

CHAPTER 17

Photon Scattering Effects in Heterogeneous Scintillator Systems

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SUMMARY

This paper describes a new experimental approach that reveals the individual contributions of sample geometry and scattering phenomena in heterogeneous flow-cell detectors. The experimental detector responses obtained using scintillating polystyrene beads with optically smooth surfaces are compared with those obtained using similar beads with highly diffuse surfaces. These comparisons are carried out for both alpha- and beta-emitting nuclides. The experimental detection efficiencies are compared to Monte Carlo simulations of the detection process. Also, a new technique will be described for the fabrication of scintillating beads.

INTRODUCTION

Flow cell scintillation detectors are used extensively for monitoring alpha- and beta-emitting nuclides in flowing aqueous or organic streams. Major applications of such cells include liquid chromatography detectors, in-line process monitors, and a variety of environmental measurement and control devices.

For low-energy emitters, two quite different approaches are used: the heterogeneous and the homogeneous flow cell. Both, however, use a scintillation process. Homogeneous flow cell systems operate by mixing a suitable liquid scintillator with all or a portion of the flowing stream. Several mixing and flow control units are used to establish stable, fixed measurement conditions. The

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cell is optically coupled to one or two photomultiplier tubes which are used to detect the scintillation output. Although this type of device can exhibit high sensitivity, it suffers from a number of problems: it uses large amounts of expensive liquid scintillator, it must provide safe disposal of its scintillator effluent, its quenching effects are unstable and unpredictable, it is difficult to maintain (mechanical and reagents), and its resolution is often poor. For these reasons the heterogeneous detector cell is usually preferred for most on-line measurement tasks.

Heterogeneous detector cells¹⁻⁴ are characterized by contacting the flowing liquid (to be measured) with a solid phase scintillator, most often in powder form. Such a flow cell must fulfill certain physical requirements for efficient operation. Obviously, detection geometry must be high in relation to the energy of the nuclide(s) to be measured. Cell volume must be as large as possible (for maximum sensitivity), consistent with the required temporal resolution of the application. The cell must be designed for minimal mixing and virtually no dead space to prevent any hold up. There may also be requirements for the shape of the cell, the surface to volume ratio, and the optical demands of coupling photodetectors.

The most efficient heterogeneous units have a tube or column that contains a solid scintillator (organic, plastic, or glass); the sample flows within the interstices of the scintillator particles or fibers. While the geometry of this device is not as good as that of the homogeneous detector, commercially available cells that use finely divided organic or glass scintillators show that it can count ¹⁴C at moderate efficiency. The tritium efficiency is, however, quite low. Other powdered materials used in cells of this type include europium-activated calcium fluoride and scintillating plastics.

Powdered scintillator detector cells also exhibit deficiencies characteristic of their design. For example, radiation generated by weak emitters degrades significantly in its passage from the sample liquid phase to the solid fluor. If the sample absorption path length is sufficiently large, and the radiation energy sufficiently low, total absorption takes place, and the event is lost to the system. Attempts to use even finer particles to improve the geometry have not improved detection efficiency as expected and routinely have made other cell characteristics worse. For example, back pressure of fine powder cells can exceed the working limits of conventional flow systems. Also, such cells with their high surface to volume ratio exhibit strong and sometimes irreversible memory effects.

Rucker et al.^{5,6} have attempted to overcome these difficulties by designing a cell that uses aligned scintillator fibers rather than the usual powder. Back pressure and memory effects improved significantly, but detection efficiency increased only slightly over previous designs. However, the results of this work prompted the idea that photon scattering within the detector, in addition to the geometry parameter, was crucial in establishing the ultimate efficiency of these devices. While smaller fluor particles lead to improved geometry, they also generate increased light scatter. The reason for this is that most of the fine-

particle scintillators have very poor surface characteristics and simultaneously exhibit extensive scattering within the particles themselves. This scatter leads to elevated absorption of the generated photons with subsequent loss of pulse height, detection efficiency, and spectral resolution. Although it appears clear that both geometry and photon scatter can diminish detector performance, it is not obvious which parameter is most important in a specific application, nor has it been demonstrated how the effects of these parameters change with different cell designs. What is clear, however, is that attempts to optimize one of the parameters often result in a degradation of the other; small particle size scintillators usually exhibit maximum scattering. Practical flow-cell implementations are often a compromise between these two, conflicting optimization constraints.

On the basis of the above cited work and other work, it is clear that scintillation efficiency, geometry, and light collection are the major parameters that determine flow cell radiation response to low-energy emitters. It also appears that using conventional powdered materials for the solid scintillator cell phase cannot improve detector geometry and reduce photon scatter simultaneously. This apparent stalemate is unfortunate since improved flow cell detectors would have a broad range of important applications. Thus, while numerous different flow radiation detectors are used daily, throughout the world, for monitoring energetic nuclides, virtually none exist for low-energy emitters. This is particularly disturbing when one notes that many of these weak emitters have significant biological application.

In order to design better flow cell radiation detectors, it became clear that more fundamental information was needed about the effects of geometry and light scatter, and the relationships between the two. This investigation was initiated to hopefully develop such information.

EXPERIMENTAL

Equipment and Reagents

All scintillation measurements were carried out using a Packard Tri-Carb liquid scintillation counter, model 4530. This unit contains a low-resolution multichannel capability used solely for a visual display of the pulse-height spectrum. Two of the spectra shown in this paper are simply photos of this display. When detailed spectral information was needed, appropriate linear signals were taken from the Packard counter and fed to a Nuclear Data multichannel analyzer system. That system included all of the standard MCA input/output and spectrum storage features. As high resolution was not needed for these studies, data were collected in a minimal 128 channels.

The clear, polystyrene spheres (three size distributions) were synthesized in the Department of Chemistry, University of Tennessee, Knoxville. These spheres were processed with conventional scintillation fluors and organic sol-

vents to produce the scintillating beads used here. The ^{14}C test solution (as aqueous carbonate) was standardized by liquid scintillation counting using the NBS hexadecane as an internal standard. ^{241}Am (as nitrate, in dilute nitric acid, pH 2 to 2.5) was assayed via 2π gas counting and confirmed in a liquid scintillation counter. All other reagents and fluors used in this study were reagent or scintillation grade.

Monte Carlo calculations were carried out on three different personal computers that all used the conventional MS-DOS operating system. Each computer was fitted with a numeric coprocessor chip (8087 or 80287) to speed the large number of floating point calculations simulation requires. Source code was written in Turbo Pascal (Borland International) that was compiled to executable files using the Turbo compiler, versions 3.01 and 4.0.

Preparation of Scintillating Beads

The untreated polystyrene beads had certain physical and optical properties that were crucial to the success of this project. First, they exhibited an extremely clear internal structure that was virtually fracture free. Also, the surface of each bead looked mirror smooth. Finally, the majority of beads assumed an almost perfect spherical shape. The visual effect through an optical microscope was similar to looking at drops of water. Although there were some spheres that were undeniably poor in optical quality, their number was small. The removal of such beads did not seem to be a viable task.

The beads were received already divided into three size distributions. There were many more beads of the larger size; these were selected for the preliminary tests directed toward endowing the beads with efficient scintillating properties. It was known that the polystyrene beads, when placed in toluene, would swell to several times their dry size. An obvious first approach was to dissolve scintillation fluors in toluene, place the beads in this solution, let them swell, filter the expanded beads, rinse them with ethanol, and air dry them so they shrink to their original size. The idea was that the solid fluors trapped within the beads would serve as efficient scintillating centers when excited by ionizing radiation. After some experimentation with different fluors and different fluor concentrations, the soak/dry technique did yield efficient scintillating beads.

A 1 g portion of dimethyl-POPOP was added to 100 mL of toluene and was allowed to mix for 24 hr at room temperature. About 3 g PPO were added to the saturated solution and the mixing was continued for 12 hr. The doubly saturated solution was separated from the excess fluors by filtration. The polystyrene beads were allowed to soak and swell in this solution for about 12 hr. The swelled beads were separated by filtration, washed with several portions of absolute ethanol, and air dried. This was the procedure used to treat all of the beads used in this study. (Some tests carried out after the start of this work have indicated that scintillation efficiency of the beads could be improved slightly by incorporating naphthalene in the soak solution. However,

Table 1. Average Bead Sizes and Size Distributions

Size	Ave. Radius (μm)	Std. Dev. (μm)
Small	28.6	2.8
Medium	68	7
Large ^a	295	36

^aThis bead size was not used for any of the nuclide measurements. It was used during the bead processing phase and is reported here for completeness.

to keep results consistent, this was not done for any of the beads studied here.)

Samples of each size distribution were examined by scanning electron microscopy (SEM) to evaluate the range of sizes in each distribution and to reveal clearly the surface characteristics and bulk structure of the beads after treatment. The size data are shown in Table 1. Figure 1 is a $300\times$ photo of the 28.6 micron cut; the highly damaged bead is obvious.

Some of the measurements carried out in this study required surface alteration of the scintillating beads from very smooth to thoroughly diffuse. A piece of fine sandpaper (8×10 in) was glued to a piece of plate glass, rough side exposed. The sample of beads to be etched was placed on the sandpaper surface along with 1 to 2 mL of distilled water. A second piece of plate glass was placed on top of the beads and gently rotated by hand to work the beads

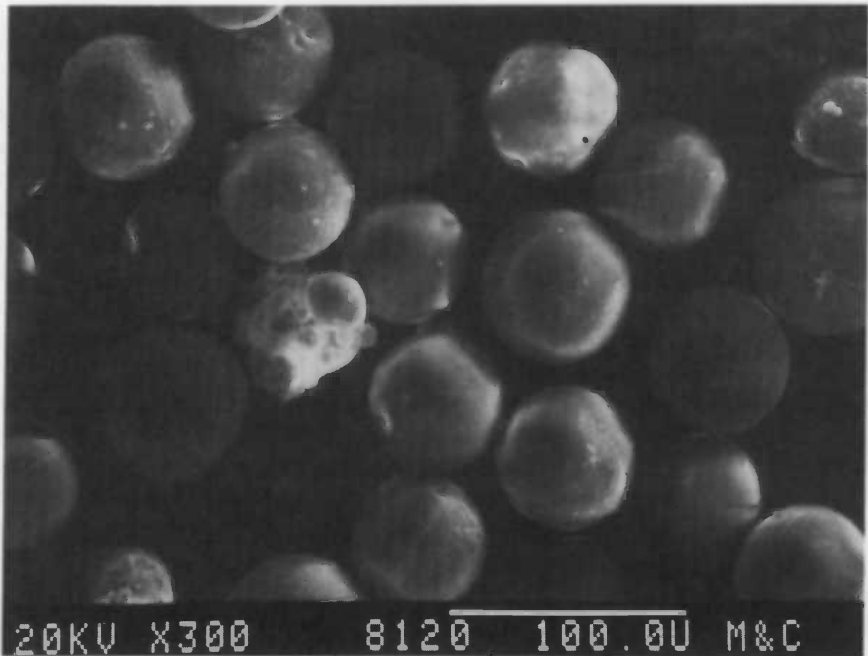


Figure 1. Photo ($300\times$) of 28.6 micron radius beads.

against the abrasive surface. As the beads are relatively soft, only two to three minutes of grinding were needed. The beads were washed into a small gas bubbler and separated from the sandpaper debris by flotation. The beads were inspected with an optical microscope; the surfaces were sufficiently etched such that it was not possible to see inside the beads. Also, no changes in the bead size could be discerned, although this was not rechecked with SEM photo.

Radionuclide Measurements

All activity measurements using the scintillating beads were carried out using an assembly similar to that shown in Figure 2. A glass tube of approximately 5 mm. diameter was cut to an appropriate length and flame sealed at one end. A small amount of white, room-temperature curing silicone rubber was placed on the inside bottom of a standard LSC glass vial. The sealed end of the tube was placed in the center of the vial and pressed into the rubber. The silicone was allowed to cure for 24 hr. For use, a selected sample of scintillating beads was transferred into the central glass rod and vibrated to aid packing. The activity to be measured was pipetted onto the beads. Water was added to the space between the vial and rod (to act as a light coupler), the vial was capped, and the assembly was gently centrifuged to draw the sample into the beads and eliminate air voids. This device was transferred to the Packard instrument for counting.

The Monte Carlo Simulations

Spheres of uniform size can be loaded into a container in two different close packed arrangements of identical efficiency: hexagonal and face centered cubic. In both cases, the spheres fill about 74% of the container, which leaves 26% void volume. It is interesting to note that 74% is not the maximum volume of space which can be occupied in the packing of spheres, although it is the maximum for symmetrical periodic arrangements. For irregular packing it can be shown that the maximum must be less than 78%.

Although crystallographic studies tend to focus on the arrangements of packed spheres, this investigation gives major importance to void geometry. Spheres that are hexagonally close packed create a "unit" void that is illustrated in Figure 3. The shaded portion is the void created by four spheres in two layers having mutual contact. When another layer of spheres is added (three total layers), the total void created is made up of two unit voids as seen through a single plane. All of the total voids in hexagonal close packing are of this type. Cubic close packing exhibits a symmetry that requires four layers rather than three. The effect on the void structure is that two different arrangements of the unit void are created. These are usually referred to in the literature as tetrahedral and octahedral interstitial holes. Both hole structures must be considered in the cubic pack simulation.

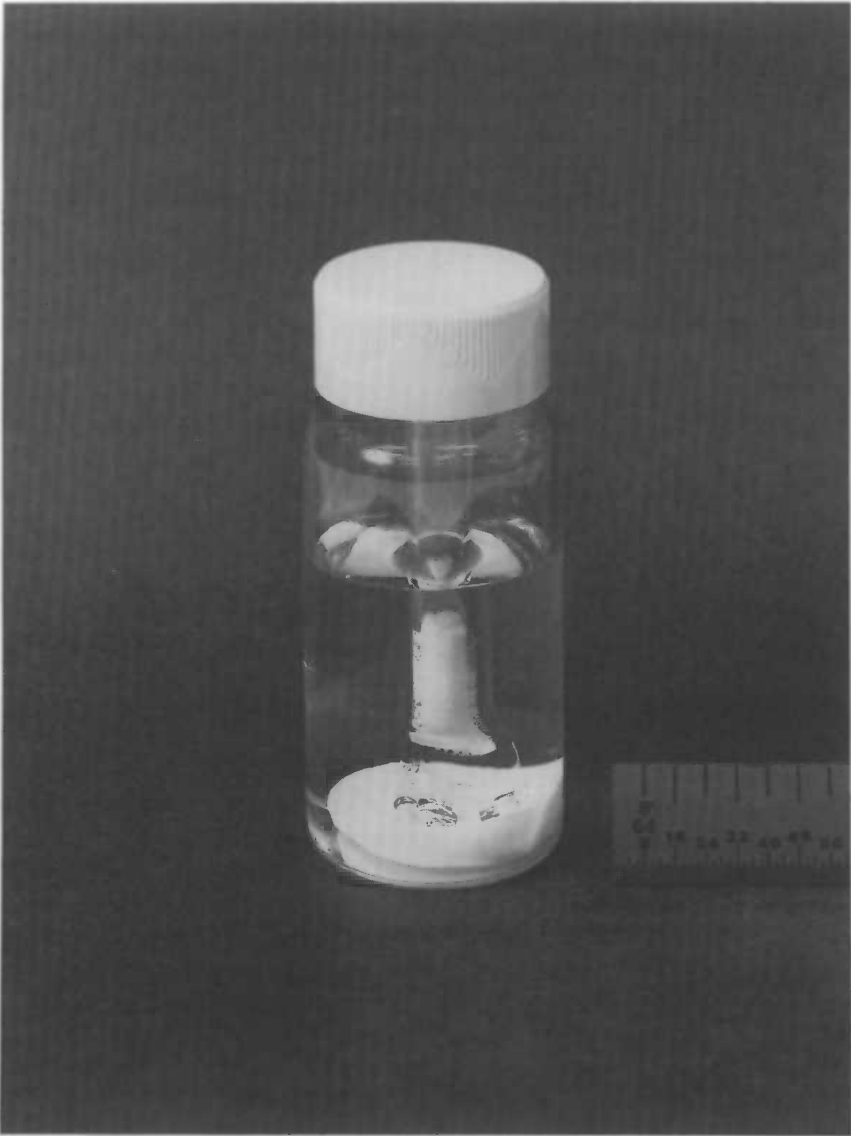


Figure 2. Counting assembly using scintillator beads.

The Monte Carlo simulation is designed to answer the following question: if scintillating spheres are close packed and if a liquid containing a radioactive emitter fills the void volume, what fraction of the decay particles are expected to reach the solid spheres? This is, of course, the geometry. Several factors must be considered in designing the simulation. These include:

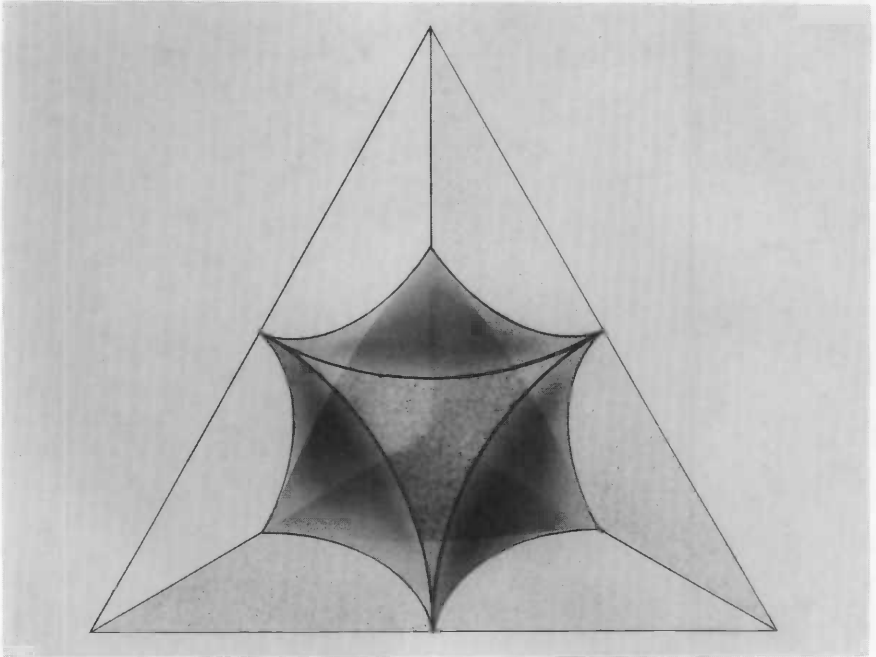


Figure 3. Diagram of void volume in hexagonal close packed spheres.

1. the emitted particle (alpha or beta)
2. the decay energy
3. range-energy relationships and absorption characteristics
4. the absorber composition
5. the sphere size
6. the detailed geometry of the voids

Four major simulations (two different but related programs) were used to develop geometry information as a function of sphere size. These were for ^{241}Am alphas and ^{14}C betas for both the hexagonal and cubic close packing arrangements. After the appropriate program is loaded, the user is asked to supply: (1) the decay energy (an average of 5.46 MeV was used for ^{241}Am , (2) the absorber density and effective atomic mass, (3) the hexagonal or cubic close packing, and (4) the number of decay events to evaluate (2000 to 5000). At this point the simulation starts and continues until the final result is obtained.

The geometrical aspects for both alpha and beta simulations are very similar. Using a fixed coordinate system, a random point is selected and tested to verify its position within the liquid phase (the void volume). This point is used as the origin of the decay event. Next, a random direction is selected to create a linear displacement from the origin point. Although these two operations appear to be relatively straightforward, much of the program run time is used

up here. The complex geometry and extensive spacial testing cause this. Also, for cubic packing, even more verification must be carried out. Processing from this point is quite different for alphas and betas.

Simulations of alphas are simplified by two important factors. Alpha radiation is monoenergetic and the emitted alpha particles travel in virtually straight lines. After the emission origin and random direction are determined, an alpha range corresponding to decay energy helps to create a vector from the event origin. The alpha range is calculated from experimental air measured alpha ranges combined with the Bragg-Kleeman⁷ rule (to correct for absorbers other than air). Finally, the vector is tested for intersection with any of the void-surrounding spheres. If intersection is not observed, and the alpha range could go to a second layer of surrounding spheres, than another algorithm is used to evaluate intersection. All events that intersect any sphere are totaled; the result is divided by the total of events tested. The outcome is the predicted geometry.

A convenient simplification can also be employed for evaluations of beta simulation response. Although betas are not monoenergetic and can travel in very convoluted paths, an empirical relationship that exists between E_{\max} and linear distance can be used to evaluate the response of an entire beta spectrum. This requires that the maximum beta range of the simulated nuclide be sufficiently long to allow at least some intersection of the beta energy distribution (from the origin of the decay event) with the solid scintillator. The technique used is described in detail in Rucker *et al.*;⁶ the geometry studied, however, is quite different from that examined here. After the degree of intersection of each beta distribution is calculated, the individual percent values are averaged to predict the geometry.

RESULTS AND DISCUSSION

The first series of tests were designed to evaluate the basic quality of the scintillating beads. The two major factors involved are photon yield and photon transmission. The baseline values of these parameters are important. If the bead emission and transmission characteristics proved substantially inferior to a quality liquid scintillator, it would have been necessary to devise an alternate procedure for bead preparation.

Aqueous samples of the ²⁴¹Am tracer were mixed with different 15 mL aliquots of Insta-Gel and Opti-Fluor liquid scintillation cocktails contained in standard size vials. The tracer was also added to bead scintillator samples contained in the assembly described above. A pulse-height spectrum was obtained for each sample. Figure 4 shows such a spectrum obtained in Insta-Gel and Figure 5 a spectrum using 68 micron beads. The marker is at the same position in both spectra.

Although the bead spectrum shows considerable energy degradation due to absorption in the liquid phase, it is quite clear that the full energy peak is both sharper and at a higher pulse height than that seen in the liquid scintillator

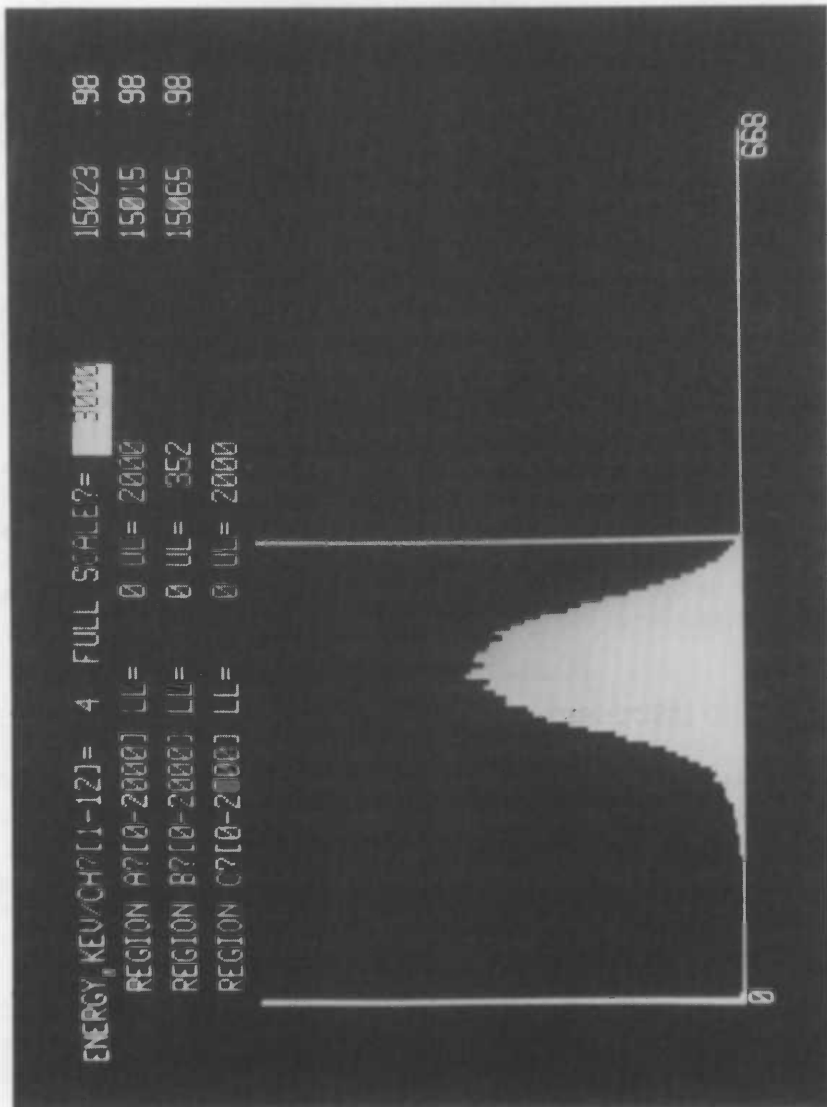


Figure 4. Pulse-height spectrum of ²⁴¹Am in Insta-Gel.

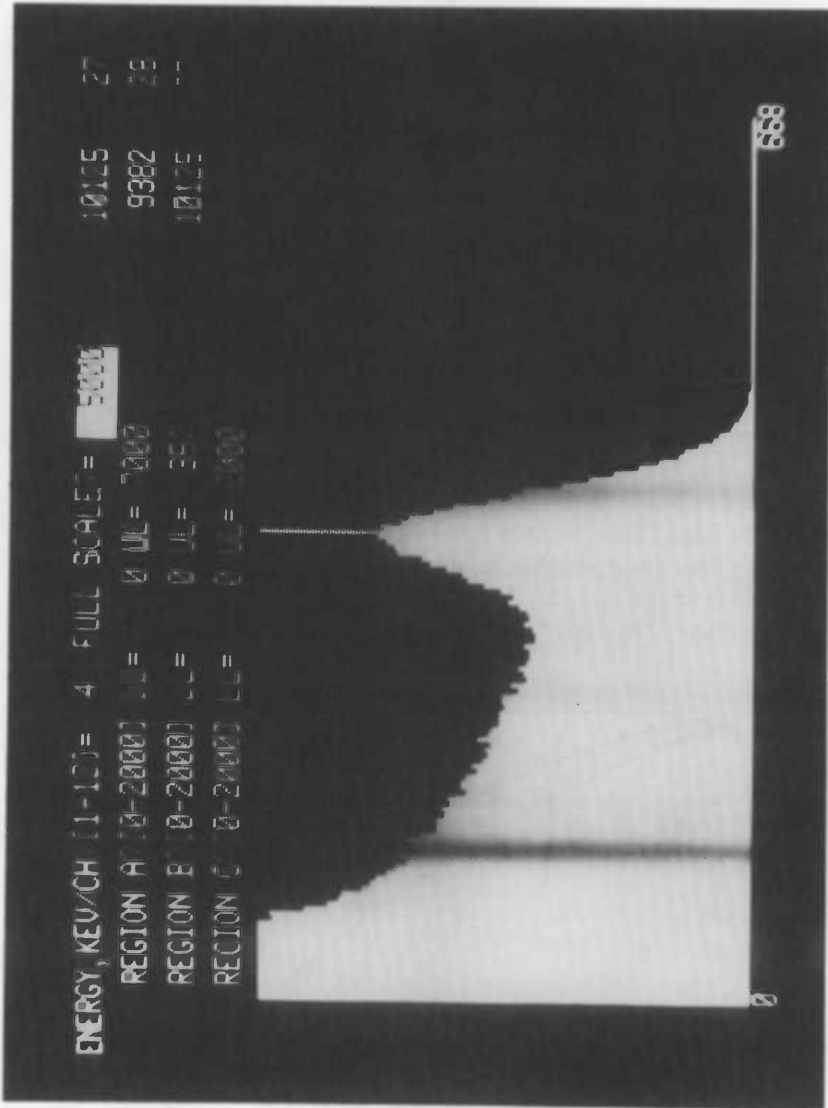


Figure 5. Pulse-height spectrum of ^{241}Am using 68 micron beads.

spectrum. This was a most surprising result. It is not really possible to determine the individual quantitative effects of photon yield and transmission from these data, but I believe it is fair to conclude that the bead scintillators do extremely well in both of these parameters. One might argue that the bead results could arise from an outstanding photon emission combined with a somewhat attenuated photon transmission characteristic. While such a conclusion might be suggested, the observed optical properties of the beads clearly argue against it.

Similar tests were made with ^{14}C tracer. Again bead results were very good, although they were more difficult to observe because of the continuous nature of the beta spectrum.

Figures 6 and 7 illustrate the results obtained with the four Monte Carlo simulations. The second order regression lines in both figures are only plotted to show point continuity. It is not suggested that they represent an analytical solution to the simulation. As might be expected, all four of the simulations tend to a geometric efficiency of one as the sphere radius goes to zero. The responses of the alpha regressions show less sensitivity to sphere radius when the radius is small; the opposite is true for the ^{14}C beta simulations. The values obtained for cubic packing are less than those obtained for hexagonal packing for both nuclides.

The Monte Carlo simulations only give an expected geometric efficiency for a given sphere size. This efficiency can be thought of as the maximum detection efficiency that could possibly be observed in the system. Of course, in real counters, results are always less than the geometry because of factors such as the minimum energy required for photon generation, presence of nonradiative

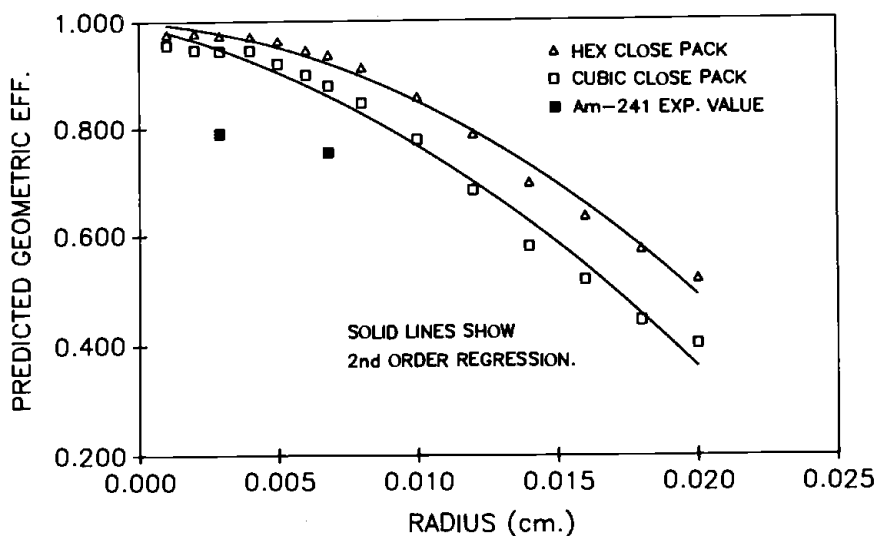


Figure 6. Monte Carlo simulation of ^{241}Am and experimental data.

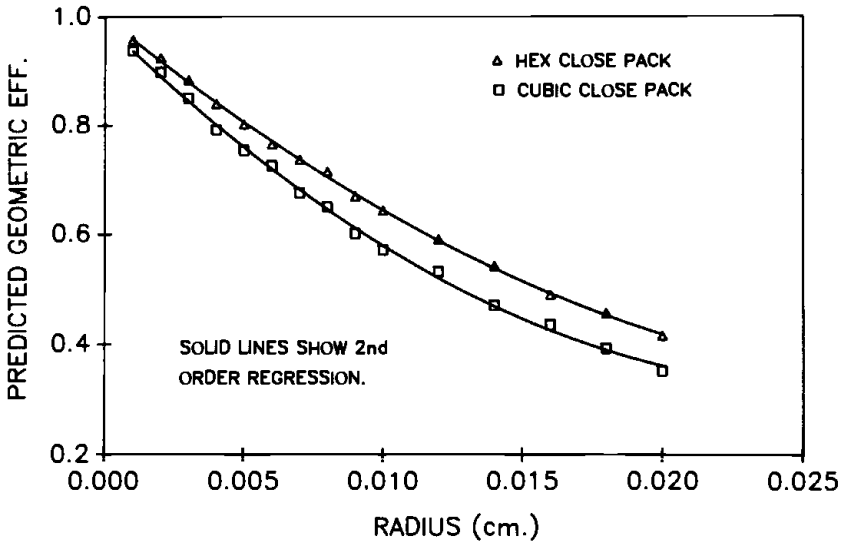


Figure 7. Monte Carlo simulation (linear plot) of ^{14}C .

absorption processes, photon collection efficiency, and electronic thresholds in the counter. Also, it would be unreasonable to assume that close packing would be of one type only or that close packing could even be achieved throughout the majority of detector volume. However, if all of these factors remain essentially constant within a given system, the validity of the simulation can be verified by comparing an experimental curve with the appropriate simulation. A shift to lower efficiency would be expected but the shape of the curves should match.

Figure 6 shows two experimental points for ^{241}Am obtained with two different size smooth-bead samples. While it is not possible to verify the curve with only two points, the experimental values do exhibit the trend of the simulation. Figure 8 shows the ^{14}C simulations replotted in a semilog format along with four experimental points. The average experimental values for the smooth beads lend additional support for the simulation results. Figure 6 also includes data obtained with etched beads that exhibit a high degree of light scattering. Along with the drastic drop in counting efficiency, one sees a surprising reversal in the response as a function of bead size. Table 2 summarizes the counting results for data shown in Figures 7 and 8.

CONCLUSIONS

Monte Carlo simulations for heterogeneous flow cell radiation detectors (fabricated with spherical scintillator beads) show somewhat different geometric response functions for alpha and beta emissions. For alpha radiation, the

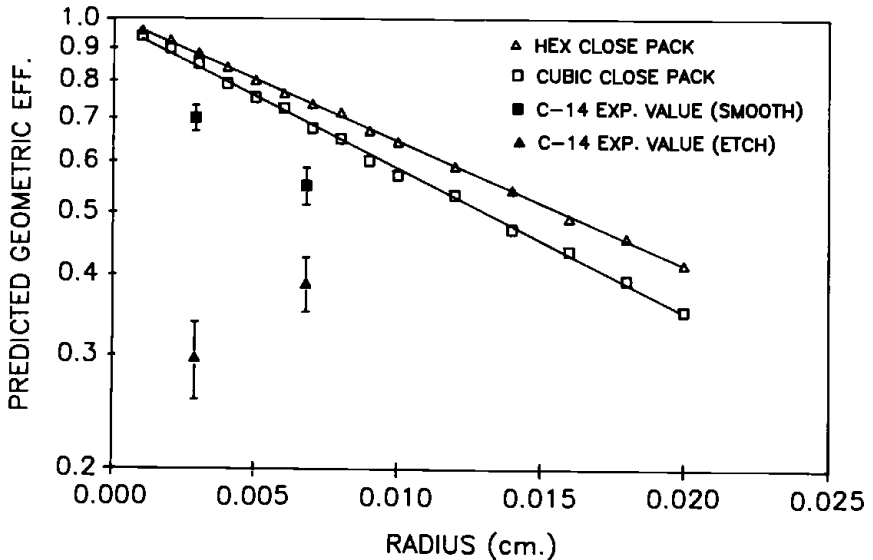


Figure 8. Monte Carlo simulation (semi-log plot) of ^{14}C and experimental data.

response is relatively flat up to about a 40μ bead radius. This implies that particles smaller than this value probably will not materially improve alpha detection efficiency in practical implementations. The experimental data observed with ^{241}Am support the shape of the observed simulation function which further strengthens the idea that ultrasmall particles are not needed. The overall maximum pulse height and spectral resolution (not counting efficiency) exceed that obtained with a typical homogeneous cocktail for aqueous samples.

Conversely, the ^{14}C response functions exhibit an increasing slope as bead radius drops. Obviously, much more attention must be directed toward bead size for low-energy beta emitters. The experimental data with smooth and rough bead surfaces demonstrates, however, that significant photon scattering is an extremely important limitation in heterogeneous cells. The minimal conditions investigated in this study show that these cells may be 3 to 4 times more sensitive to photon scatter and absorption than to geometry. The conclusion is

Table 2. Counting Efficiency of ^{241}Am and ^{14}C With Scintillating Beads

Nuclide	Bead Radius (μm)	Bead Surface	Counting Eff. (ave.)
Am-241	28.6	Smooth	0.79
Am-241	68	Smooth	0.75
C-14	28.6	Smooth	0.70
C-14	68	Smooth	0.55
C-14	28.6	Etched	0.30
C-14	68	Etched	0.39

clear that the development of high-sensitivity heterogeneous flow cell detectors may ultimately be determined more by the optical rather than physical properties of the scintillator cell.

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