



Cocktail Mismatch Effects in $4\pi\beta$ Liquid Scintillation Spectrometry: Implications Based on the Systematics of ^3H Detection Efficiency and Quench Indicating Parameter Variations with Total Cocktail Mass (Volume) and H_2O Fraction

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Detection efficiency changes for ^3H by $4\pi\beta$ liquid scintillation (LS) spectrometry cannot be adequately monitored by quench indicating parameters when the quench changes are the result of multiple causal factors (e.g. simultaneously varying cocktail sizes and composition). In consequence, some kinds of cocktail mismatches (between LS counting sources) introduce errors that result from efficiency changes that cannot be fully accounted for by quench monitoring compensations. These cocktail mismatch effects are examined for comparative ^3H measurements and for ^3H -standard efficiency tracing methods for the assay of other β -emitting radionuclides. Inherent errors can occur in both types of radionuclidic assays, as demonstrated with realistic case examples, unless cocktails are *very closely* matched. The magnitude of the cocktail mismatch effect (and attendant errors) can range from being virtually negligible (particularly for high-energy β -emitting nuclides and for slight single-variable cocktail composition mismatches) to being very significant for high-precision metrology and standardizations (particularly with easily quenched, low-energy β emitters and for mismatches due to both varying cocktail constituents and concentrations). The findings presented here support the need to understand fully the quenching systematics of a given LS system (combination of cocktails and spectrometer) and the need for very careful control of cocktail preparations. © 1997 Published by Elsevier Science Ltd

Introduction

Collé (1997), in a companion paper, reports on the systematic variations in detection efficiency ϵ and quench indicating parameters (QIPs) in $4\pi\beta$ liquid scintillation (LS) spectrometry of ^3H as functions of total cocktail mass m and H_2O mass fraction f . The work was based on experimental evaluations of ϵ and a QIP (called the Horrocks number H , which is derived from the downward spectral shift of the Compton edge of an external γ -ray source with increasing cocktail quenching) for a matrix of 33 carefully prepared cocktails having varying m and f . The study revealed that ^3H efficiency variations that were induced by m and f changes were not fully tracked by inverse H dependencies on m and f , and that the ϵ versus H quench curves exhibited some peculiar irregularities for m -dependent quenching (at near constant f). It clearly demonstrated that efficiency changes cannot be adequately monitored (or adjusted) by QIPs when the quench changes are

induced by multiple causal factors, such as by simultaneous differences in cocktail sizes and compositions.

This paper examines the significant implications of this earlier work. It addresses the repercussive inherent errors in radionuclidic assays performed by LS spectrometry that result from cocktail mismatching effects. The analyses given here focus on how cocktail mass (or volume) and composition mismatches between LS counting sources affect both comparative ^3H measurements (with or without quench curve corrections) and ^3H -standard efficiency tracing for other β -emitting nuclides. Realistic case examples, derived from the previously given ^3H data of Collé (1997), are used to illustrate the effects of cocktail m and f mismatches.

Overview of the Previous Experimental Work

The cocktails used in the previous study (Collé, 1997) were prepared by gravimetric additions of three

components: a commercial scintillation fluid with mass m_c ; blank water (to vary the H_2O fraction) with mass m_w ; and an aliquant of a tritiated water standard with known 3H activity concentration and mass m_s . An additional 33 matched blanks (for background counting subtractions) with nearly identical composition, but without m_s , were also prepared. Comparisons of the QIP determinations for the two sets of 33 blanks and 3H cocktails were also useful in evaluating the ability to replicate cocktail preparations. The prepared 3H cocktails (and 33 matched blanks) formed a matrix of compositions with varying total cocktail mass $m = m_c + m_w + m_s$ and H_2O mass fraction $f = (m_w + m_s)/m$. The relative standard uncertainty in any determination of m or f was estimated to be about $\pm 0.1\%$. The matrix of cocktails sliced across seven m values and across five f values. The m slices ranged from about 3 to 21 g in nominal 3 g increments. The f slices comprised two transparent solution cocktail compositions: $0.002 \leq f \leq 0.02$ and $f \simeq 0.14$; and three translucent gel cocktail compositions: $f \simeq 0.27$, $f \simeq 0.34$ and $f \simeq 0.52$. The former two sets of solution cocktails nicely complement the m -varying single composition 3H data given by Zimmerman and Collé (1997) for an aqueous fraction of about $f \simeq 0.05$.

The ϵ and H determinations for each cocktail were based on five replicate measurements that were performed over the course of about 8 days. The 3H detection efficiencies ranged from about $\epsilon \simeq 0.18$ for the most quenched cocktail (at minimum $m \simeq 3$ g and maximum $f \simeq 0.52$) to $\epsilon \simeq 0.48$ for the least quenched cocktail (with $f \simeq 0.005$ at an optimal $m \simeq 9$ g cocktail size). The uncertainties in ϵ , in terms of a relative standard deviation of the mean [coefficient of variation $v_m(\epsilon)$] for 4 degrees of freedom, were typically about $v_m(\epsilon) \simeq 0.2\%$ [with a slight m dependence that exhibited increased $v_m(\epsilon)$ at large m]. The QIP determinations for the various cocktails (varying inversely with ϵ) ranged from about $H \simeq 64$ to $H \simeq 191$, again, respectively, for the least and most quenched sources. The uncertainties associated with the QIP determinations, in terms of a standard deviation of the mean $s_m(H)$, were largely of fixed magnitude $s_m(H) \simeq 0.3$, and independent of m and f as well as the magnitude of H itself (see below).

The principal findings of this earlier study were: (1) that H was not only strongly influenced by f -varying chemical quench changes (as expected), but was also dependent on m ; (2) that at least some part of the complex m dependence on H must be due to some external effect beyond any internal quenching in the cocktail (probably the subtended solid angles for the geometrical arrangement amongst the external γ -ray source used for the quench monitoring, the cocktail volume in the LS vial, and the photomultiplier tubes); (3) that the uncertainty (measurement replication precision) in making an H determination appeared to be independent of m and f , as well as the

magnitude of H itself, which suggests that this uncertainty is largely of fixed magnitude (for a given LS system) and controlled by the precision in locating the channel-number position of the Compton edge irrespective of the magnitude of the Compton-edge shift with quenching; (4) that ϵ had an obvious monotonic functionality with the increased chemical quenching associated with increasing f , and had a complex dependence on m that somewhat paralleled (inversely) the H versus m dependence; (5) that the uncertainties (replication precision) in determining ϵ were slightly dependent on m (cocktail size) at near constant f , but were largely invariant of f (cocktail composition) at near constant m ; (6) that the "optimum" (i.e. maximum efficiency) $m \simeq 9$ g cocktail size for solution cocktails agreed with a canonically accepted value of 8–12 mL, but for gel cocktails the maximum efficiency shifted to larger m values as f increased; (7) that the dependence of both H and ϵ with changes in m tended to "flatten" with increasing f (i.e. $\partial\epsilon/\partial m|_f$ and $\partial H/\partial m|_f$ were much less at large f values than at small ones); (8) that the ϵ dependencies on m and f were not fully tracked by the inverse H dependencies on m and f ; (9) that observed discrepancies in the ϵ versus H quench curves for variable m (at near constant f) exhibited a peculiar "folding over" of the quench curve; and (10) that quench variations induced simultaneously by multiple factors (e.g. m and f) exhibit a very complex ϵ versus H behavior that is largely a result of having multiple families of superimposed quench curves.

Effects of Cocktail m and f Mismatches on Comparative 3H Measurements

The above described effects of m and f on the determination of QIP and detection efficiencies can have significant repercussions on the accuracy of comparative 3H measurements unless cocktails are very closely matched. Two situations may be considered: direct comparative measurements without QIP-adjusted quench corrections; and comparative measurements which are adjusted for slight variations in QIP. Inaccuracies due to the effects of cocktail m and f mismatches occur in both.

Without QIP-adjusted quench corrections

Consider the simplest kind of comparative measurement in which a prepared cocktail of an aqueous 3H standard (having a massic activity A_s) with a corrected (for background, deadtime losses, radioactive decay, etc.) counting rate R_s (for a gravimetrically-determined sample aliquant of mass g_s) is directly compared to some unknown 3H solution having a corrected counting rate R_x for a cocktail with a sample mass g_x . If the two cocktails are perfectly matched in terms of m and f (i.e. $m_x = m_s$,

and $f_x = f_s$), then one could simply derive the massic activity for the unknown solution from

$$A_x = R_x/g_x \epsilon_x = R_x/g_s \epsilon_s = (R_x/R_s)(g_s/g_x) A_s \quad (1)$$

on the assumption that the two detection efficiencies ϵ_x and ϵ_s are exactly equal.

Going one step further, we can consider what occurs if the two cocktails are slightly mismatched in terms of m and/or f . For a cocktail mass (volume) mismatch of $\delta m = (m_x - m_s)$ and aqueous mass fraction mismatch of $\delta f = (f_x - f_s)$, the efficiency for the unknown with respect to that for the standard will be

$$\epsilon_x = \epsilon_s + \delta m (\partial \epsilon_s / \partial m)_f + \delta f (\partial \epsilon_s / \partial f)_m \quad (2)$$

which will result in a "true" massic activity of

$$\ll A_x \gg = R_x/g_x [\epsilon_s + \delta m (\partial \epsilon_s / \partial m)_f + \delta f (\partial \epsilon_s / \partial f)_m] \quad (3)$$

The absolute relative error in A_x (expressed in %), which would result from the mismatches in m and f , is then

$$e(A_x) = 100 \cdot [(\epsilon_s + \delta m (\partial \epsilon_s / \partial m)_f + \delta f (\partial \epsilon_s / \partial f)_m) / \epsilon_s - 1] \quad (4)$$

The magnitude of $e(A_x)$ would obviously depend on the extent of the δm and δf mismatches and on how sensitive ϵ_s is to changes in m and f (i.e. on the partial derivatives $\partial \epsilon_s / \partial m|_f$ and $\partial \epsilon_s / \partial f|_m$).

The introduction of these errors in detection efficiency due to the cocktail m and f mismatches can also be understood by a very simple example that shows the construction of hypothetical quench curves (Fig. 1). Point A in the figure is given by the

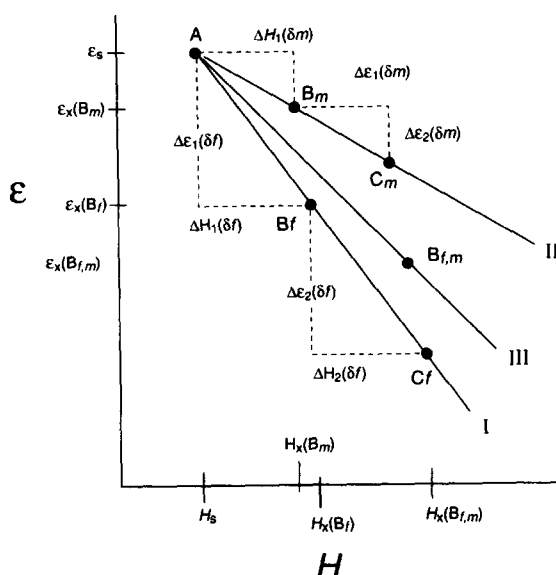


Fig. 1. Illustrative construction of hypothetical quench curves for changes in efficiency $\Delta \epsilon$ and quench indicating parameter ΔH due to quenching imposed by δm and/or δf cocktail mismatches (refer to text for notations). It demonstrates the errors [differences between ϵ_s (at point A) and ϵ_x (at points B_f , B_m , $B_{f,m}$)] in comparative LS measurements introduced by such δm and δf mismatches.

coordinates ϵ_s and H_s for a measured efficiency and QIP H for a standard cocktail. With a quench change due to a mismatch $\delta f = (f_x - f_s)$ between some unknown solution and the standard, the efficiency for the unknown (point B_f) is [from Eq. (2)] $\epsilon_{x1} = \epsilon_s + \Delta \epsilon_1(\delta f)$ where $\Delta \epsilon_1(\delta f) = (f_{x1} - f_s)(\partial \epsilon / \partial f)_m$. Analogously, the other coordinate of point B_f is $H_{x1} = H_s + \Delta H_1(\delta f)$ where $\Delta H_1(\delta f) = (f_{x1} - f_s)(\partial H / \partial f)_m$. Additional points (e.g. C_f) for sequential δf mismatches can be similarly derived: $\epsilon_{x2} = \epsilon_{x1} + \Delta \epsilon_2(\delta f)$ and $H_{x2} = H_{x1} + \Delta H_2(\delta f)$, etc. to complete construction of an f -varying quench curve (labelled I in Fig. 1). One can obtain a similar type of curve (II) due to a mismatch $\delta m = (m_x - m_s)$: with $\epsilon_{x1} = \epsilon_s + \Delta \epsilon_1(\delta m)$ where $\Delta \epsilon_1(\delta m) = (m_{x1} - m_s)(\partial \epsilon / \partial m)_f$ and $H_{x1} = H_s + \Delta H_1(\delta m)$ where $\Delta H_1(\delta m) = (m_{x1} - m_s)(\partial H / \partial m)_f$ for point B_m , and $\epsilon_{x2} = \epsilon_{x1} + (m_{x2} - m_{x1})(\partial \epsilon / \partial m)_f$ and $H_{x2} = H_{x1} + (m_{x2} - m_{x1})(\partial H / \partial m)_f$ for point C_m , etc. It is easy to envisage yet a third curve (III) due to simultaneous mismatches in both δf and δm : with $\epsilon_x = \epsilon_s + (f_x - f_s)(\partial \epsilon / \partial f)_m + (m_x - m_s)(\partial \epsilon / \partial m)_f$ and $H_x = H_s + (f_x - f_s)(\partial H / \partial f)_m + (m_x - m_s)(\partial H / \partial m)_f$ for the point labelled $B_{f,m}$ in Fig. 1. The three points identified as B_f , B_m and $B_{f,m}$ [with efficiencies $\epsilon_x(B_f)$, $\epsilon_x(B_m)$ and $\epsilon_x(B_{f,m})$] are thus those due to mismatches in m , f , and both m and f , respectively. The differences between these three ϵ_x values and ϵ_s reflect the possible errors in A_x . Hence, such a direct comparative measurement (without any QIP-adjusted quench correction) of any two cocktails (e.g. an unknown and a standard) which are presumed to be matched, but have even slight mismatches, will of necessity lead to some finite error in determining the efficiency.

To appreciate the magnitude of the possible error $e(A_x)$, we can consider some numbers for a very realistic case. Imagine an experiment where we take two drops of a pycnometer-dispensed standard aliquant having a gravimetrically-determined mass $g_s \approx 27$ mg, and three drops of an unknown solution with $g_x \approx 55$ mg. The mass per unit drop differs in this case because two different (but reasonably matched) pycnometers were used. We also chose to use differing numbers of drops for the aliquants to match more closely counting rates (and thereby "counting errors" for equal counting times). Let us further suppose that both the standard and unknown aliquants were added to vials containing a nominal 9 g of commercial scintillation fluid to form relatively simple, clean solution cocktails. Routinely, the mass (or volume) of the scintillant is not dispensed with a precision that is better than a few tenths of 1%, so we could easily have happened to obtain two dispensed masses of 8.977 and 9.023 g. In reality, the precision in the dispensed scintillant masses could be considerably poorer (several percent) since most laboratories rarely make efforts to control accurately the mass (or volume) of such dispensings. Nevertheless, we then have for our case: $m_s = (8.977 + 0.027)$ g; $m_x = (9.023 + 0.055)$ g;

$f_s = (28 \text{ mg})/(9.004 \text{ g}) = 0.0031$; and $f_x = (55 \text{ mg})/(9.078 \text{ g}) = 0.0059$, which results in mismatches of $\delta m = 0.074 \text{ g}$ and $\delta f = 0.0028$. For these conditions, the ^3H efficiency is around $\epsilon \approx 0.48$, and (from Collé, 1997) $\partial\epsilon/\partial m|_{f \approx 0.005} \approx -0.0018$ and $\partial\epsilon/\partial f|_{m \approx 9} \approx -0.72$. Substitution of these values into our error expression [Eq. (4)] yields $e(A_x) \approx 0.45\%$. The relative contributions to $e(A_x)$ are 0.03% for the δm mismatch and 0.42% for δf . Hence, we find that the effect of m and f mismatches between the cocktails for the standard and for the unknown solution for our conjectural (almost idealized) experiment leads to a bias error of nearly half of one percent.

We can consider a second example (for the gel cocktail region) where efforts are even made to match closely the cocktail compositions because of vast differences in the massic activities of the standard and unknown solution. For this case, let us assume that we have the same dispensed scintillant masses of 8.977 and 9.023 g. To the latter we add $g_x = 3.500 \text{ g}$ of an unknown ^3H solution, so that $m_x = 12.523 \text{ g}$ with $f_x = 0.2795$. The standard cocktail uses the same $g_s = 28 \text{ mg}$ as before, but we try to match f_s to f_x by the addition of blank H_2O (of mass g_w). For the matching we strive for $g_w = (g_x - g_s) = 3.472 \text{ g}$. However, since we perform the addition by dispensing from a graduated 5 mL syringe, we actually obtain $g_w = 3.377 \text{ g}$ (which again could be substantially worse in routine practice). The standard cocktail then has $m_s = 12.382 \text{ g}$ and $f_s = 0.2750$, which corresponds to mismatches of $\delta m = 0.141 \text{ g}$ and $\delta f = 0.0045$. With reasonable values of $\epsilon \approx 0.32$, $\partial\epsilon/\partial m|_{f \approx 0.28} \approx -0.0025$ and $\partial\epsilon/\partial f|_{m \approx 12} \approx -0.27$ (from Collé, 1997), the relative error in A_x from Eq. (4) is $e(A_x) \approx 0.49\%$. The contributions to $e(A_x)$ in this case are 0.11% for the δm mismatch and 0.38% for δf .

The above two examples were almost idealized in that all of the cocktails contained identical constituents (only H_2O in the scintillant), and in that the m and f mismatches can easily be manyfold greater in routine laboratory practice (unless great care is taken to control all components that are added to the cocktails, including the scintillation fluid). The magnitudes of the error $e(A_x)$ can be substantially greater if the cocktails are mismatched because of additions of other constituents like mineral acids and dissolved salts. The two examples also treated cases in the least sensitive regions of $\partial\epsilon/\partial m|_f$ dependence at the relatively flat, maximum efficiency portion of the ϵ versus m curves (refer to figures in Collé, 1997). The usually dominant $\delta f(\partial\epsilon/\partial f|_m)$ component is fairly sensitive in all regions, but generally less so with gel cocktails.

The error $e(A_x)$ can of course be diminished by randomization if one prepares and measures multiple cocktails at near constant m and f such that the $\delta m = (m_x - m_s)$ and $\delta f = (f_x - f_s)$ mismatches are both positively and negatively valued. However, the error will only decrease by a factor of \sqrt{n} for n

similarly prepared cocktails. Even if one used $n = 10$ such cocktails in which δm and δf were randomized, the approximate 0.5% error in the above two examples (for comparative measurements with one set of cocktails) would only reduce to about a few tenths of one percent. No such \sqrt{n} reduction in $e(A_x)$ will occur, of course, if the cocktails have a consistent mismatch, such as if all the standard cocktails have a slightly lower (or higher) aqueous fraction than all the unknown solution cocktails. This is often a usual occurrence because of the nature of cocktail preparation procedures.

The relative error expression of Eq. (4) can also be used to assess realistically the uncertainties due to possible δm and δf mismatches even when the cocktails are presumed to be matched (and with randomized possible mismatches). One merely needs to make reasonable estimates of the magnitudes of the possible δm and δf mismatches (e.g. by knowing the bounds of dispensing precisions, etc.) and have knowledge of the $\partial\epsilon_s/\partial m|_f$ and $\partial\epsilon_s/\partial f|_m$ systematics for the system of their cocktails and spectrometer.

With QIP-adjusted quench corrections

Substantial improvements in obtaining a correct efficiency for comparative measurements will result if QIP-adjusted quench corrections are made. However, even in these cases and depending on the systematics of the employed LS system, the efficiency error as given by $e(A_x)$ may still not necessarily disappear. This too can be demonstrated with a very simple hypothetical case that considers just a cocktail m mismatch.

Imagine, again, a ^3H standard cocktail having a measured efficiency ϵ_s and a QIP of H_s (point A in Fig. 2) which is one point on a previously established quench curve I. The curve is intended to make quench corrections for composition differences f between the standard and some unknown solution by considering the differences in the two measured QIPs (H_s and H_x) for the standard and unknown. The curve (I) is just reflective of the changes $\partial\epsilon_s/\partial f|_m$ due to f differences (at constant m), and may be considered to have some functional form $\epsilon_s = Q[H_s]$ for a function Q . Now consider that the unknown solution cocktail is presumed to be matched to the standard, but in reality actually has a slight m mismatch of $\delta m = (m_x - m_s)$. The experimentally observed QIP for the unknown would be

$$H_{x(\delta f, \delta m)} = H_s + \delta f(\partial H/\partial f|_m) + \delta m(\partial H/\partial m|_f). \quad (5)$$

After all, if the standard and unknown were indeed perfectly matched for all affecting parameters, then H_x would have to be exactly equal to H_s (within the QIP measurement precisions). Given the observed H_x , the QIP-adjusted efficiency $\epsilon_{x(\delta f)}$ for the unknown (point B in Fig. 2) is then incorrectly inferred to be $\epsilon_{x(\delta f)} = Q[H_{x(\delta f, \delta m)}]$, or algebraically $\epsilon_{x(\delta f)} = (H_{x(\delta f, \delta m)} - H_s)(\partial\epsilon_s/\partial f|_m)$, since the change in QIP [and $\epsilon_{x(\delta f)}$] was presumed to be only due to a slight change in f (at

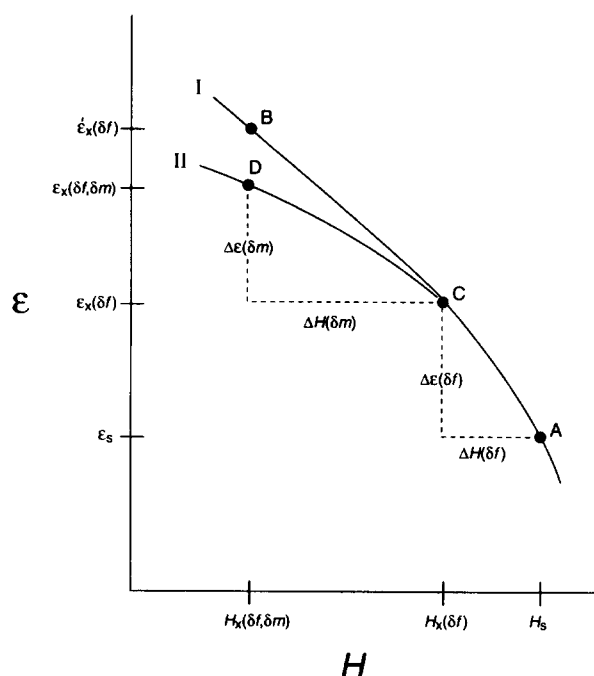


Fig. 2. Illustration of a comparative LS measurement with a QIP-adjusted quench correction which demonstrates the error $[\epsilon_{x(\delta f)} - \epsilon_{x(\delta f, \delta m)}]$ introduced by a δm cocktail mismatch on for an f -varying quench curve (I) given by $\epsilon = Q_f[H]$. The δm mismatch results in a superimposed quench curve (II) given by $\epsilon = Q_m[H]$. Refer to text for explanatory detail and notation.

constant m). If the cocktails were perfectly matched for m , then the experimentally observed QIP for the unknown would have been $H_{x(\delta f)} = H_s + \delta f(\partial H / \partial f|_m)$, for just the change in composition parameter f (which also lies on curve I at point C in Fig. 2). Alternatively, on considering the additional change in QIP and efficiency due to the δm mismatch, we recover the observed QIP: $H_{x(\delta f)} + \delta f(\partial H / \partial f|_m) = H_{x(\delta f, \delta m)}$; and have $\epsilon_{x(\delta f, \delta m)} = \epsilon_{x(\delta f)} + [H_{x(\delta f, \delta m)} - H_{x(\delta f)}](\partial \epsilon_{II} / \partial H) = \epsilon_s + \delta f(\partial \epsilon_I / \partial f|_m) + \delta m(\partial \epsilon_{II} / \partial m|_f)$. Point D of Fig. 2 is given by these $H_{x(\delta f, \delta m)}$ and $\epsilon_{x(\delta f, \delta m)}$ coordinates. The segment defined by points C and D can be considered to be a secondary quench curve (labelled II) obtained with varying m (at constant f), and having a functional form $Q_m[H]$. The existence and nature of such multiple families of superimposed quench curves was addressed at length by Collé (1997). To aid in understanding the above example (and the following one), Fig. 2 also denotes the $\Delta H(\delta f)$ and $\Delta H(\delta m)$ changes in H due to the δf and δm impositions, and the $\Delta \epsilon(\delta f)$ and $\Delta \epsilon(\delta m)$ changes due to δf and δm . The difference between the incorrectly-inferred efficiency $\epsilon_{x(\delta f)}$ (at point B) and $\epsilon_{x(\delta f, \delta m)}$ (at point D) is the bias error in efficiency as introduced by the mismatch in m .

The magnitude of these efficiency errors [or in the previously defined $e(A_i)$], even with QIP-adjusted quench corrections, may be appreciated by a reconsideration of our second example given above

for the gel-cocktail comparative measurement. For simplicity and convenience of discussion, let us look again at just the effect of an m mismatch, under the assumption that our applied quench corrections are solely being made because of f_x to f_s differences. This is a most favorable and highly idealized situation. Yet, it will adequately demonstrate that the cocktail mismatch effect still remains. One can perform the necessary arithmetic on the previously given, gel-cocktail example to confirm that the bias error in A_x (or ϵ_x) under these conditions will still be about 0.1% (which is a significant error or uncertainty component for most radionuclidic metrology laboratories). Figure 3 exhibits the quench correction (and arithmetic exercise) for this case. The numerical values for this example are similarly adopted from Collé (1997). With $\epsilon_s = 0.32$ and $H_s = 130$ as starting conditions (point A), the "true" known ϵ_x and H_x are, from that given previously by Eqns (2) and (5), $\epsilon_x = 0.3184$ and $H_x = 130.67$ (point D). The incorrectly-inferred efficiency $\epsilon_{x(\delta f)}$, obtained from assuming that all of the quench change is due to δf , is $\epsilon_{x(\delta f)} = 0.3187$ at $H = 130.67$ (point B). Point C of Fig. 3 denotes the division between the Q_f and Q_m (defined previously) quench curves, such that the change in efficiencies between points A and C and between C and D, is $\Delta \epsilon(\delta f)$ and $\Delta \epsilon(\delta m)$, respectively [with corresponding QIP changes of $\Delta H(\delta f)$ and $\Delta H(\delta m)$]. Notational comparisons with Fig. 2 may be useful. The 0.1% difference between $\epsilon_{x(\delta f)}$ (point B) and ϵ_x (point D) is the efficiency error due to the δm mismatch between cocktails.

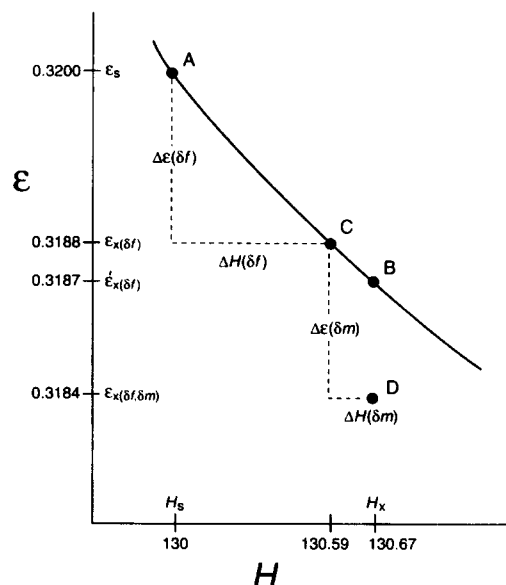


Fig. 3. Illustrative numerical example of a comparative ^3H measurement for gel cocktails ($f \approx 0.28$) with a QIP-adjusted quench correction. It demonstrates the error $[\epsilon_{x(\delta f)} - \epsilon_{x(\delta f, \delta m)}]$ due to a $\delta m = 0.141$ g cocktail mismatch (for $m \approx 12.5$ g) on an f -varying ($\partial \epsilon / \partial f|_m \approx -0.27$ and $\partial H / \partial f|_m \approx 134$) quench curve I. Refer to text for additional details.

With QIP-adjusted quench corrections, the $e(A_x)$ error (or in ϵ_x) arises because of differences in $\partial\epsilon/\partial H$ for the Q_f and Q_m quench curves. If changes in ϵ exactly tracked with changes in H irrespective of the imposed agent that caused the quenching (i.e. if $\partial\epsilon/\partial H$ was invariant and identical for both δf and δm changes), then the error would not occur.

The foregoing example is indeed very idealized in being very conservatively based. Firstly, because it does not involve extreme situations, but rather considers a realistic case involving a fairly careful cocktail preparation procedure. Secondly, it addresses only the two (m and f) considered here. Usually the mismatching error is not due to a relatively small effect like a δm mismatch, but rather is due to differences in the cocktail constituents (acids, salts, etc.) as well as their respective concentrations. Even the most carefully controlled cocktail preparations invariably exhibit QIP and efficiency differences because of these constituent mismatches.

The mismatching error for this quench correction case, as for the preceding examples, can be diminished through randomization with multiple cocktails, but only if there is not a systematic, consistent cocktail mismatch between standards and unknown solutions (which often occurs in practice).

The error analysis procedures used here can also, as before, be invoked to assess realistically the uncertainty due to possible cocktail mismatching when quench corrections are made. Even with very carefully controlled cocktail preparations (and with $4 \leq n \leq 10$ multiple replicate cocktails), the magnitudes of these uncertainties are often of the order of $\pm 0.05\%$, and can be substantially greater depending on the cause and degree of mismatching.

Effects of Cocktail m and f Mismatches on ^3H -standard Efficiency Tracing for Other Radionuclides

One of the more commonly invoked methodologies for ^3H -standard efficiency tracing is the CIEMAT/NIST protocol (Grau Malonda and Garcia-Toraño, 1982), originated by the Centro de Investigaciones Energeticas, Medioambientales y Tecnologicas (CIEMAT) and the National Institute of Standards and Technology (NIST) laboratories, which utilizes various updated and revised versions of the CIEMAT-developed EFFY code (Garcia-Toraño and Grau Malonda, 1985; Grau Malonda *et al.*, 1985; Garcia-Toraño, 1993) to determine the detection efficiencies for cocktails of the traced radionuclide under known varying quench conditions by following the experimentally-determined efficiencies for closely-matched cocktails of a ^3H standard. The methodology has been described in numerous publications by Coursey and coworkers (Coursey *et al.*, 1985, 1986, 1989, 1991). Details of its practical application, as recently invoked and considered here, are given by

Zimmerman and Collé (1997); Collé and Zimmerman (1996a,b).

In the CIEMAT/NIST method, experimentally-determined ^3H efficiencies ϵ_x are related to EFFY-code generated "figures of merit" M : $\epsilon_x = F_1[M]$. The parameter M is used to characterize the quenching and overall detection efficiency of the LS counting system (cocktails plus spectrometer). These same M values are then related to similarly calculated efficiencies ϵ_x for the traced radionuclide (either with or without QIP-adjusted quench corrections): $\epsilon_x = F_4[M]$. This is the method's procedure for the efficiency tracing at its simplest conceptual level. In effect, the two F_1 and F_4 functions operate like a kind of universal quench correction curve that accounts for differences in the detected portions of the β spectra for the ^3H standard and traced radionuclide. Several sequential examples can be treated to appreciate the effect of cocktail mismatches on this tracing.

First, we can consider an idealized situation where a series of ^3H -standard cocktails (having varying quenching) are used to trace the efficiencies ϵ_x for a matching set of cocktails for some other β -emitting radionuclide under the assumption that the two sets of cocktails are perfectly matched in terms of size and composition. Let us suppose that both sets have constant H_2O fraction f_1 (i.e. $f_{s1} = f_{x1}$). In practice, one generally prepares a set of near identical ^3H cocktails and another near identical set of traced radionuclide cocktails, and varies the quenching within both sets by the controlled introduction of some imposed chemical quenching agent like CCl_4 or CH_3NO_2 . In this first cut, we will dispense with any adjustments for small QIP differences since we are assuming that the cocktails are matched and thereby have identical quenching. Figure 4 shows the typical function relationships F_1 and F_4 between ϵ and M for ^3H and some higher-energy β -emitter (like ^{60}Ni) as obtained from the EFFY code. The solid points on the ^3H curve represent the experimentally-determined ^3H efficiencies $\epsilon_s(f_{s1})$ (for composition f_1) and their corresponding M values. The traced efficiencies $\epsilon_x(f_{x1})$ (also for composition f_1) are then obtained directly from application of these M values to the $\epsilon_x = F_4[M]$ relation. For example, the experimentally-determined ^3H efficiency at point A is used to establish the value M_1 which in turn establishes efficiency ϵ_x at point B.

Now, consider what occurs if there is a $\delta f = (f_1 - f_2)$ mismatch between the standard and traced radionuclide cocktails such that the standards have a composition f_2 which is greater than f_1 . All of the experimentally-determined ^3H efficiencies will shift by $\epsilon_s(f_{s2}) = \epsilon_s(f_{s1}) + \delta f(\partial\epsilon_s/\partial f)$ on the $M = F_1[\epsilon_x]$ curve because of greater quenching by the imposed δf . These shifts are labelled $\Delta\epsilon(\delta f)$ in Fig. 4. Our original $\epsilon_s(f_{s1})$ value at point A, for example, will decrease by $\Delta\epsilon(\delta f)$ to $\epsilon_s(f_{s2})$ with figure of merit M_2 at point C. The incorrectly-inferred detection efficiency for the

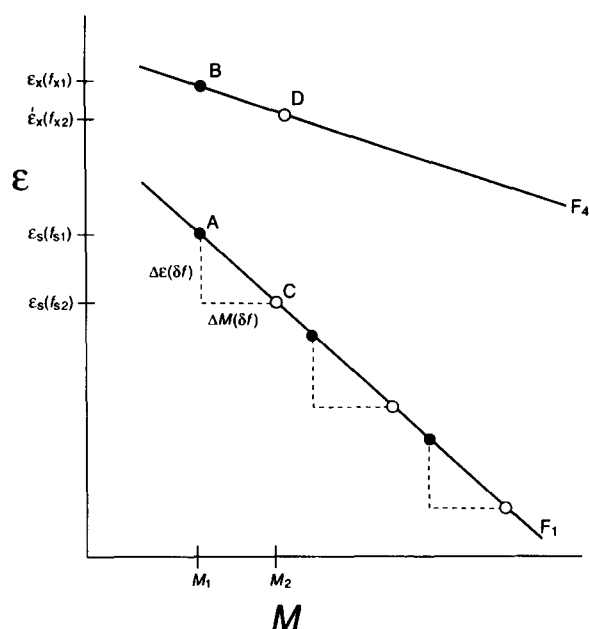


Fig. 4. Illustration of the error $[\epsilon_x(f_{s2}) - \epsilon_x(f_{s1})]$ in the ^3H -standard efficiency tracing of another β -emitting radionuclide due to a δf cocktail mismatch (without a QIP-adjusted quench correction). F_1 and F_4 are the functions defining the relation between the figure of merit M and the efficiencies for ^3H and the traced radionuclide: $M = F_1[\epsilon_s]$ and $\epsilon_x = F_4[M]$. Refer to text.

traced radionuclide would be $\epsilon_x(f_{s2}) = F_4[M_2]$ at point D. The efficiency difference between $\epsilon_x(f_{s1})$ (at point B) and $\epsilon_x(f_{s2})$ (point D) is the error due to the δf mismatch. The magnitude of the error in this case depends on the degree of mismatch δf , on $\partial \epsilon_s / \partial f$, and on the relative sensitivities of the ϵ versus M dependencies for F_1 and F_4 . As an example, a 1% change in ϵ_s due to some δf mismatch would result in about a 0.6% error in ϵ_x for ^{63}Ni under most normal $\partial \epsilon_s / \partial f$ and $\partial \epsilon_x / \partial f$ quenching ranges. For tracing of higher-energy β -emitting nuclides (e.g. ^{36}Cl , ^{89}Sr , etc.), the effect of such mismatches (and corresponding ϵ_s changes) decreases, of necessity, because of much smaller changes in $\epsilon_x = F_4[M]$ with changes in ϵ_s .

With the above understandings, we can examine, as a second example, what the possible mismatch effect is when QIP adjustments are made. Here, the adjustments are made by first relating the experimentally-observed QIP values for the set of standard cocktails to M values (as shown in Fig. 5) through the combined use of the relations between H_s and ϵ_s and M ($\epsilon_s = F_2[H_s]$ and the $M = F_1[\epsilon_s]$ function) to obtain a new relation $M = F_3[H_s]$. For example: point A in Fig. 5(a) has an efficiency $\epsilon_s(A)$ and QIP of $H_s(A)$; $\epsilon_s(A)$ defines $M(A)$ from $M = F_1[\epsilon_s]$ (Fig. 4); thus establishing the correspondence between $M(A)$ and $H_s(A)$ in Fig. 5(b). Other M to H correspondences, such as for points B, C, etc. in Fig. 5, would be obtained similarly. To do the QIP adjustment, one assumes that the $M = F_3[H_s]$ function is valid for any other traced radionuclide

irrespective of the differences in the underlying β spectra and in the sources of quenching. This is a critical assumption that we will subsequently examine. With the assumption, however, attainment of the QIP-adjusted efficiency ϵ_x for a cocktail of the traced radionuclide is then straightforward. The observed QIP H_x (which may differ slightly from the H_s for the matched standard cocktail because of slight differences in δf quenching) is used to obtain an adjusted $M_x = F_3[H_x]$, from which one in turn obtains ϵ_x from the EFFY-code generated $\epsilon_x = F_4[M_x]$. Now, returning to Fig. 4, we can consider the mismatch $\delta f = (f_{s2} - f_{s1})$ with observed QIP values of H_{s2} and H_{s1} . With the previous perfect matching for $f_{s1} = f_{s1}$, we can assume $H_{s1} = H_{x1}$, and thereby can establish H_{x1} with respect to H_{s2} : $H_{x1} = H_{s2} - \delta f(\partial H / \partial f)$ [from the given $H_{s2} = H_{s1} + \delta f(\partial H / \partial f)$]; and with $M_1 = F_3[H_{x1}] = F_3[H_{s2} - \delta f(\partial H / \partial f)]$ and $\epsilon_{x1} = F_4[M_1]$,

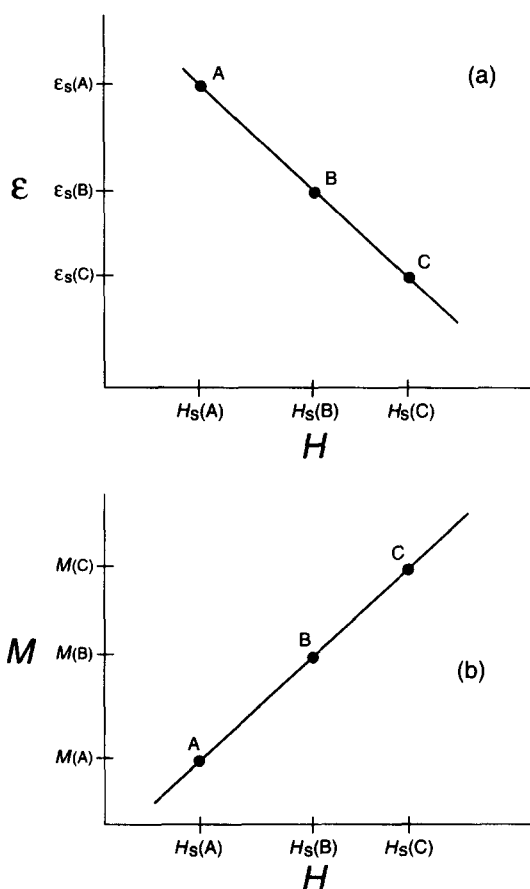


Fig. 5. Illustration of the ^3H -standard efficiency tracing of another β -emitting radionuclide with a QIP-adjusted quench correction for a cocktail mismatch δf . The upper trace (a) relates the ^3H efficiency ϵ_s to the quench indicating parameter H ($\epsilon_s = F_2[H_s]$); while the lower trace (b) relates the figure of merit M to H ($M = F_3[H_s]$) through the relation $M = F_1[\epsilon_s]$. The example (refer to text for details) demonstrates the recovery of a correct quench-corrected efficiency ϵ_x for the traced radionuclide (as given in Fig. 4) if δf is the only unmatched source of quenching in the ^3H and traced radionuclide cocktails.

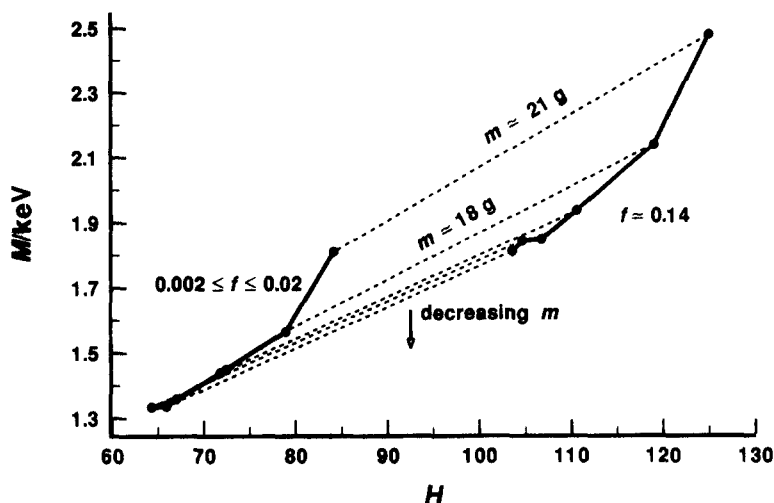


Fig. 6. Experimental evaluation of the function $M = F_3[H]$ for two sets of ^3H solution cocktails with near constant f ($f \leq 0.02$ and $f \approx 0.14$) and varying m . Experimentally observed values of the quench indicating parameter H for each cocktail are plotted against values of the figure of merit M that were obtained from EFFY-code calculations for each cocktail's experimentally determined ^3H efficiency ϵ_i : $M = F_3[H]$. The solid curves are for $F_3(f \leq 0.02)$ and $F_3(f \approx 0.14)$ functions with varying m ($3 \leq m \leq 21$ g), whereas the broken curves are for various $F_3(m)$ functions at near constant m with variable f . The results clearly demonstrate that the $M = F_3[H]$ function is dependent on the causal agent of quenching.

we find that the QIP adjustment completely recovers the correct efficiency (point B in Fig. 4). This finding, however, depends on the assumption as to the independence of the function F_3 with any source of quenching. It requires that any change ΔH in QIP, such as those due to $\Delta H(\delta m)$ and $\Delta H(\delta f)$ (as given by Collé, 1997) will manifest in comparable changes in M , i.e. when $\Delta H(\delta m) = \Delta H(\delta f)$, the change in M must be $\Delta M = F_3[\Delta H(\delta m)] = F_3[\Delta H(\delta f)]$. Changes in M are also given by $\Delta M = F_3[\Delta \epsilon_i]$, so we have $\Delta M = F_3[\Delta \epsilon_i] = F_3[\Delta H(\delta m)] = F_3[\Delta H(\delta f)]$. However, it has been more than adequately demonstrated by Collé (1997) (in examining the ϵ versus H tracking, and quench curves) that efficiency changes do not perfectly scale with changes in H for different cocktail sizes and composition (i.e. for different causal agents of quenching). Therefore, the assumption (and entire basis of the efficiency tracing) is untenable unless the cocktails are very closely matched. They must be matched closely enough to guarantee the sufficiency of the independence of the $M = F_3[H]$ relation with all possible imposed sources of quenching in the two sets of cocktails. The parameter M in the CIEMAT/NIST model can adequately account for differences in β spectra, detection thresholds, and for quench differences when the quenching changes result from the same causal factor. It cannot fully adjust for quench changes caused by different agents (e.g. those due to the simultaneous introduction of different cocktail sizes, differences in cocktail composition concentrations, or different cocktail constituent components).

The failure of the assumption as to the independence of $M = F_3[H]$ under certain quench-varying conditions is easy enough to demonstrate with

available data. Figure 6 shows the systematics of M values (as obtained by Collé (1997) from the experimentally-determined ^3H efficiencies ϵ_i for the two sets of solution cocktails) versus the corresponding experimental H_i values. The value of M for each ϵ_i was obtained from the $M = F_3[\epsilon_i]$ relation as generated by EFFY2 code calculations and as given in functional form by Grau Malonda *et al.* (1985). The findings shown in Fig. 6 are fully consistent with comparable calculations using the more recent, revised EFFY4 code (Garcia-Torano, 1993), although the actual magnitudes of M for a given ϵ_i differ between codes. The two solid curves in Fig. 6 are the F_3 functions for near constant f ; $F_3(f < 0.02)$ and $F_3(f \approx 0.14)$ with quench variations induced by changes in m . The broken curves approximate the F_3 functions for constant m with variable- f quench changes. Evidently, with serious m and f mismatches in cocktails for the ^3H standard and traced radionuclide, one would be very hard pressed to establish exactly which F_3 function (in Fig. 6) one should use.

As a final practical example, we can examine the efficiency tracing of a low-energy β emitter like ^{63}Ni against ^3H in which the two solutions (^{63}Ni and ^3H) have considerably different constituent components. This is a typical occurrence. A set of nearly identical ^3H -standard cocktails is prepared using about 50 mg of tritiated water in a nominal 9 g of scintillant. The cocktails also contain controlled additions of varying quantities Δq of an imposed quencher solution (say 15–150 mg of a 10% solution of CH_3NO_2 in ethanol) to vary the quenching and thereby develop a suitable quench curve for the tracing. This quench curve is designated as curve I in Fig. 7(a). Point A is for the

least-quenched cocktail and is given by $\epsilon_{s(w)}$ and $H_{s(w)}$. Since all the cocktails in the set were nearly identical except for the imposed CH_3NO_2 quencher solution, all subsequent points on the quench curve are given by $\epsilon_{s(w)} + \Delta\epsilon_{s(w)}(\delta q)$ and $H_{s(w)} + \Delta H_{s(w)}(\delta q)$. For the efficiency tracing, another set of nearly identical ^{63}Ni cocktails is prepared by using 50 mg aliquants in 9 g of scintillant with the same controlled additions Δq of CH_3NO_2 quencher solution. One might initially suppose that these two sets of cocktails, as prepared, constitute reasonably closely-matched cocktails. They do not. The ^{63}Ni solution probably consists of something like 1 mol/L HCl and a carrier concentration of $80 \mu\text{g Ni}^{+3}$ per gram of solution. These cocktails exhibit quench curve II in Fig. 7(a) where point B is defined by $\epsilon_{x(a)}$ and $H_{x(a)}$, and where all subsequent points are given by $\epsilon_{x(a)} + \Delta\epsilon_{x(a)}(\delta q)$ and $H_{x(a)} + \Delta H_{x(a)}(\delta q)$. Now, imagine what would result if the ^3H and ^{63}Ni cocktail compositions were exactly reversed (i.e. the ^3H cocktails contained 50 mg aliquants of 1 mol/L HCl and $4 \mu\text{g Ni}^{+3}$ and the ^{63}Ni cocktails contained only 50 mg H_2O). Quench curve I for ^3H would be displaced to curve III due to the additional quenching from the imposed HCl and Ni^{+3} . Point A on curve I, for example, would shift to point C on curve III with coordinates $\epsilon_{s(a)}$ and $H_{s(a)}$. Somewhat comparably, quench curve II for ^{63}Ni would be displaced to curve IV due to the lessened quenching in the absence of the HCl and Ni^{+3} . In this case, for example, point B on curve II [with $\epsilon_{x(a)}$ and $H_{x(a)}$] would shift to point D on curve IV [with $\epsilon_{x(w)}$ and $H_{s(w)}$]. Translating the corresponding $\Delta\epsilon_s$ and $\Delta\epsilon_x$ efficiency changes into ΔM changes results in the two

distinct $M = F_3[H]$ functions given in Fig. 7(b): one $F_{3(w)}[H]$ for the water compositions [from curves I and IV in Fig. 7(a)], and one $F_{3(a)}[H]$ for the acid compositions (from curves II and IV). If the aqueous ^3H cocktails operate with $F_{3(w)}$ (from quench curve I) and ^{63}Ni cocktails operate with $F_{3(a)}$ (from curve II), then the efficiency tracing will of necessity result in bias errors in the traced ϵ_x values. It is, therefore, irrefutable that the efficiency tracing protocol is valid only if both sets of cocktails operate with either the $F_{3(w)}$ or $F_{3(a)}$ function. There is a relatively simple way to accomplish the necessary matching. For this example, one can add 50 mg of a blank carrier solution containing 1 mol/L HCl and $4 \mu\text{g Ni}^{+3}$ to the ^3H cocktails, and add 50 mg of blank H_2O to the ^{63}Ni cocktails (the latter addition for matching total cocktail size and water fraction to those in the ^3H cocktails). In this way, both sets of cocktails will operate from the same F_3 function. Regrettably, based on this author's observations, this kind of obvious cocktail matching seems to be infrequently performed in routine practice.

These constituent-varying cocktail mismatches do introduce systematic errors in the efficiency tracing even when QIP-adjusted quench corrections are made. Based on work performed in this laboratory for the efficiency tracing of ^{63}Ni with ^3H for a ^{63}Ni standardization (Collé and Zimmerman, 1996b), the above example would introduce a relative bias error of at least 0.2% in the traced massic activity of ^{63}Ni . The magnitude of this relative error (had it been present in the ^{63}Ni standardization) would have been nearly one half of the combined standard uncertainty

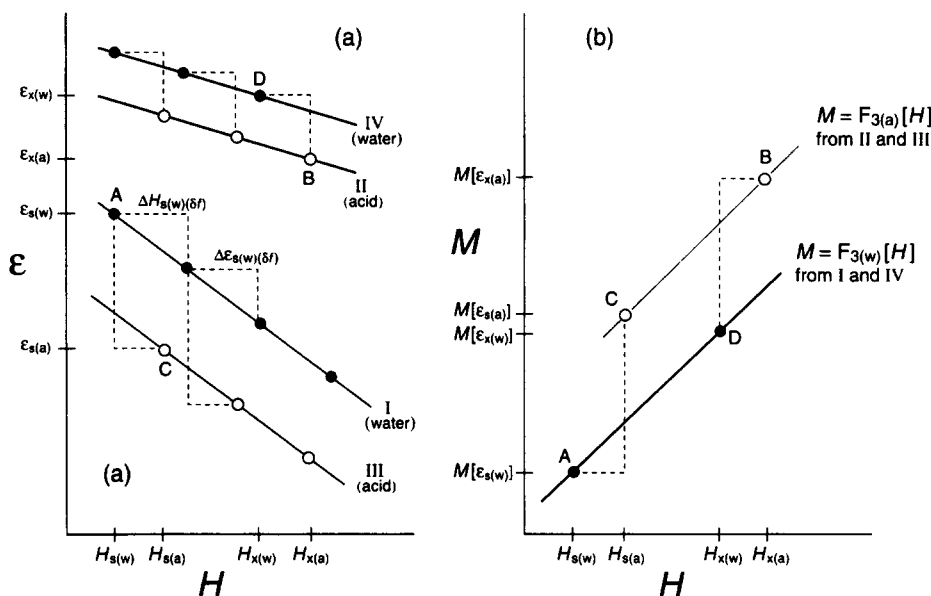


Fig. 7. Illustration of the ^3H -standard efficiency tracing of ^{63}Ni for sets of cocktails containing differing constituents (water and acid compositions). The efficiency changes $\Delta\epsilon$ and QIP changes ΔH along any of the four quench curves [I–IV in the upper trace (a)] are the result of additions of varying quantities Δq of an imposed chemical quencher. The corresponding $M = F_3[H]$ functions for the two compositions are given in the lower trace (b). A bias error in ϵ_x results unless both the ^3H and ^{63}Ni cocktails operate with the same F_3 function. Refer to text for discussion.

(0.46%) for the standardization (Collé and Zimmerman, 1996b). The error was largely eliminated through the use of carefully and rigorously matched cocktails.

Admittedly, the mismatching effects discussed here are much smaller (almost negligible) for tracing higher-energy β emitters (like ^{36}Cl , ^{10}Be , ^{89}Sr , etc.) and when the constituent composition differences are not too severe. Nevertheless, it will always result in the needless introduction of an error that can be simply obviated by rigorous matching of cocktails in all regards (constituents, concentrations and sizes).

Even in the absence of such known bias errors, estimates of the uncertainty in the efficiency tracing due to possible cocktail mismatches can be obtained using the same general principles outlined previously for the comparative measurements. It is more difficult in this case in that the uncertainty propagates through four functional dependencies (F_1 , F_2 , F_3 and F_4), but is still doable. With estimates as to the possible magnitude of the cocktail mismatches, and knowledge of the $\partial\epsilon_s/\partial H_s$ and $\partial\epsilon_x/\partial H_x$ systematics for the LS system (i.e. the combination of cocktails and spectrometer), one can perform a sensitivity analysis for the effect of the mismatch through the four functions to arrive at the uncertainty in the traced ϵ_x .

Concluding Notes

The above detailed analyses (and accompanying examples) of the changes in ^3H efficiency ϵ and quench indicating parameter H as a function of the total cocktail mass m and H_2O mass fraction f demonstrate the significant repercussions on the inherent accuracy of assays performed by LS spectrometry unless cocktails are very closely matched. Cocktail mismatching errors can occur not only in comparative ^3H measurements using developed quench curves, but also in the more exacting ^3H -standard efficiency tracing methods. Use of the "figure of merit" M in the CIEMAT/NIST tracing model to relate a ^3H efficiency to that for some other β -emitting nuclide, for example, is untenable unless the two sets of cocktails for the ^3H and traced radionuclide are closely matched for composition constituents.

The errors arise from the inability to perform adequate quench monitoring compensations when the quenching results from multiple causal factors, such as with simultaneously varying cocktail constituents, compositions and sizes. The cocktail mismatch effects (and attendant errors) will be most prevalent for mismatches resulting from both varying cocktail constituents and concentrations, and for easily quenched low-energy β -emitting nuclides. The

magnitudes of the bias errors can be in the range of significance for high-precision radionuclidic metrology and standardization activities. The errors are less significant (often negligible) for slight cocktail mismatches and for less quench-dependent high-energy β emitters.

Even with reasonably matched cocktails, the uncertainties associated with possible cocktail mismatches can be assessed by careful evaluations of the quenching systematics of the LS system (i.e. the combination of cocktails and spectrometer).

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