



Cocktail Volume Effects in $4\pi\beta$ Liquid Scintillation Spectrometry with ^3H -standard Efficiency Tracing for Low-energy β -emitting Radionuclides

B. E. ZIMMERMAN and R. COLLÉ

Physics Laboratory, National Institute of Standards and Technology,* Gaithersburg, MD 20899, U.S.A.

(Received 7 March 1996; in revised form 18 June 1996)

The effect of total liquid scintillation (LS) cocktail volume (or mass) in the $4\pi\beta$ LS spectrometry of β -emitting radionuclides has been investigated. The magnitude of such possible volume effects on the apparent activity of low-energy β -emitting radionuclides, as determined by the CIEMAT/NIST ^3H -standard efficiency tracing method, as well as any systematic trends in the relative detection efficiencies of low-energy β -emitters were studied. The radionuclides chosen for the study, ^{63}Ni and ^{36}Cl , were traced against ^3H . Detection efficiency losses, as a function of total LS cocktail volume, were found to be energy-dependent. Because of the low $E_{\beta,\text{max}}$ for the decay of ^3H and ^{63}Ni , systematic losses in the efficiency with increasing cocktail mass, as well as at extremely low (<5 g) masses were observed. The determination of quench-indicating parameters, even for cocktails of uniform composition, were also found to be volume-dependent. Despite a relatively large (17%) variation in the ^3H counting efficiency over the volume range 1-20 mL in 22 mL vials and a corresponding 7% variation in the ^{63}Ni counting efficiency, the CIEMAT/NIST method was able to trace the observed ^{63}Ni activity to about 0.1%. No volume effect on the observed relative efficiency of ^{36}Cl was found. The best condition for repeatability in the determination of the massic activity of a single sample was found to be when the volume is 8-12 mL in a 22 mL vial. The effect of total LS cocktail volume on the efficiency-traced massic activities was found to have no clear, consistent trend and proved difficult to quantify. Nonetheless, two approaches to estimating the magnitude of the effect are presented and indicate that it is extremely small ($<0.1\%$) and was within the statistical variation of the measurements. Published by Elsevier Science Ltd. All rights reserved

Introduction

Liquid scintillation spectrometry and sample volume effects

In performing radionuclidic assays, the most important factor is the determination of detection efficiency that is necessary to relate the observed number of counts to the actual number of nuclear disintegrations. For such measurements of pure β -emitting radionuclides, liquid scintillation (LS)

spectrometry has become one of the most popular techniques, especially for low-activity samples, due to the high (4π) geometrical efficiency obtained by combining the *sample* of radionuclide with a *scintillator*,† and possibly an introduced quenching agent, to form an LS *cocktail*. This cocktail acts as the detector medium. However, effects due to properties of the sample itself can lead to diminished efficiency. These effects are collectively known as *quenching*.

Some degree of quenching is present in every LS sample. *Color quenching* occurs when the photons emitted by the fluor are absorbed in the solution before reaching the photomultiplier tube (PMT) or are shifted to energies insufficient to produce photoelectrons. *Chemical quenching* occurs when the β -particle energy that is transferred to the solution through collisions with solvent molecules in the sample is diminished before reaching the fluor. This is most often the case when either an excited solvent

*The National Institute of Standards and Technology is an agency of the Technology Administration, U.S. Department of Commerce.

†In the context of this paper, the term *scintillator* is taken to mean the commercially available *scintillation* fluids which contain a solvent and a fluor, as well as surfactants, chemical waveshifters and emulsifiers which are added to increase efficiency, acid loading capability, etc.

molecule or the β -particle itself transfers energy to a 'nonparticipating' molecule (such as water) by collision. Since not all of the energy of the β -particle is transferred to the fluor molecules, counting efficiency is lowered since fewer photoelectrons than would otherwise be expected will result from that event.

One way to minimize chemical quenching is to ensure that more fluor molecules are available to transfer the energy from the excited solvent molecules before being intercepted by nonparticipating sample molecules. This implies that a much greater proportion of fluor molecules in the cocktail relative to 'inert' molecules (such as water, additives to the fluor such as surfactants and secondary solutes, or the radionuclide itself) is more desirable. This would, of course, involve custom-mixed fluors and would preclude the routine use of commercial fluors—an extremely inefficient approach.

Furthermore, one cannot simply prepare a cocktail with an arbitrarily high fluor concentration. It has been shown (Dammers-DeKlerk, 1958) that the fluorescence yields of some scintillator solutions quickly decrease, at what those authors considered relatively high (10^{-2} – 10^{-1} mol L $^{-1}$) concentrations. The mechanism for this appears to be an interaction between an excited fluor molecule and one that is not excited, forming an excited dimer complex that de-excites either by a radiationless transition or by fluorescence at a different wavelength for which the PMT is insensitive.

A 'brute force' approach to minimize quenching is to use the largest possible volume of cocktail, and to thereby maximize the number of fluor molecules. However, it has been noted (Horrocks, 1974) that the total amount of sample plays an important role in that the response of the PMT is not constant across its surface. While it may seem that a maximum amount of solution might be the best condition under which to count (to cover as much of the surface area of the PMT as possible), this is not what is usually recommended by 'authoritative sources' (Kessler, 1989; Kobayashi and Maudsley, 1974). Instead, the middle of the PMT is found to be the most sensitive, and the optimum sample volume is one which places the meniscus near the middle of the face of the PMT. For 'standard' vials (nominally 22 mL), this translates into 8–12 mL of sample.

Depending upon the nature of the radionuclide being studied (and under what conditions it is being studied), it is not always possible to prepare LS samples with the canonical 8–12 mL volume. This is especially true of environmental and other low-activity samples (Collé and Thomas, 1993; Moghissi, 1970). In order to achieve reasonable precision in counting some of these types of samples, it is often necessary to use very large sample volumes.

Surprisingly, little has appeared in the literature concerning volume effects on LS efficiencies for radionuclides. Differences in counting efficiencies

between 2 and 12 mL samples in 12 mL vials and 4 and 13 mL samples in 22 mL vials of 10–11% and 5–6%, respectively, were observed for ^3H by Kobayashi and Maudsley (1974). This observation might be due to the sample level being sufficiently low in the 2 and 4 mL samples so as to be below the sensitive region of the PMT.

The effect of volume on samples of ^{14}C was investigated by Knoche *et al.* (1979). In the first part of that study, a series of cocktails ranging in volume from 1–23 mL was counted and the efficiency determined. It was observed that the efficiency rose from ~85.5 to 88.3% for the 1–5 mL samples, remained at 88.3% for cocktail volumes 5–16 mL, then decreased back to 85.5% for the 17–23 mL samples. This shape of the observed curve can be attributed to geometrical effects. The low-volume samples may suffer from the 'height effect'; that is, that the sample level is too low to be in the sensitive region of the PMT.

The higher-volume samples appear to exhibit a 'volume quenching' effect, which could possibly be due to absorption of the photons emitted by the fluor by other molecules in the sample. Those authors conjectured after calculating a 'standard' (sic) quench-indicating parameter (ESCR, discussed below) for each of the volume samples, that use of such a parameter in conjunction with a quench-correction curve could recover the apparent loss in efficiency. The additional height of these samples may also have the effect of adding a 'dead region' in which a portion of the cocktail is situated above the useful region of the PMT. By using the ESCR quench indicating parameter, they were able to predict the efficiency as a function of volume to within 1%.

While this level of precision may be acceptable for some applications, it would certainly be more desirable to be able to recover the true activity of a sample to a higher degree. Thus, the goal of the present investigation was to determine if more sophisticated methods of efficiency determination, namely the CIEMAT/NIST ^3H -standard efficiency tracing method, could provide better results. Additionally, we hoped to ascertain what influence, if any, β -endpoint energies have on this volume effect.

To this end, we have studied three radionuclides to determine the magnitude of the uncertainties introduced into an efficiency-tracing scheme and to study the components of these uncertainties. We employed ^3H as a tracer and noted the effect on the activity determination, via the CIEMAT/NIST ^3H efficiency tracing method, on the low-energy (66.95 keV) β -emitter ^{63}Ni and the relatively high-energy (709.2 keV) β -emitter ^{36}Cl .

Determination of quench

Many methods are available to correct LS data for quenching effects. Most of these relate the counting efficiency of the system to some 'quench-indicating parameter' (QIP). One such QIP is the External

Source Channels Ratio (ESCR), which uses the fact that the Compton electron pulse height spectrum produced by exposure of the sample to an externally-placed γ -ray source such as ^{137}Cs or ^{133}Ba will be quenched by the same mechanism as the β -spectrum of the radionuclide being studied (Horrocks, 1974). The ESCR is calculated by summing the number of counts in two different energy windows in the resulting Compton spectrum and taking their ratio. If this is done for a set of standard solutions of the radionuclide of interest, then a curve of efficiency vs ESCR can be plotted, from which the efficiency for the unknown sample of that radionuclide can be found if the ESCR is known.

The ESCR suffers from the drawbacks of requiring a set of standards with varying amounts of quenching to be prepared for each radionuclide to be studied. In addition, this QIP has a rather small dynamic range (dependent on the degree to which the spectrum is shifted) and may require discriminator setting changes if large quench ranges are used. Additionally, this QIP exhibits a volume-dependence in that small volumes exhibit shape changes in the low-energy region, making ESCR determination unreliable for such samples.

In order to deal with these deficiencies, Horrocks developed the 'H number' parameter (Horrocks, 1974), which is also based on the external γ -ray source Compton spectrum method. The parameter is determined by calculating the difference (in channels) between the inflection point of the Compton edge of a quenched sample vs that of an 'unquenched' (sic) standard. Besides the inherent difficulty of defining an 'unquenched' sample, this QIP has the potential to suffer in monitoring low-volume and color-quenched samples, both of which exhibit a flattening of the Compton spectrum (a statistical effect due to fewer counts), thereby making determination of the inflection point more difficult. However, with the advent of more sophisticated computer algorithms to calculate derivatives and transforms and increased memory capacity in modern LS spectrometers, this problem is much more tractable.

Another commonly-used QIP is the *tSIE*, a proprietary method used by Packard Instruments (Kessler, 1989) which utilizes a mathematical transform of the external γ -ray source Compton spectrum to monitor quench. A curve is fit to the transformed Compton spectrum and the coefficients of the resulting fit are used to derive the *tSIE* value. It is claimed that this transform eliminates uncertainties due to spectral distortions caused by wall effects, color quenching, and volume effects.

Determination of efficiency

One of the earliest ways to perform quench corrections involved developing an efficiency curve as a function of QIP for a standard of the radionuclide to be measured. This may work for applications in

which a traceable standard exists (^3H , ^{14}C , etc.), but obviously not for those which seek to quantify radionuclides which have not yet been standardized. Also, this method relies on the reproducibility of the QIP from the time the efficiency curve is developed to the time the unknown is analyzed. Unless the standard is run right before analyzing the unknown, instrumental drifts can call the reliability of the efficiency curve into question, since it is doubtful that the same QIP will correspond to the same efficiency over a few weeks or even over a few days.

A systematic study of sources of uncertainty in applying this method using ESCR as a QIP was carried out by Neame (1978). In that study, the author found that variations in the cocktail volume in a 20 mL vial from 1–20 mL could cause as much as a 10% discrepancy between the calculated and predicted efficiencies. In addition, this difference was found to be inconsistent, sometimes falling within the limits of experimental uncertainty. The author also confirms the notions that a quench-correction curve of this type must be made prior to studying the unknown sample and that the curve must be re-determined anytime the cocktail conditions have changed, so that the standard and unknown are counted under as identical conditions as are possible.

Other methods of efficiency correction are also available, such as the triple-to-double coincidence ratio (TDCR) method (Pochwalski *et al.*, 1988; Simpson and Meyer, 1992, 1994), which claims to implicitly include quenching corrections, but this method requires a three-PMT instrument or a custom setup.

Many modern commercial LS instruments are equipped with two or more methods to perform efficiency corrections using internally-stored quench curves or by extrapolating a precalibrated curve of efficiency of a standard vs an integral spectrum of the sample of interest to 100% efficiency (Kessler, 1989 and Burns and Steiner, 1991). While the uncertainties quoted by these manufacturers (<4%) may be adequate for most biological or medical applications, this is certainly not acceptable for cases in which high precision is required, such as the development of radionuclidic standards.

Most LS measurements at NIST use two-PMT instruments in conjunction with the CIEMAT/NIST ^3H efficiency tracing method. The remainder of this paper will concentrate on this approach.

The CIEMAT/NIST ^3H efficiency tracing method

The CIEMAT/NIST ^3H efficiency tracing method (Coursey *et al.*, 1986, 1989, 1991) is a protocol by which the LS counting efficiency for a sample of interest under known, varying quenching conditions is obtained by following the efficiency of a closely-matched (in terms of cocktail composition) standard. Tritium is a good candidate for this standard because of its low β energy, which makes it very sensitive to quenching effects.

In order to describe the overall efficiency of the counting system, a 'figure of merit' M is employed. This parameter describes the energy (in keV) required to produce one photoelectron at the first dynode of the PMT. For a decay event with energy E from the β -spectral distribution, the fraction of energy lost due to heat absorption outside the solution (i.e. the container walls) is given by $1 - W(E)$, while the fractional energy loss due to secondary interactions within the solution ('quenching') is given by $1 - Q(E)$. The energy remaining, and thus available to produce photoelectrons, is then $EQ(E)W(E)$ and represents the unquenched, or effective, energy of the decay event. The average number of photoelectrons produced at the first dynode of the PMT is then

$$\bar{n} = M^{-1}EQ(E)W(E) \quad (1)$$

For low energies (<100 keV), β -particles with the distribution of these photoelectrons are assumed to follow Poisson statistics (at higher β -energies the distribution is normal). Thus the probability of detecting x photoelectrons from a mean number of photoelectrons \bar{n} can be calculated by

$$P(x, \bar{n}) = \frac{\bar{n}^x}{x!} \exp(-\bar{n}) \quad (2)$$

and the probability of detecting zero electrons (the 'non-detection probability') is just

$$P(0, \bar{n}) = \exp(-\bar{n}) \quad (3)$$

where the probability distributions are normalized to 1. The detection probability for a single PMT is then $(1 - \exp(-\bar{n}))$. Hence, for a two-PMT system in coincidence, the expected efficiency above the detection threshold is given by

$$\begin{aligned} \hat{\varepsilon}(E) &= \{1 - \exp[-\bar{n}]\}^2 \\ &= \{1 - \exp[-M^{-1}EQ(E)W(E)]\}^2 \quad (4) \end{aligned}$$

This efficiency, however, still only applies to events *above* the detection threshold. In order to include events below the threshold, an extrapolation to zero detection threshold must be made.

This is achieved in the CIEMAT/NIST method by relating this probabilistic efficiency, $\hat{\varepsilon}$ to one that can be determined experimentally. The calculation model for this transformation is embodied in the code EFFY4, which is an updated and revised version of EFFY2 (García-Torano and Grau Malonda, 1985; Grau Malonda *et al.*, 1985). The program calculates the efficiency for a given M by first calculating the shape of the β spectrum for a particular nuclide through the Fermi distribution function $P(Z, E)dE$ (not to be confused with the Poisson probability

distribution $P(x, n)$, given above). By comparing the number of particles emitted to the number of those that would most likely be detected, the efficiency can be calculated by the relationship

$$\varepsilon = \frac{\int_0^{E_{\max}} \{1 - \exp[-M^{-1}EQ(E)W(E)]\}^2 P(Z, E)dE}{\int_0^{E_{\max}} P(Z, E)dE} \quad (5)$$

where the integrals represent the total number of counts (numerator) or β -particles (denominator) over the energy from 0 keV to the β endpoint.

In practice, the procedure consists of running EFFY4 to obtain a table of M vs ε (accomplished by numerical integration of equation (5)) for each of the nuclides involved in the study, including the standard. The efficiency of the standard is then experimentally determined and a corresponding value of M is read from the table. The precision in the determinations is based on the step size between successive M -values used when running EFFY4. A fit of M vs 'quench indicating parameter' (QIP) is obtained for the standard. Since the QIP is assumed to be independent of nuclide (identical QIPs are obtained for all radionuclides under identical quenching conditions), the same equation can be used to obtain M for each of the other nuclides based on the measured QIP for each nuclide determined under the same conditions as that of the standard. By performing this fit, it is possible to make the necessary (small) adjustments to the figure of merit between samples which are slightly mismatched in composition, volume, or any other condition that leads to slightly different quenching. Based on the M calculated from this equation, the efficiency for that particular nuclide can be obtained for those quenching conditions using the tables generated by EFFY4.

Experimental

A set of liquid scintillation cocktails containing 5, 7.5, 10, 12.5, 15, 17.5 and 20 mL of Beckman Ready-Safe* scintillator were prepared for each of the three radionuclides ^3H , ^{36}Cl , and ^{63}Ni and for a set of blanks containing only distilled water. Glass vials with a nominal 22 mL volume were used. Although the scintillator was added volumetrically to the cocktail, an average mass per mL of the scintillator was obtained by averaging the masses of two 2.5 mL additions. Gravimetric additions of about 15 mg of either distilled water, a ^3H (tritiated-water) standard (NIST SRM 4927E (NIST, 1991), gravimetrically diluted with H_2O by a factor of 6.0697), or a ^{63}Ni solution standard (NIST SRM4226C (NIST, 1996)) were made for each of the scintillator volumes. The cocktails were prepared in such a way so as to

*Certain commercial equipment, instruments, or materials are identified in this paper to foster understanding. Such identification does not imply recommendation by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

nominally match the count rate of each. Due to the lower mass activity of the ^{36}Cl standard solution (NIST SRM 4943 (NBS, 1984)), about 40 mg were gravimetrically added to that set of scintillator volumes. The relative standard uncertainty on the mass for any of the gravimetric additions of ^3H , ^{63}Ni , or ^{36}Cl to the cocktails was estimated to be about 0.05%. Distilled water was added to each of the cocktails containing radionuclide to ensure that the aqueous fraction in each sample was close to 5%. Cocktails containing ^{63}Ni in an aqueous fraction less than a few % (prepared with any of five different commercial scintillation fluids) have been found by the present authors to be either unstable or incorrectly traced by the CIEMAT/NIST method (Zimmerman and Collé, 1997; Collé and Zimmerman, 1996). These observations, however, are at variance with reports from other laboratories (Cassette, 1996; Los Arcos, 1996), who employed ^{63}Ni solutions with smaller Ni^{+2} concentrations. Additional experiments to evaluate this effect are currently underway.

In order to eliminate any possible experimental bias due to detector system or quench determination method, measurements were performed using two LS systems. The first was a Packard TriCarb2500TR LS analyzer, which employs two PMTs in coincidence mode, linear signal amplification for pulse height analysis of spectra, and an external ^{133}Ba γ -ray source for quench determinations. The QIP was *tSIE*. The second system was a Beckman LS7800 LS counter equipped with two Hamamatsu R331-05 PMTs, also operated in coincidence mode, but with logarithmic signal amplification. The QIP was the Horrocks *H*, which was determined with an externally-placed ^{137}Cs γ -ray source.

Each cocktail was counted once in each spectrometer for 120 minutes live time. All of the samples at a given volume were counted before counting the next volume sample. About 4×10^6 counts were recorded for each of the radionuclides during a single counting cycle. Most of the cocktails were counted for additional counting cycles.

EFFY4 calculations were carried out on a PC-clone equipped with a 90 MHz Pentium processor and 16 MB of RAM. The code was modified to permit very large arrays to be carried through the calculation and the output was modified to print only a two-column file of efficiency vs figure of merit. This modified code was recompiled using a 32 bit compiler and run to generate tables for ^3H , ^{63}Ni , and

^{36}Cl with figure of merit increments of 0.0001 through the entire range of observed ^3H efficiencies. The β -spectral distribution for each radionuclide was calculated over intervals of 0.01 keV in each case using the latest available data from the ENSDF database (ENSDF, 1995; Martin, 1995). Typical calculation times of 10–15 min were required to generate each of the three tables.

Results and Discussion

All counting data were first adjusted for background and decay-corrected to a reference time of 1200 EST July 21, 1995. Efficiencies for each of the ^3H cocktails were calculated from the experimental count rates and were used to obtain figures of merit (*M*) as calculated by EFFY4. A third-degree polynomial fit of *M* as a function of QIP was obtained for each spectrometer and was used to calculate an *M* for each of the ^{36}Cl and ^{63}Ni samples based on the measured QIP for that sample. These *M*-values were then used to obtain efficiencies for those samples from EFFY4 calculations. For cases with multiple counting cycles, the final calculated activities were averaged.

Relative volume effects on efficiencies

As expected, the efficiency of the ^3H generally decreased with increasing sample mass.* This is seen in Fig. 1 and is due to both internal quenching effects in the cocktail and geometrical effects arising from the change in height of the cocktail relative to the PMTs. More important, however, is how the ^{63}Ni and ^{36}Cl efficiencies change relative to the ^3H . The relative efficiencies as a function of cocktail mass are shown in Fig. 2. As can be seen, the rate of change in efficiency is different for the ^{63}Ni and ^3H samples and is nearly unchanged for the ^{36}Cl . This would suggest that the volume effect on efficiency is energy-dependent, i.e. it is dependent on the radionuclide and its decay energy.

The energy dependence of the efficiency for a given sample mass is not surprising. According to the theory of Birks (1958), the specific light output dL/dx (in photons) from a scintillation event is

$$\frac{dL}{dx} = \frac{S\left(\frac{dE}{dx}\right)}{1 + kB\left(\frac{dE}{dx}\right)} \quad (6)$$

where *x* is the path length of the detected particle (in units of $\text{mg}\cdot\text{cm}^{-2}$), *L* is the light output in photons, dE/dx is the energy loss of the particle through the cocktail over a given distance in the cocktail, *S* is the scintillation efficiency of the scintillator (in $\text{cm}^2 \text{MeV}^{-1} \text{mg}^{-1}$), and *kB* is a quenching parameter ($\sim 9 \text{ mg cm}^{-2} \text{MeV}^{-1}$). Integrating equation (6)

*Because all of the samples in this investigation were prepared gravimetrically rather than volumetrically, we refer to sample *mass* instead of *volume* when referring to our specific samples. The sample density is nominally 1 g mL^{-1} , so the reader can readily approximate the volume of the cocktail/radionuclide mixture in the 22 mL vial.

over the total amount of deposited energy, the total light output is

$$L(E) = S \int_0^E \frac{dE}{1 + kB \left(\frac{dE}{dx} \right)} \quad (7)$$

If we now define a fractional loss g of photons due to geometrical (solid angle) effects and a fractional loss f due to photon absorption by the fluor or other components of the cocktail, the number of photons actually incident on the PMT as a function of β -particle energy, $n(E)$, becomes

$$n(E) = gfS \int_0^E \frac{dE}{1 + kB \left(\frac{dE}{dx} \right)} = gfSQ(E) \quad (8)$$

The function $Q(E)$ is the ionization quenching function found in equation (1). This ionization function has a much greater effect on radionuclides with low β endpoints since $Q(E)$ is most sensitive in the low-energy part of the β -spectrum. If the wall effect ($W(E)$) is neglected (appropriate for low-energy β -emitters), and combining the other terms such that $M = gfS$, we have essentially derived equation (1), but now have a more meaningful description of the figure of merit. The figure of merit can thus include any sources of photon losses and one can compute $Q(E)$ by numerical integration of equation (8) with the appropriate choice of parameters k and B . Therefore, once the choice of model for ionization quenching is established, the figure of merit can embody any other detection losses that are not

included in that model, including geometry, optical factors, or other quenching mechanisms.

Figure 3 shows the theoretical (as calculated by EFFY4) and experimental ratios of the ^3H and ^{63}Ni efficiencies (calculated by comparing the observed count rate to the certified activity for both radionuclides) as a function of M for the ^3H sample. The decreasing slope of the ratio of these efficiencies corresponds to the behavior of the efficiencies observed in Fig. 2. Similar behavior is expected for the ratios of the ^3H and ^{63}Ni efficiencies relative to those of ^{36}Cl . Each of the different experimental M values corresponds to a different cocktail mass and can be viewed as a different quenching condition. As can be seen in Figs 4 and 5, the figure of merit traces the QIP, and thus the quenching, to a very high degree.

Sample geometry is not explicitly included in the EFFY4 code and the code relies on a semiempirical function to compute $Q(E)$. As such, any loss of photons (or energy deposited into the system not accounted for by $Q(E)$) is reflected in the figure of merit M , which would simply need to be recalculated to reflect these effects. The data in Fig. 3 suggest that the use of a 'figure of merit' can compensate for nearly any condition which has the effect of quenching the sample that occurs exclusively of those effects embodied in $Q(E)$. While this most often includes geometrical and optical effects and quantum efficiencies of the fluor and PMTs, it can also account for ionization quenching effects not embodied in the function chosen to model $Q(E)$. Thus comparison of this figure of merit parameter to some physical quantities should be viewed with caution unless the model for $Q(E)$ is well-understood.

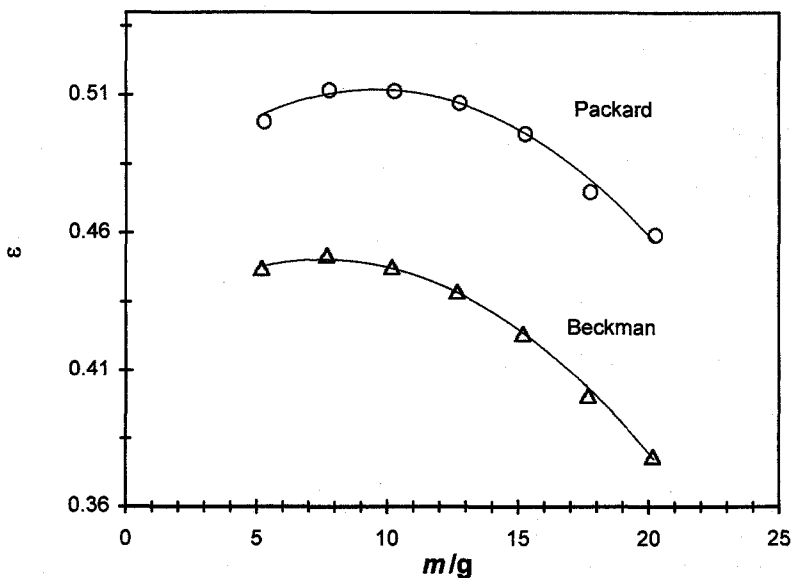


Fig. 1. Measured ^3H efficiencies ϵ for LS samples containing NIST SRM 4927E ^3H solution as a function of sample mass (volume) m (g) for the Beckman and Packard spectrometers. The lines through the data represent second-order polynomial fits, but are only intended to guide the eye.

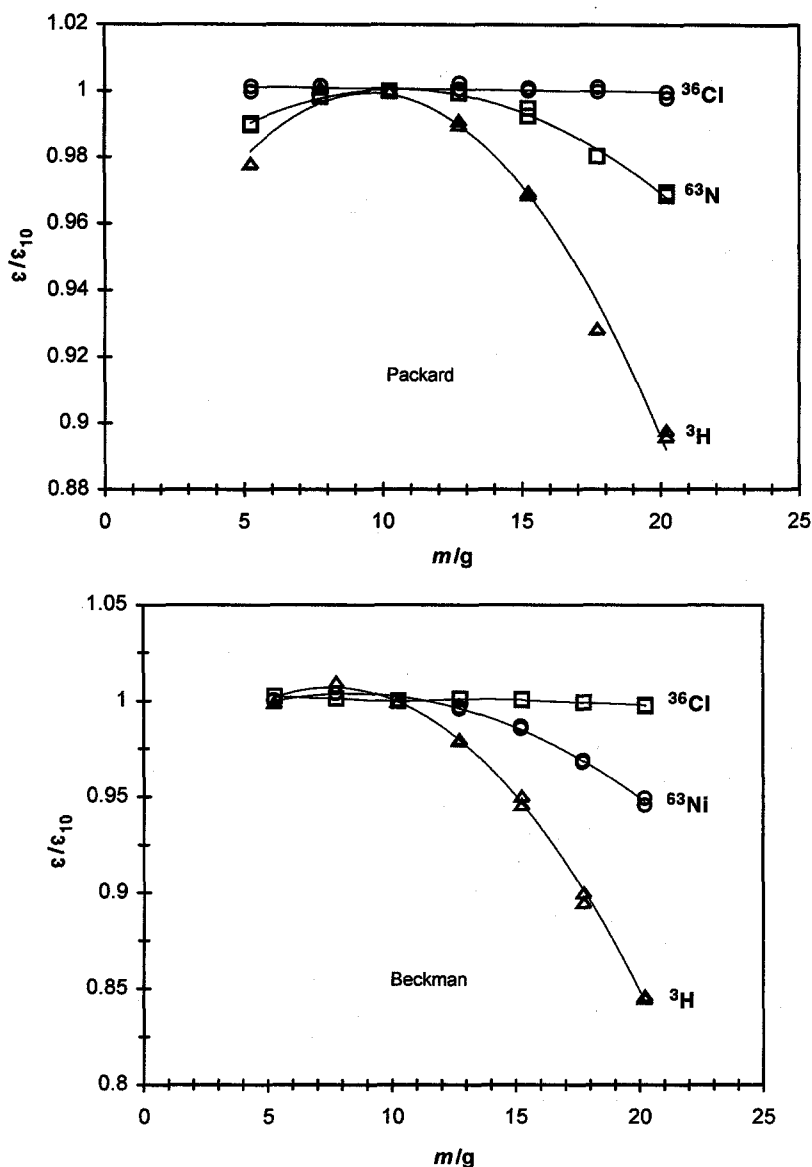


Fig. 2. Relative efficiencies ϵ/ϵ_{10} of ^3H , ^{36}Cl , and ^{63}Ni standard solutions from the (a) Packard and (b) Beckman spectrometers as a function of sample mass m (g). The efficiency values are normalized to the value of the (nominal) 10 g sample for each radionuclide.

With this in mind, a quench correction can be applied without knowledge of the actual quenching mechanism. In the application of the CIEMAT/NIST method, the physical meaning of M is irrelevant, since it is only used as a 'dummy variable' to make the transition from the efficiency of ^3H to that of the radionuclide of interest. The assumption, of course, must be that the conditions (composition, sample mass, vial type, etc.) of the samples are identical since the requirement is that the figure of merit for the system is the same for all samples.

Effect on ^3H efficiency traced-massic activities

The massic activities C_A of the ^{36}Cl and ^{63}Ni volume samples as calculated via the CIEMAT/NIST ^3H efficiency tracing method are shown in Fig. 6. The most striking result is that despite the large changes in the ^3H and ^{63}Ni efficiencies over the entire mass range, the derived massic activities were excellently traced. Clearly there is a problem with reproducibility in the ^{63}Ni samples with both volume and spectrometer as variables. This is most noticeable in those samples with masses below 10 and above

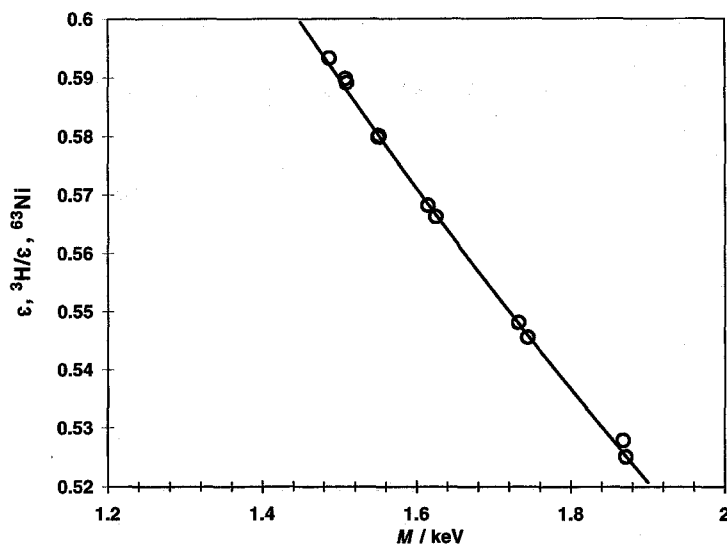


Fig. 3. Experimental (circles) and theoretical (line) ratio of the efficiency of ^3H to that of ^{63}Ni at values of the figure of merit determined for the ^3H samples. The theoretical ratios were calculated with data obtained from EFFY4 calculations. Experimental efficiencies were calculated from the observed count rates and the NIST-certified activity values for the two standards. Data were acquired on the Beckman spectrometer.

17.5 g. The average of all the samples gives a C_A of 50.58 kBq g^{-1} with relative uncertainty $s = 0.25\%$ which was obtained from propagating the typical standard deviation of the mean for between-cycle repeatability (of the massic activity) on the same sample and the standard deviation (of the massic activity) for the variability between samples. Using only the three samples in the 10–15 g range, the average C_A is 50.60 kBq g^{-1} , with $s = 0.11\%$. Both values are identical within their experimental uncertainties, but the somewhat smaller s on the

latter value suggests that greater precision (or more consistent values) is obtained in this case. This would appear to confirm the canonical rule of using around 10 mL of total sample to get the most consistent results although the argument is not entirely compelling given the magnitude of the uncertainties. It is important to point out that both values are in excellent agreement with the NIST-certified value (decay-corrected to 50.55 kBq g^{-1}) within experimental uncertainties. The latter certified value has a comparable statistical uncertainty of $s = 0.16\%$ and

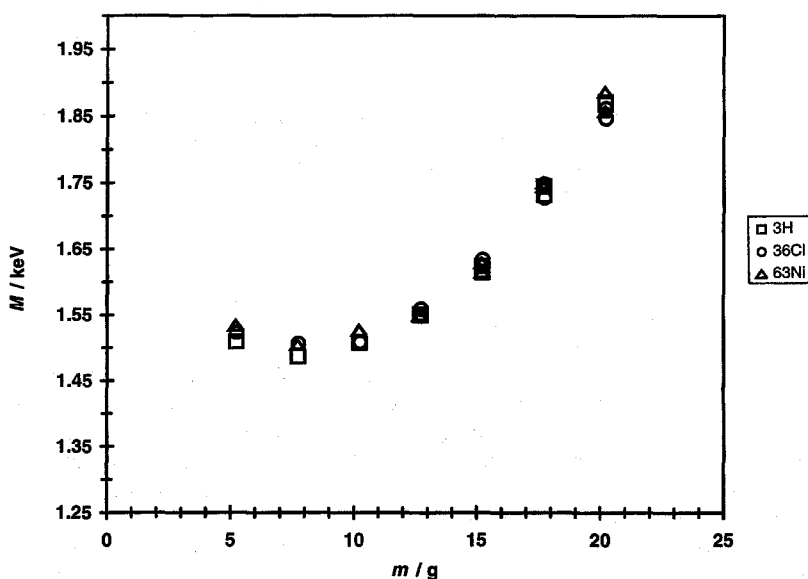


Fig. 4. Experimentally-determined figures of merit M (keV) as a function of total cocktail sample mass m (g) for standard solutions of ^3H , ^{63}Ni and ^{36}Cl .

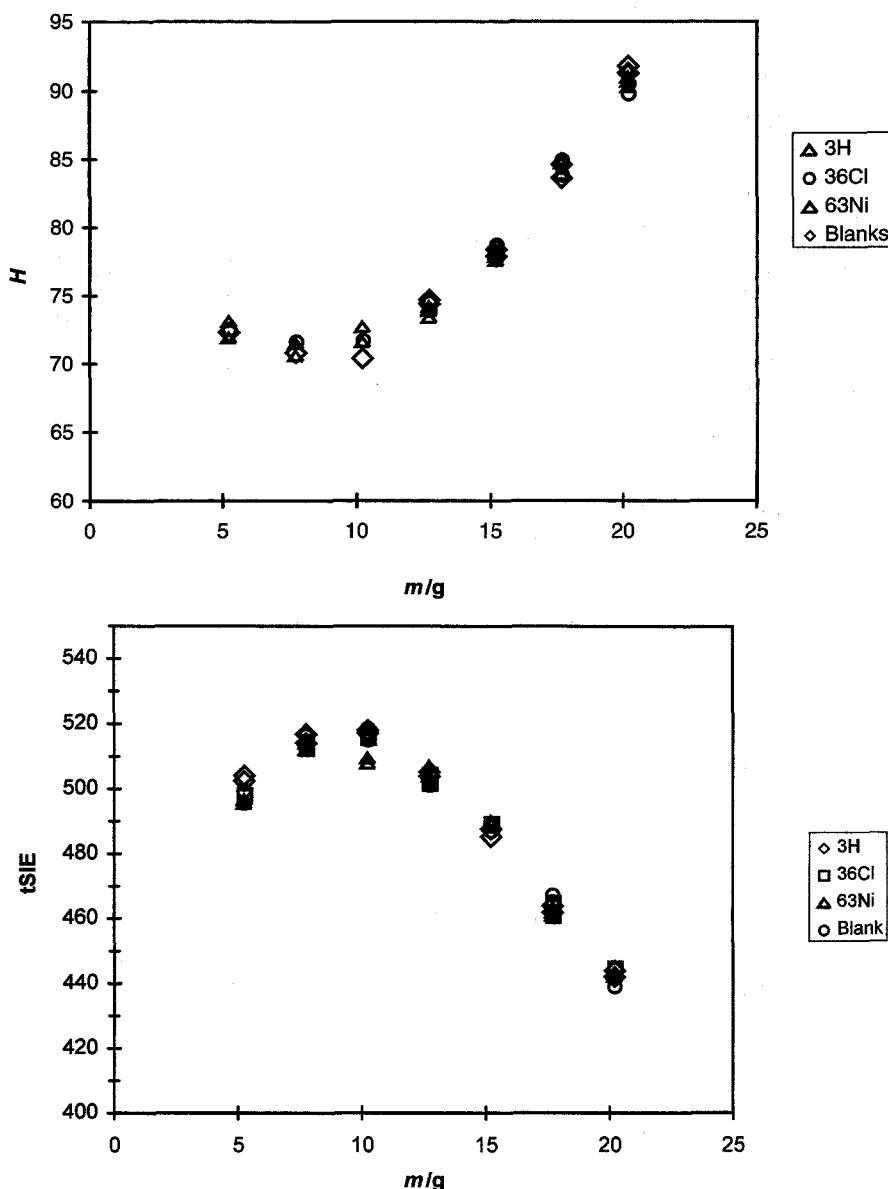


Fig. 5. Measured (a) H and (b) $tSIE$, for LS cocktails contain solutions of standards of ^3H , ^{36}Cl and ^{63}Ni and background blanks as a function of sample mass m (g).

a relative combined standard uncertainty u of 0.46%.

The results of the efficiency tracing appear to be much better for the ^{36}Cl samples, although some degree of scatter is also observed. In spite of the fact that there appears to be a sharp decrease in the apparent activity in the 20 g sample for ^{36}Cl relative to the 5–17.5 g samples, the overall agreement with the certified value is quite good. The average ^{36}Cl C_A calculated using all of the measurements is found to be 10.96 kBq g^{-1} with $s = 0.12\%$. The NIST-certified value for the SRM from which these samples were prepared is $10.95 \text{ kBq g}^{-1} \pm 0.09 \text{ kBq g}^{-1}$ —a difference of only 0.1% and within the experimental

uncertainty. If one neglects the 20 g sample the same average value of 10.96 kBq g^{-1} is obtained, but with a lower uncertainty, $s = 0.08\%$.

Both of the above results appear to indicate an inability to correctly account for the efficiencies of ^{63}Ni at both extremes of sample mass. Only the largest sample volume presented a problem for the ^{36}Cl . In the case of ^{63}Ni , the problem is particularly pronounced at low sample volumes.

Figure 7 shows the experimental efficiency for ^3H as a function of the QIP determined at that efficiency. While the Beckman exhibits fairly good linearity in being able to relate the efficiency to the QIP (the square of the correlation coefficient for a linear fit

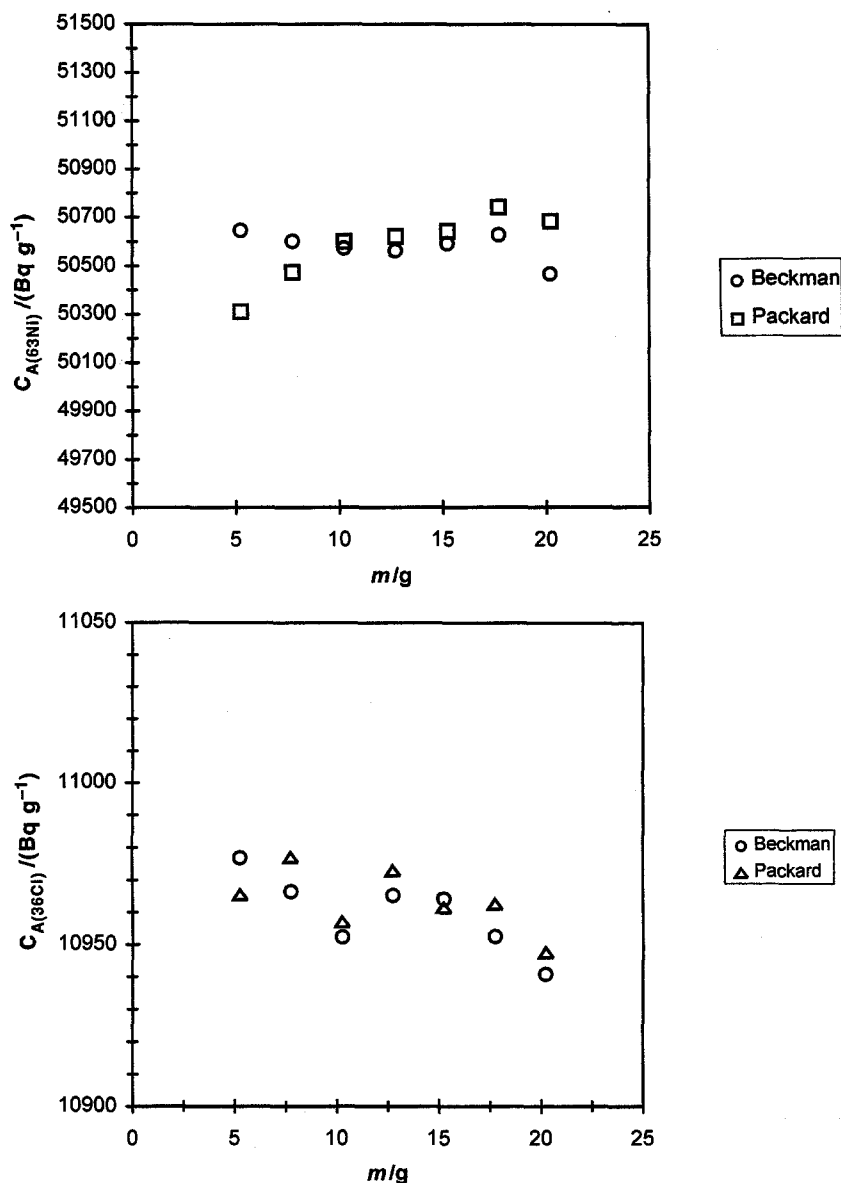


Fig. 6. Massic activity of (a) ^{63}Ni , $C_{A,63\text{Ni}}$ (b) ^{36}Cl , $C_{A,36\text{Cl}}$, samples as a function of sample mass m (g) counted in the Beckman and Packard spectrometers. Uncertainties (either the standard deviation of the mean for replicate counts or the Poisson 'counting error') in the measured massic activities for each of the radionuclides lie within their respective data symbols.

$r^2 = 0.9994$ and standard error of estimate (Crow *et al.*, 1960)* for that fit $s_{\text{fit}} = 0.00072$), the results for the Packard are relatively poor. For a given ^3H efficiency, the spread in $tSIE$ values from linearity is relatively large ($r^2 = 0.9832$, $s_{\text{fit}} = 0.0029$). The

inability to determine a consistent $tSIE$ value is especially evident at low volumes (corresponding to high $tSIE$ numbers).

Since it is not only the ^3H QIP that is used, but also that of the radionuclide being studied, it is imperative that there be a consistent calculation of QIP. Since all of the samples were prepared so as to be as closely-matched as possible, a QIP determined for ^3H should be more or less equal to those calculated for the other radionuclides. Figure 8 shows the QIP for ^{36}Cl and ^{63}Ni as a function of the ^3H QIP. As can be seen, both spectrometers appear to have problems calculating a consistent set of QIPs at low

*The standard error of the estimate is a measure of the variance of the data from a regression (of any function), in this case indicating the variance from linearity. For a set of data (x_i, y_i) to which is fitted a function $y_i' = f(x_i)$, the standard error of the estimate s_{fit} can be expressed as $s_{\text{fit}} = (\sum (y_i - y_i')^2 / (n - 2))^{1/2}$ for n degrees of freedom.

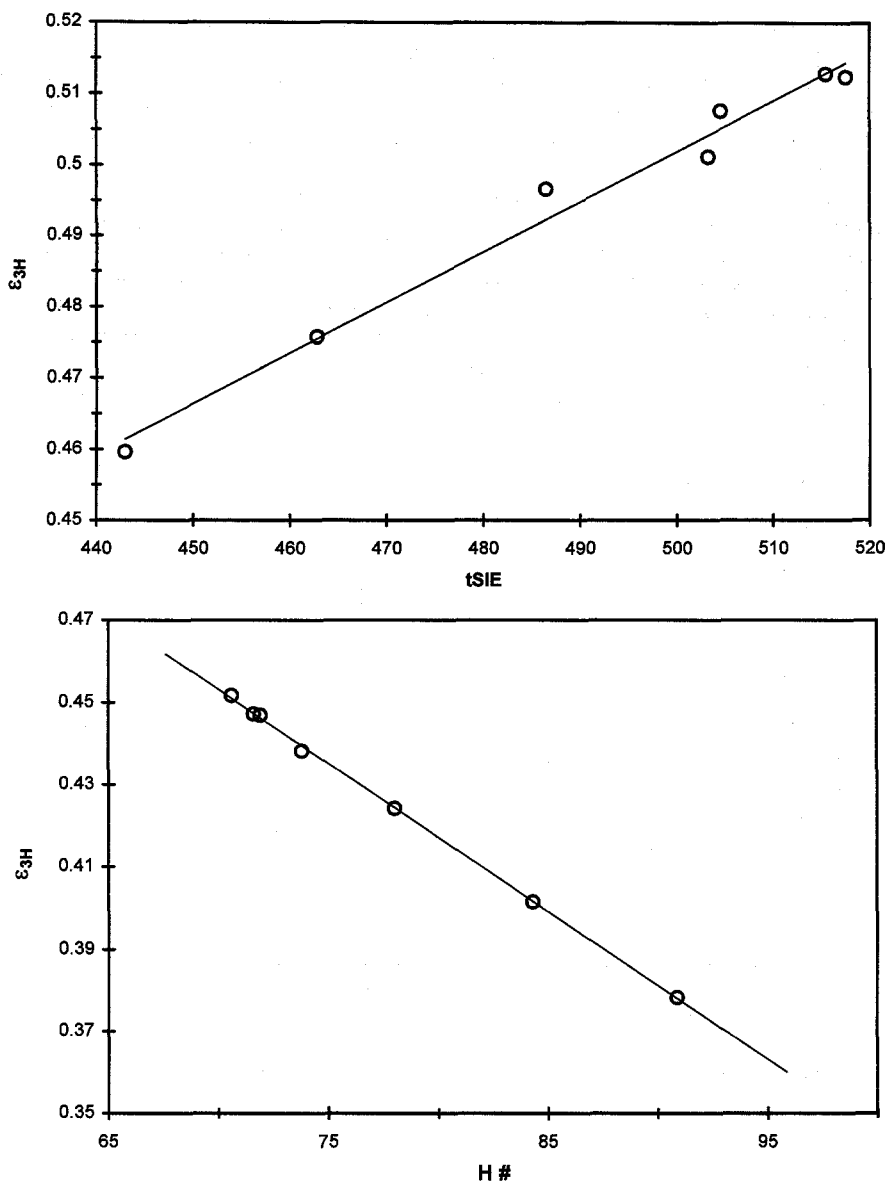


Fig. 7. Average experimental ${}^3\text{H}$ efficiency $\epsilon_{3\text{H}}$ of NIST ${}^3\text{H}$ standard as a function of average (a) $t\text{SIE}$ and (b) H . Greater quenching is indicated by a higher H and lower $t\text{SIE}$. The lines represent linear fits to the data.

volumes as evidenced by the data corresponding to minimum quenching.

The inability to correctly determine the QIP is of utmost importance, since it is through this parameter that the figure of merit M is calculated. While it is clear that the ${}^{36}\text{Cl}$ efficiency is relatively insensitive to small changes in M , the ${}^{63}\text{Ni}$ efficiency is quite sensitive to M , and thus the QIP. Propagating even a difference of 3 $t\text{SIE}$ units ($\sim 0.6\%$) can cause a 0.2% change in the efficiency and massic activity. Several of the measurements in this investigation exhibited variances in the $t\text{SIE}$ value of this magnitude.

As noted, the magnitude of the volume effect on

the efficiency-traced massic activity C_A for either ${}^{63}\text{Ni}$ or ${}^{36}\text{Cl}$ is nearly within the random variability of the measurements across the entire 5–20 g cocktail mass range. This is evidenced by the small differences between the obtained C_A at any given mass and the NIST-certified massic activity. Similarly, without recourse to 'known' massic activity values, one can compare the C_A at any mass to a mean C_A obtained by either averaging over all masses (5–20 g) or averaging over the masses in midrange (10–15 g). The absolute differences from either of these comparisons are typically about 0.1%, excepting a few worst cases on the extremes of sample mass. Table 1 illustrates the results for the latter case comparison. The sign

of the differences may be easily established by examination of Fig. 6. Multiplication of the tabulated absolute differences by a factor of 0.9 yields estimates of the relative standard deviation (with one degree of freedom) for the replication precision in determining the efficiency-traced C_A . Comparisons of individual C_A values with that for $C_{A(m)}$ averaged over all sample masses is nearly indistinct from that given in Table 1.

Although the efficiency traced mass activities C_A are nearly invariant of cocktail mass, the reproducibility within various mass ranges is distinctly different. Table 2 summarizes the observed dispersions about mean $C_{A(m)}$ values that have been obtained by averaging over three cocktail mass

ranges. As indicated, the precision is best in the middle (nominal 10–5 g) range, and decidedly poorer at both the lower (5–10 g) and higher (15–20 g) ranges. The effect is particularly evident for the ^{63}Ni measurements obtained with the Packard spectrometer.

As indicated in Fig. 6, the efficiency-traced mass activities C_A do not exhibit any gross systematic trends as a function of cocktail mass, even though both the individual efficiencies (Figs 1 and 2) and quench indicating parameters (Fig. 3) for ^3H , ^{36}Cl and ^{63}Ni did. Furthermore, the observed volume effects on C_A are relatively small, except at cocktail mass extremes, and are often nearly lost within the

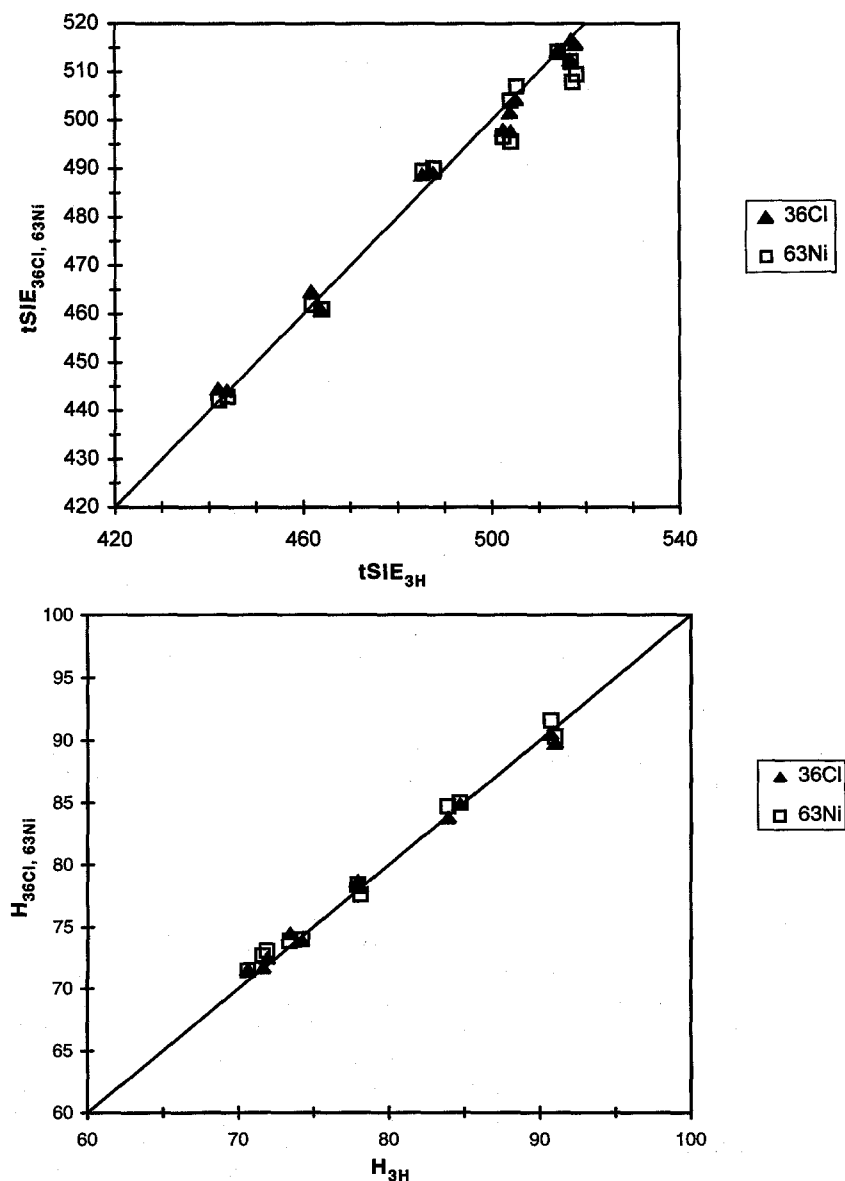


Fig. 8. Quench indicating parameters (QIP) (a) $tSIE$ and (b) H of ^{36}Cl and ^{63}Ni as a function of QIP for ^3H solution with matched sample composition and mass. The lines through the data are 'helper lines' and indicate a slope of unity.

Table 1. Absolute differences between the efficiency-traced massic activity C_A for ^{36}Cl and ^{63}Ni with two spectrometers at various cocktail masses and that for a mean value $C_{A(m)}$ obtained by averaging the results for samples in the 10–15 g midrange

Nominal cocktail mass (g)	Absolute differences (in %) between C_A and $C_{A(m)}$			
	For ^{36}Cl		For ^{63}Ni	
	Beckman	Packard	Beckman	Packard
5.3	0.15	0.02	0.14	0.61
7.7	0.05	0.12	0.05	0.29
10.3	0.08	0.06	0.01	0.04
12.7	0.04	0.08	0.03	0.001
15.2	0.03	0.02	0.03	0.04
17.7	0.07	0.01	0.10	0.23
20.2	0.18	0.15	0.22	0.12
Median value	0.07	0.06	0.05	0.12
Mean value	0.09	0.07	0.08	0.19

statistical variation of the measurement precision. As a result, a simple and explicit quantification of the volume effect on C_A is difficult. It is even more difficult to quantify the effect of cocktail volume on the uncertainty in C_A . Nevertheless, two related approaches can be invoked to at least establish some crude limits on the magnitude of the volume effect, and on its contribution to the uncertainty in C_A .

Firstly, one can compare the differences between the average $C_{A(m)}$ values for the various cocktail mass ranges given in Table 2. Excepting the case for ^{63}Ni measurements with the Packard spectrometer, the average $C_{A(m)}$ decreases by between 0.02 and 0.07% (for a 5 g mass change) in going from 5 to 10 g masses to 10 to 15 g masses and to 15 to 20 g masses. The Packard measurements on ^{63}Ni exhibit a larger and reverse effect; viz. a 0.3% increase in going from 5 to 10 g masses to 10 to 15 g masses, and a 0.1% increase in going from 10 to 15 g masses to 15 to 20 g masses. Obviously then, for any reasonable change in the cocktail mass from the presumed optimal 8–12 g value, the effect on C_A must be very small ($<0.1\%$) and the relative uncertainty contribution must be virtually negligible ($<0.01\%$).

Secondly, one can consider the overall change in C_A per unit cocktail mass, dC_A/dm , as obtained from linear regressions of the data of Fig. 6. As seen in the ^{36}Cl data of Fig. 6, C_A generally (and somewhat systematically) decreases with increasing cocktail mass. The ratio of the fitted slope dC_A/dm to the average $C_{A(m)}$ is $(dC_A/dm)/C_{A(m)} = (-0.011 \pm 0.004) \% \text{ g}^{-1}$ for the Beckman spectrometer and

$(-0.010 \pm 0.006) \% \text{ g}^{-1}$ for the Packard spectrometer. Examination of Fig. 6 indicates that the use of linear regressions for the ^{63}Ni data is less supportable. Nevertheless, they are: $(dC_A/dm)/C_{A(m)} = (-0.013 \pm 0.008) \% \text{ g}^{-1}$ for the Beckman and $(+0.048 \pm 0.010) \% \text{ g}^{-1}$ for the Packard. Again, confirming that found with the first approach, the ^{63}Ni data for the Packard exhibits a larger and reverse volume effect. The relative uncertainty in C_A due to a cocktail volume effect for any of these cases may be directly approximated by multiplying an invoked Δm uncertainty in cocktail mass by the $(dC_A/dm)/C_{A(m)}$ values to give a relative uncertainty contribution $u = \Delta m(dC_A/dm)/C_{A(m)}$.

From the above, one may, therefore, conclude that the cocktail volume effect on the efficiency-traced massic activity (as determined with the CIEMAT/NIST method) is relatively negligible, and nearly within the measurement precision of this work. Not surprisingly, the volume effect is most prevalent at the extremes of low and high cocktail masses. This is evidenced by either decreases or increases in the efficiency-traced massic activity at the mass extremes compared to that obtained in the midrange of cocktail masses, and by much poorer measurement precision at the extremes. At these extremes, the volume effect also appears to be both radionuclide (β -endpoint energy) dependent and spectrometer dependent. Except at the cocktail volume extremes, the volume effect on the efficiency-traced massic activity C_A is generally much less than $0.1\% \text{ g}^{-1}$ change in the cocktail mass, and the volume effect on the relative uncertainty in C_A is less than 0.01% .

Conclusions

An apparent energy-dependent effect on LS detection efficiency due to cocktail volume is observed in samples with volumes ranging from 5 to 20 mL in 22 mL vials. In general, the efficiencies tend to decrease with increasing sample volume. The detection efficiency for ^3H over this volume range was found to vary by about 17%. At higher β -energies, the efficiency variations were about 7% for ^{63}Ni (having a mean β energy of $E_{\beta(\text{max})} = 66.95 \text{ keV}$) and virtually nonexistent for ^{36}Cl ($E_{\beta(\text{max})} = 709.2 \text{ keV}$). This effect can be viewed in terms of loss of energy to the cocktail prior to being absorbed by the fluor molecules and the of absorption of photons produced during a decay event.

The determination of quench indication parameters (both H and $tSIE$), even for cocktails of nearly identical composition, was also found to systematically vary as a function of cocktail volume. The functional form of both H and $tSIE$ vs cocktail volume appears parabolic with either minimum H or maximum $tSIE$ occurring at about 8 mL. The relative range in H over the 5–20 mL volume range was about 28%, while that for $tSIE$ was about 16%. This observed volume effect on the quench indicating

Table 2. Relative standard deviations of the mean s_m on the efficiency-traced massic activity C_A for ^{36}Cl and ^{63}Ni with two spectrometers at various cocktail mass ranges. The values of s_m are indicative of the dispersion about a mean $C_{A(m)}$ obtained by averaging the results over the three cocktail mass ranges

Nominal cocktail mass (g)	s_m (in %) for $C_{A(m)}$ averaged over the given cocktail mass range			
	For ^{36}Cl		For ^{63}Ni	
	Beckman	Packard	Beckman	Packard
5–10	0.10	0.10	0.07	0.44
10–15	0.01	0.01	0.04	0.04
15–20	0.12	0.12	0.21	0.21

parameters (QIP) was originally considered surprising. One would presume that any QIP is merely a measure of the degree of quenching in the cocktail, and that the degree of quenching is in turn merely dependent on the composition of the cocktail. Yet, it turns out that this is not wholly the case since the two measures of quenching, as obtained with two commercial LS spectrometers, can exhibit widely different QIP values for samples of identical composition and with only changes in cocktail volume. When one considers the more global concept of 'quenching' (to include factors other than chemical effects), geometrical effects must be included. Evidently, the QIP determinations, like the efficiency, are dependent on geometrical effects. Therefore, the use of QIPs in the application of the CIEMAT/NIST method is only valid when the cocktail volumes of the ^3H standard and the radionuclide being studied are identical.

Irrespective of these volume effects on LS detection efficiency and on the determination of QIP, the CIEMAT/NIST ^3H -standard efficiency tracing method was found to correct for these effects very well. The method excellently traced the massic activity of both ^{63}Ni and ^{36}Cl over nearly the entire 5–20 mL volume range. The only exceptions were at the extremes of very low and very high cocktail volumes, particularly for the lower β -energy emitter ^{63}Ni . Such extremes of volume should be avoided since nonoptimum PMT response and Compton electron productions with the external γ -ray source are most probable under those conditions.

Comparison of experimental data and numerical calculations using an assumed geometry and model of the mechanism for ionization quenching show that additional losses contributing to a decrease in detection efficiency can be compensated for through the use of a 'figure of merit'. The physical meaning of the 'figure of merit', M , depends on the model chosen to account for apparent energy losses in the system. Once the mechanism for ionization quenching is fixed, M can then embody any other losses due to geometry and energy losses not included in the assumed ionization quenching model.

Acknowledgements—The authors wish to thank Dr B. M. Coursey for many stimulating discussions regarding LS spectrometry and the CIEMAT/NIST method.

References

- Birks J. B. (1958) *The Theory and Practice of Scintillation Counting*. Pergamon Press, London.
- Burns P. D. and Steiner R. (1991) *Advanced Technology Guide for LS6000 Series Scintillation Counters*, Beckman Instruments, Inc., Fullerton, Connecticut, Appendix 8.

- Cassette P. (1996) Laboratoire primaire des rayonnements ionisants (LPRI), private communication.
- Collé R. and Thomas J. W. L. (1993). *J. Res. Natl. Inst. Stand. Tech.* **98**, 653.
- Collé R. and Zimmerman B. E. (1996). *Appl. Radiat. Isot.* **47**, 677.
- Coursey B. M., Mann W. B., Grau Malonda A., Garcia-Toraño E., Los Arcos J. M., Gibson J. A. B. and Reher D. (1986). *Appl. Radiat. Isot.* **5**, 403.
- Coursey B. M., Lucas L. L., Grau Malonda A. and Garcia-Toraño E. (1989). *Nucl. Inst. Meth.* **A279**, 603.
- Coursey B. M., Cessna J., Garcia-Toraño E., Golas D. B., Grau Malonda A., Gray D. H., Hoppes D. D., Los Arcos J. M., Martin-Casallo M. T., Schima F. J. and Unterwieser M. P. (1991). *Appl. Radiat. Isot.* **9**, 865.
- Crow E. L., Davis F. A. and Maxfield M. W. (1960) *Statistics Manual*. Dover, New York.
- Dammers-DeKlerk A. (1958). *Mol. Phys.* **1**, 141.
- Evaluated nuclear structure data file (ENSDF) (1995) On-line database, Nuclear Data Center, Brookhaven National Laboratory, Upton, New York.
- Garcia-Toraño E. and Grau Malonda A. (1985). *Comp. Phys. Comm.* **36**, 307.
- Grau Malonda A., Garcia-Toraño E. and Los Arcos J. M. (1985). *Int. J. Appl. Radiat. Isot.* **2**, 157.
- Horrocks D. L. (1974) *Applications of Liquid Scintillation Counting*. Academic Press, New York.
- Kessler M. J. (1989) *Liquid Scintillation Analysis: Science and Technology*. Packard Instrument Co., Meriden, Connecticut.
- Knoche H. W., Parkhurst A. M. and Tam S. W. (1979). *Int. J. Appl. Radiat. Isot.* **30**, 45.
- Kobayashi Y. and Maudsley D. V. (1974) In *Liquid Scintillation Counting: Recent Developments* (Stanley P. E. and Scoggins B. A., Eds), pp. 192–193. Academic Press, New York.
- Los Arcos J. M. (1996) Centro de Investigaciones Energéticas Medioambientales y Tecnológicas (CIEMAT), private communication.
- The latest evaluated ^{63}Ni β -endpoint energy was provided by M. Martin, Nuclear Data Project, Oak Ridge National Laboratory, Oak Ridge, Tennessee, private communication.
- Moghissi A. A. (1970) In *The Current Status of Liquid Scintillation Counting* (E. D. Bransome, Jr, Ed.), pp. 86–94. Grune and Stratton, New York.
- National Bureau of Standards (NBS) (1984) Certificate, standard reference material 4943, radioactivity standard chlorine-36, NBS, Gaithersburg, Maryland.
- National Institute of Standards and Technology (NIST) (1996) Certificate, standard reference material 4226C, radioactivity standard nickel-63, NIST, Gaithersburg, Maryland.
- National Institute of Standards and Technology (NIST) (1991) Certificate, standard reference material 4927E, radioactivity standard hydrogen-3, NIST, Gaithersburg, Maryland.
- Neame K. D. (1978). *Anal. Biochem.* **91**, 323.
- Pochwalski K., Broda R. and Radoszewski T. (1988). *Appl. Radiat. Isot.* **39**, 165.
- Simpson B. R. S. and Meyer B. R. (1992). *Nucl. Inst. Meth.* **A312**, 90.
- Simpson B. R. S. and Meyer B. R. (1994). *Nucl. Inst. Meth.* **A339**, 14.
- Zimmerman B. E. and Collé R. (1997) The standardization of ^{63}Ni by $4\pi\beta$ liquid scintillation spectrometry with ^3H -standard efficiency tracing. *J. Res. Natl. Inst. Stand. Tech.* In press.