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Preparation of solid water-equivalent radioactive standards

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Abstract

The use of a superabsorbent polymer to prepare water-equivalent volume standards by solidification without the need of irradiation to effect the polymerization process, is described. Less than 40 g of the polymer is needed to solidify 1 litre of solution. Monte Carlo simulations of the gamma-ray escape probability indicate that the mixture is water-equivalent to better than 1.0%. During preparation, the solidified material can be mixed until homogeneity is achieved. Comparative measurements made before and after solidification confirmed the homogeneity and demonstrated water equivalence.

Keywords: Radioactive volume standards; Water-equivalent standard; Solid standard; Superabsorbent polymer

1. Introduction

Radioactive water standards prepared in Marinelli beakers can pose a problem due to potential leakage that can both compromise the standard and present a safety hazard. These difficulties can be circumvented by solidifying the standard such that it remains fundamentally water-equivalent. A technique for achieving this based on polymerization of acrylamide has been previously reported by Sahagia and Grigorescu (1992). A drawback of this method is the requirement that the volume standard be placed in a strong gamma radiation field to effect the polymerization process.

This paper describes an alternative procedure that avoids the need to irradiate the standard. This entails the use of a small quantity of a superabsorbent polymer, namely lightly crosslinked polyacrylate. The polymer granules are simply added to the radioactive solution and thoroughly mixed to achieve homogeneity during the solidification process. Extensive measurements have confirmed the solid standard to be both homogeneous and water-equivalent.

2. Monte Carlo simulations

A literature survey indicated that the amount of polyacrylate needed to solidify a source would be between 5% and 20% (Garner et al., 1997) compared to the 40% polyacrylamide used by Sahagia and Grigorescu (1992). Based on the close match obtained using polyacrylamide, it was anticipated that polyacrylate would be suitable for producing reasonably water-equivalent sources.

Calculations of γ-ray escape probabilities were then used to predict the degree of water-equivalence of polyacrylate mixtures. This was achieved using a locally written Monte Carlo program (Simpson, 1994) that simulates the probability of a γ-ray escaping from a source. The required elemental mass attenuation coefficients were taken from Hubbell (1982) and combined according to the weight fractions of the elements constituting the specific materials.

For the exploratory Monte Carlo simulations, the density of the polyacrylate/water mixture was assumed to be 1 g/ml. During actual source preparation the density of the utilized polyacrylate mixture (2.55% polymer by weight) was measured to be 1.013 g/ml. This density was used in all Monte Carlo simulations presented in this paper.

Although volume standards are generally prepared in Marinelli beakers, plastic bottles are also in common

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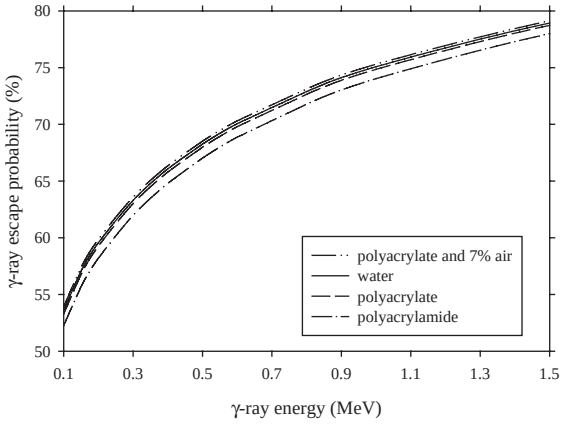

Fig. 1. Results of Monte Carlo simulations of the γ-ray escape probabilities for water, polyacrylamide, polyacrylate and a polyacrylate and air mixture described in Section 3.2.

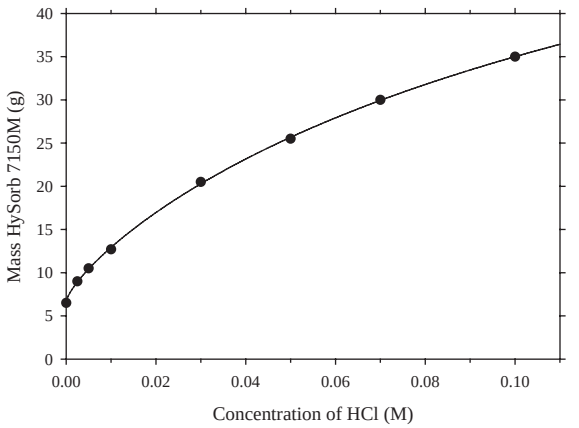

Fig. 2. The amount of polyacrylate needed to solidify 1 litre of acidic solution as a function of acid concentration.

use. A simple cylindrical shape with suitable dimensions was thus used for the Monte Carlo simulations. It is shown in the appendix that, for similar materials, changes in the relative escape probabilities are small over a wide range of path lengths. Since the average path length that a γ-ray travels through a Marinelli beaker does not differ much from that through the cylinder simulated, the relationship between the γ-ray escape probabilities of the polymer and water as predicted for the cylinder is a valid approximation for that of the Marinelli beaker.

The results of the Monte Carlo simulations of the γ-ray escape probabilities from water and 2.55% polyacrylate used in the present investigation are presented in Fig. 1, together with the Monte Carlo results of 40% polyacrylamide. The results clearly indicate that the attenuation of γ-rays by the selected polymer corresponds to that of water somewhat more closely than the attenuation by the previously studied polyacrylamide.

3. Solidified volume sources

3.1. Details regarding the selected polymer

Based on the promising outcome of the Monte Carlo simulations, lightly crosslinked polyacrylate was obtained for experimental investigation. The actual product used for these tests was HySorb 7150M from BASF Aktiengesellschaft. It is a polyelectrolite and belongs to the class of superabsorbent polymers. The crosslinking renders this polymer insoluble in water, while the ionic nature draws water into the polymer network to dilute the ionic strength. This allows the polymer to absorb up to 3000 times its weight in pure water (Garner et al., 1997). When an acid- or salt-containing solution is added to polyacrylate, the polymer network preferentially absorbs the charged particles and less water is required to dilute the ionic strength. Since sources are generally acidic in nature and contain varying amounts of acid, the amount of HySorb needed to solidify a litre of acidic solution was determined as a function of acid concentration. These results are presented in Fig. 2. A correctly solidified mixture consisted of opaque granules that did not flow. The addition of less of the polymer resulted in a mixture that was wet and still flowed, while the addition of too much produced a crumbly product with the appearance of crushed ice.

3.2. Source preparation

Two comparable 1-litre Marinelli liquid standards were prepared gravimetrically from a master solution containing 156.34 kBq ^{152}Eu, 16.23 kBq ^{137}Cs and 42.01 kBq ^{60}Co per litre on 14 January 2003. About 40 ml of the stock solution was used per source and the sources acidified to a hydrochloric acid concentration of 0.05 M. The one standard remained in liquid form, while the other was solidified according to the procedure described below.

The mass and the exact liquid level of the source to be solidified were recorded, after which the solution was decanted into a suitable container. An accurately weighed quantity of HySorb, of the order of 25.5 g (see Fig. 2), was added to the solution and the resulting mixture stirred thoroughly for about 5 min until completion of the solidification process. The stirring was crucial to ensure the even distribution of the radionuclide ions attached to the polymer membrane walls. Without it, a definite concentration gradient was observed with more of the radionuclides at the bottom of the source.

Due to the addition of polyacrylate and introduction of air whilst stirring, the volume of the radionuclide mixture increased by about 8.5%, so that not all could be returned to the original Marinelli beaker without altering the geometry of the source. The beaker was filled to the previously marked liquid level, taking care to pack the granules as tightly as possible. Subsequent measurement indicated that the mixture comprised about 7% of air by volume. The activity of the source was attained by comparison of the mass returned against the original mass of liquid plus polymer. In summary, the final product comprised distinct granules interspersed with air. Nevertheless, the mixture remained intact and did not flow even when the container was tilted through 90°.

4. Experimental

4.1. NaI measurements

Measurements were made on a 1-litre Marinelli source both before and after solidification. A NaI(Tl) detector (50×50 mm) was used, facing the side of the beaker, measuring the upper, center and lower layers of the source in turn. For each layer, the source was measured in four orientations differing by about 90°, labeled North, East, South and West, respectively. Counts were recorded integrally above a threshold set at about 80 keV. Results from these measurements are summarized in Fig. 3 and indicate that the radioactivity was uniformly distributed within the layers. The effect of the different measurement geometries on the detection efficiency can be clearly seen.

The homogeneity and degree of water-equivalence was determined by comparing the mean count-rate of the solid source in each of four measurement geometries against measurements made on the source in liquid form. The measurements made with the liquid source were normalized to the radionuclide concentration of the solid source to compensate for the fraction of the solid source that was not returned to the Marinelli beaker. The results in Table 1 show that, on average, counts from the solid source were about 0.6% less than from the liquid source.

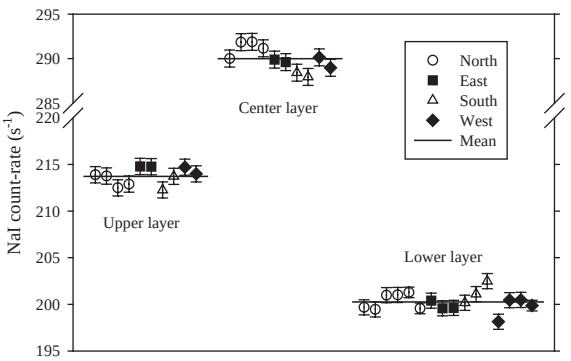

Fig. 3. Summary of γ-ray measurements of the solidified Marinelli source. Uncertainties are counting statistics only and all measurements were corrected for background.

Table 1
Summary of NaI measurements to confirm homogeneity and water-equivalence. Specified uncertainties are due to counting statistics only

Measurement geometry[a]	Count-rate of solid (s^{-1})[b,c]	Count-rate of liquid normalized to solid (s^{-1})[b]	Difference between solid and liquid (%)
Upper layer	213.7±0.3	213.1±0.3	0.3
Center layer	290.0±0.3	291.5±0.3	−0.5
Lower layer	200.3±0.2	201.9±0.2	−0.8
Lengthwise	211.7±0.3	214.6±0.3	−1.4

[a] The rates vary for each layer because of efficiency differences due to the changed geometry.
[b] All measurements were corrected for background.
[c] The count-rates are the averages of the various orientations measured for each geometry as displayed in Fig. 3.

To check that the solidified source was water-equivalent over the entire energy range, NaI γ-ray spectra were collected measuring the center layer of both the liquid and solid forms. The difference between the two spectra was consistent with zero within the statistical variation.

Destructive tests on the solid source were performed 2 months after the initial solidification by counting 13 cylindrical vials each containing 45 g of the source material sampled throughout the beaker. The tests demonstrated homogeneity to within 1%, thereby also indicating that the solid was stable over time.

4.2. HPGe measurements

Finally, measurements were made to gauge the practical situation of utilizing the solid Marinelli standard to calibrate a HPGe detector. The solidified source and a comparable liquid source were counted successively 3 times for a total of 3 h per source and the acquired spectra analyzed in the usual way to obtain the peak areas corresponding to the major photopeaks.

After normalization of the peak areas to the same radioactivity concentration, the data were used to determine the solid/water efficiency ratios as a function of energy (Fig. 4). Due to cancellation of parameters making up the efficiencies, the ratios are equivalent to the ratios of the γ-ray escape probabilities and so the data can be compared with the Monte Carlo calculations shown in Fig. 1. It is apparent that the

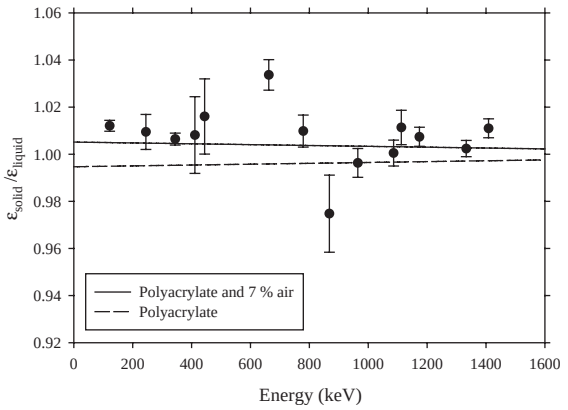

Fig. 4. Plot of HPGe solid/liquid detection efficiency ratios (solid circles) and the solid/liquid γ-ray escape probabilities as calculated by Monte Carlo simulations (lines).

experimentally determined values are fully consistent with the trend predicted for the polymer/air standard, conclusively demonstrating the water-equivalence. For completeness sake, the situation without the incorporation of air by stirring is also shown in the figure.

5. Conclusions

A procedure to prepare water-equivalent volume sources has been described. The method is based on the addition of a superabsorbent polymer to the liquid with subsequent mixing to produce a homogeneous solid source. Extensive measurements together with Monte Carlo simulations have indicated the suitability of utilizing the solid source as an excellent standard for the efficiency calibration of detectors measuring liquid samples.

Appendix A

The use of the *average* path length is a good indicator to assess the effect on the escape probability ratios when volume dimensions other than that specified for the Monte Carlo calculations are considered.

The probability for a γ-ray escaping from the medium making up a source, $J(E)$, is calculated from

$$J(E) = e^{-[\mu(E)/\rho]\rho t}, \quad \text{(A1)}$$

where $\mu(E)/\rho$ is the mass attenuation coefficient for a γ-ray of energy E, ρ is the density of the material and t is the distance the γ-ray travels through the volume. The distance t is a function of both the point of production and the direction in which the γ-ray is ejected.

The ratio of the γ-ray escape probabilities from the polymer and water (J_p/J_w) is given by

$$\frac{J_p}{J_w} = e^{[(\mu(E)/\rho)_w\rho_w - (\mu(E)/\rho)_p\rho_p]t} \equiv Y^t. \quad \text{(A2)}$$

The fractional difference between the ratios, δ, indicates the size of the effect on J_p/J_w as t is increased or decreased by a factor f. Thus,

$$\delta = Y^{(tf-t)} - 1. \quad \text{(A3)}$$

The Monte Carlo calculations were based on a cylinder with a radius of 45 mm, which is a general radius for a 1-litre bottle, and a height of 157.18 mm to give a volume of 1 litre. The average path length was calculated to be 43.8 mm. To gauge the effect of t being different from this value in practice, calculations were made with $f = 0.5$ and 2. The results are presented in Table 2.

Table 2
The minimal effect on the relative γ-ray escape probability, J_p/J_w, of changing the path length is demonstrated for a range covering a factor two over the energy range of interest

Energy (keV)	Escape probability for $t = 43.8$ mm		Fractional difference δ in J_p/J_w (%)	
	Polymer, J_p	Water, J_w	$f = 1/2$	$f = 2$
100	0.533	0.536	0.3	−0.6
600	0.698	0.701	0.2	−0.4
1500	0.787	0.789	0.1	−0.3

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