratio can be straightforwardly derived as follows. With the intercept of Y at $X = 0$ given by $Y_0 = A_{1(t)}$ and with $I_0 = A_{2(t)}/A_{1(t)}$, equation (2) can be rearranged in terms of

$$Y/Y_0 = 1 + I_0 X \quad (6)$$

from which $X = (Y/Y_0 - 1)/I_0 = f_{\Delta Y}/I_0$. With $X = (\epsilon_2/\epsilon_1)\exp[(\lambda_1-\lambda_2)t_{\min}]$, the time interval t_{\min} as a function of X may be expressed as $t_{\min} = [\ln X - \ln(\epsilon_2/\epsilon_1)]/(\lambda_1 - \lambda_2)$ which results in

$$t_{\min} = [\ln(f_{\Delta Y}/I_0) - \ln(\epsilon_2/\epsilon_1)]/(\lambda_1 - \lambda_2) \quad (7)$$

Figure 13, for the case of $^{33}\text{P}/^{32}\text{P}$ mixtures, illustrates this calculation of the time interval t_{\min} needed to obtain a fractional change $f_{\Delta Y}$ for various $I_0 = A_{33(t)}/A_{32(t)}$ impurity ratios. The calculation assumes an efficiency ratio of $\epsilon_2/\epsilon_1 = 0.954$ (see Table 4 for typical values). Since t is a logarithmic function of X , t_{\min} is linear on a logarithmic $f_{\Delta Y}$ axis, just as a plot of X versus $f_{\Delta Y}$ would simply be linear as given by equation (6). If one somewhat arbitrarily selects $f_{\Delta Y} = 0.05$ (a 5% change in Y_0 such that $Y/Y_0 = 1.05$) as providing adequate resolution, then Figure 14 shows the time interval needed as a function of the impurity ratio I_0 . As indicated, assays with very low impurity ratios, e.g., $I_0 < 0.02$, require very long measurement time separations (> 40 d) which are usually longer than most normal LS cocktail stabilities. Above about $I_0 > 0.05$, the resolutions are rather easily achieved over short times.

Use of simple Monte-Carlo-like simulations to predict resolution precisions

The above estimation of the required time interval t needed to resolve the two components does not, of course, specify the actual precision (i.e., the fitted-parameter uncertainties) in which the two components will be determined. This will depend upon the number of measurements and the time spacing between measurements (frequency), as noted previously; as well as on the number of independent counting sources, on how well the detection efficiencies are determined (or on how variable they are), on the inherent variations between counting sources, and on the inherent precision in determining the counting rates R . One can, however, model the measurement process using the linear transform of equation (6) to perform Monte-Carlo-like simulations that will allow one to estimate the likely fitting precision that will be obtained under a given set of experimental conditions. This can be of use, for example, in choosing between alternative experimental designs. It might be employed, for example (in the case of high impurity ratio I), to ascertain whether 48 equally-spaced (R_i, t_i) measurements over 2 d would give comparable fitting precision to that obtained with considerably less measurements over 8 d. With some necessary assumptions, such a simulation can be directly performed by: (i) calculating the values of X for the chosen time intervals t (and efficiency values) of the proposed design; (ii) calculating the "true" values of $Y_T = (Y/Y_0)_T = 1 + I_{T(t)}X$ for an expected (assumed) impurity ratio $I_{T(t)}$; (iii) assuming that the transformed rates Y (with respect to Y_0) at each X datum is sampled from a population that has a particular

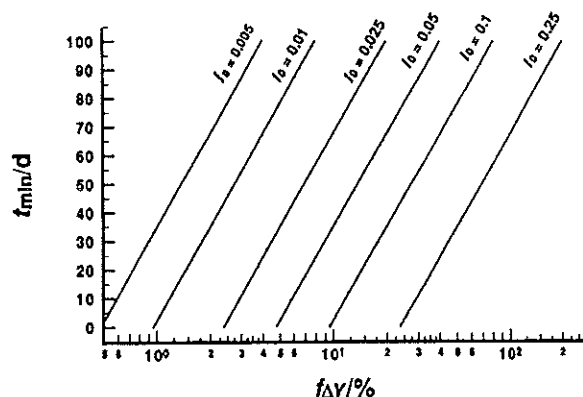


Figure 13 Calculations of the estimated time intervals t_{\min} needed to obtain a fractional change $f_{\Delta Y}$ in Y for various $I_0 = A_{330g}/A_{320g}$ impurity ratios as it would apply to the resolution of $^{33}\text{P}/^{32}\text{P}$ mixtures.

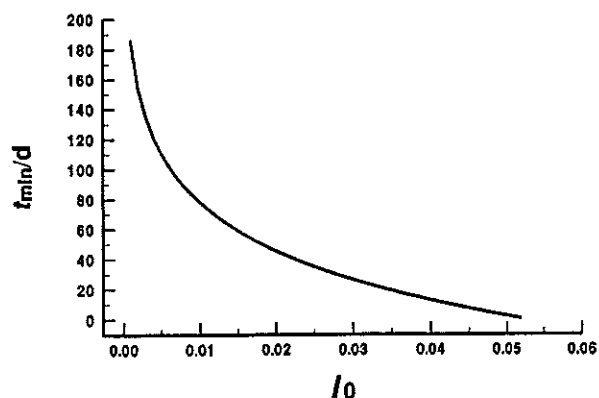


Figure 14 Calculated results for the estimated time intervals t_{\min} needed to obtain a fractional change $f_{\Delta Y} = 0.05$ as a function of the impurity ratio $I_0 = A_{330g}/A_{320g}$ as it would apply to the resolution of $^{33}\text{P}/^{32}\text{P}$ mixtures.

standard deviation s_Y (which can be estimated from typical LS within- and between-cocktail counting precisions as obtained in your laboratory under similar cocktail composition and timing conditions); (iv) calculating sampled values $Y_s = (Y/Y_0)_s = Y_1(1 + s, \sigma)$ at each X using random numbers σ sampled from a normal distribution having a mean $\mu = 0$ and variance $\sigma^2 = 1$; and (v) fitting the (X, Y_s) pairs to equation (6) to obtain I_{SC} as a fitted parameter. If we repeat this calculational process many times for each design, then it will become apparent (from the fits and from the scatter in the sampled Y_s values) which design will result in a more precise I_0 determination.

This kind of simulation has recently been employed with considerable efficacy in designing several counting experiments for the assay of ^{32}P intravascular brachytherapy sources.³⁷

Concluding thoughts

The various examples given here have hopefully demonstrated the considerable usefulness of this simple transformation for graphically analyzing two-component decay data, e.g. for resolving a ^{33}P impurity in ^{32}P solutions. The transform itself has virtually no utility for actually performing the fits of measurement data to the function consisting of the sum of two exponential decay terms to extract, as fitted parameters, the two component activities. Rather, it offers an extremely powerful way of graphically observing the quality of a resolution (and/or the absence of a resolution). Fitted uncertainties, and other statistical estimators such as adjusted correlation coefficients, are notorious in masking the quality of such fits, or the quality of the input measurement data; and can rarely detect experimental or calculational blunders. Graphical displays of the linearly-transformed data can detect such problems, and recently have within this laboratory! The simple transform can also be employed to advantage in helping to establish experimental designs, e.g. in selecting the measurement-time interval that is needed to adequately resolve two components.

Endnotes

*1

It seems hard to imagine that this kind of simple data transformation is really an original conception, and that it has not previously appeared somewhere in the literature. Its existence in print, however, is unknown to this author. Moreover, this data analysis technique is not covered in any of the usual and standard texts and reference works on radionuclidic metrology, such as the sampling of 20 citations given as reference 1. Nearly all of these give an example of the decomposition of a two-component decay curve, but they treat it by either doing a graphical subtraction on a semilogarithmic plot of the activity (or counting rate) versus time or suggesting the use of least-squares-fit methods to

perform the calculations. Neither approach provides a very direct evaluation of the quality of the resolution.

*2

Readers may find it of interest to note that most ^{32}P sources invariably also contain an ^{124}Sb impurity whose origin is inexplicable. The $^{124}\text{Sb}/^{32}\text{P}$ impurity ratio is generally in the range of 10^{-6} to 10^{-8} for relatively freshly-prepared ^{32}P supplies. This finding is based on over a decade of γ -ray spectrometry results from this laboratory⁷ with many different commercial sources of ^{32}P . The ^{124}Sb impurity is not only almost always observed, but it is largely the only γ -emitting impurity ever observed.

*3

An alternative approach to assaying ^{32}P is, of course, by Cerenkov counting in which any ^{32}P impurity would not be detected since its maximum β^- endpoint energy $E_{\beta(\text{max})} = 248.5$ keV is below the velocity threshold (263 keV) for producing Cerenkov radiation in aqueous solutions (see, for example, references 3-5). This requires, however, an independent determination of the Cerenkov counting efficiency for ^{32}P such as by the methodology of Grau Carles and Grau Malonda.⁶ The Cerenkov efficiency for ^{32}P (typically in the

range of 0.2 to 0.5) is not only lower than the LS efficiency, but is also much more variable with changes in the counting conditions or solution compositions. Furthermore, if one wanted to also evaluate the ^{32}P content of the solution, then one would still have to perform LS counting along with the Cerenkov counting which would result in the need to determine all three efficiencies.

*4

The acronym CIEMAT/NIST refers to the two laboratories that collaborated in developing the protocol for this LS spectrometry tracing methodology; viz., the Centro de Investigaciones Energeticas, Medioambientales y Tecnologicas (CIEMAT) and the National Institute of Standards and Technology (NIST). The method has been described in numerous publications by Grau Malonda, Coursey, et al.^{7,11} Details on its practical application, as it is presently invoked in this laboratory, are given by Collé and Zimmerman.^{12,17} The protocol utilizes various updated and revised versions of the CIEMAT-developed EFFY code^{18,20} to determine the detection efficiencies for cocktails of the traced radionuclide (under known and varying quench conditions) by following the experimentally-determined efficiencies for closely-matched cocktails of ^3H . Tritium (^3H) is recommended

to serve as the matched (in terms of cocktail composition and quenching) standard since extrapolations to the lower-energy portions of the β spectra are more sensitive than that obtained with higher-energy β -emitting standards like ^{14}C .^{8,10} The critical importance of cocktail matching between the standard cocktails and those of the traced radionuclide has been treated by Collé.¹⁶ Similarly, the need to understand the cocktail-composition systematics (e.g., effects of the aqueous mass fraction f_w ,^{12,15,21}), as it affects cocktail stability and what has been termed cocktail "tractability", is critical.^{22,24} A detailed uncertainty model for the CIEMAT/NIST method's measurement process has been developed by Collé and Zimmerman.¹³

*5

An additional cocktail (H1) with an mass fraction of H_2O of $f_w \approx 0.01$ was also prepared, but was found to exhibit asystemic behavior and was considered to be "intractable",²³ in that its apparent efficiency and QIP variations did not tract in a predictable and regular functional dependence on f_w compared to the other cocktails in the series. The irregularities with this cocktail were particularly noticeable after the cocktail series had "aged" for the trial 2 measurements. Similar problems with low f_w cocktails have been previously observed (cf., 12), but this was a surprising finding since it was the first time it was observed for a high-energy β emitter like ^{32}P .

*6

This example is also interesting in that the very large ^{33}P content of the solution allowed a direct determination of the relative ^{33}P and ^{32}P activity components by spectral stripping procedures, whose results comported well with that obtained from the resolved decay data given here.³⁷

Acknowledgments and Disclaimers

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endorsement by NIST, nor does it imply that the materials or equipment identified are the best available for the purpose.

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