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FLUORESCENT ION EXCHANGE RESINS*

by

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FLUORESCENT ION EXCHANGE RESINS

INTRODUCTION

The development of a scintillating, cation exchange resin has been previously reported.(1,2) However, it will be helpful to review briefly the reasons for undertaking the synthesis of such a resin.

The many and varied applications of ion exchange resins are well known to technical people from academic to industrial laboratories. Two very important properties of ion exchange resins are their ability to concentrate ions from aqueous solutions of widely varying chemical conditions and their selectivity for certain elemental and complex, ionic species. The physical and chemical stability of these resins further contribute to their utility in analytical, synthetic and process chemistry.

Plastic fluors are less widely known and used, but their applications have greatly increased in their short history since 1950.(3) Already organic scintillators have been routinely employed in both physical and chemical measurements in the detection of alpha, beta, gamma and neutron particles. Although crystal scintillators give a better pulse height resolution and a greater light output, the relative ease of preparation, low cost of materials and the wide range of sizes and shapes of plastic scintillators favor their use in many applications.

Thus the combination of ion exchange and fluorescent properties in one resin should facilitate radiochemical procedures. The principle of concentrating radioactivity from aqueous solutions of low specific activity into a small volume allows for a higher detection efficiency. Further chemical procedures are not required for counting after the radioactivity is adsorbed on the resin since the " activated resin" can serve as the prepared sample. With the appropriate apparatus for monitoring purposes, the counting can take place as the activity is being integrated.

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(1) Heimbuch, A. H., Trans. Am. Nuclear Soc. 4, No. 2, 251 (Nov. 1961).
(2) Heimbuch, A. H., Gee, H. Y., U. S. Atomic Energy Commission Report, NYO-9138 (April 1962).
(3) Schorr, M. G., and Torney, F. L., Phys. Rev. 80, 474 (1950).

EXPERIMENTAL

After attempts were made to introduce ion exchange groups into existing plastic phosphors, it became apparent that a cross-linked polymer matrix would be the most desirable, if not necessary, for a scintillating, ion exchange resin. The linear polymer matrix of commercial phosphors made them unsuitable because of the unstability toward reaction media and the voluminous swelling of the resultant product in water. A suspension-type polymerization process was then developed whereby a fluorescent, spherical bead was made which contained the appropriate fluors dissolved in solid solution in cross-linked polyvinyltoluene. The plastic bead was subsequently treated chemically to introduce the anion, or cation, exchange groups.

Synthesis of fluorescent, ion exchange beads.

The first step in making either the anion or cation exchange resin was the synthesis of a fluorescent, plastic bead. The bead was made by a suspension-type polymerization process which first involved the dissolution of the appropriate fluors in a monomeric solution of vinyltoluene (or styrene) and divinylbenzene. After heating, with stirring, to 100-110°C, the solution was transferred to an aqueous medium at 80°C where the polymerization took place as an oil-in-water suspension. The details of this procedure have been previously described.(2) The resulting resin was an optically clear, scintillating, spherical bead in the size range of 0.1 to 1.0 mm in diameter.

The chemical composition of the bead is schematically illustrated by structural formulae in Figure 1. The monomer mixture was composed of vinyltoluene-divinylbenzene-ethylvinylbenzene in a molar per cent ratio of 83:10:7. Divinylbenzene was obtained in 55% purity which contained ethylvinylbenzene to the extent of 35%. All monomers were predominantly the meta and para isomers. The divinylbenzene served to cross-link the polymer chains which gave greater chemical and physical stability to the resin.

The primary solute (fluor) used was p-terphenyl at a concentration of 3.5 per cent the weight of the monomers. The waveshifter, or secondary solute, was used at a level of 0.1 per cent the weight of the monomers. Initially, 1,4-bis-[2-(5-phenyloxazolyl)]-benzene, known as POPOP, was used as the waveshifter for the cation resin. However, 9,10-diphenylanthracene was later used for both cation and anion resin synthesis since POPOP was not stable to the reaction

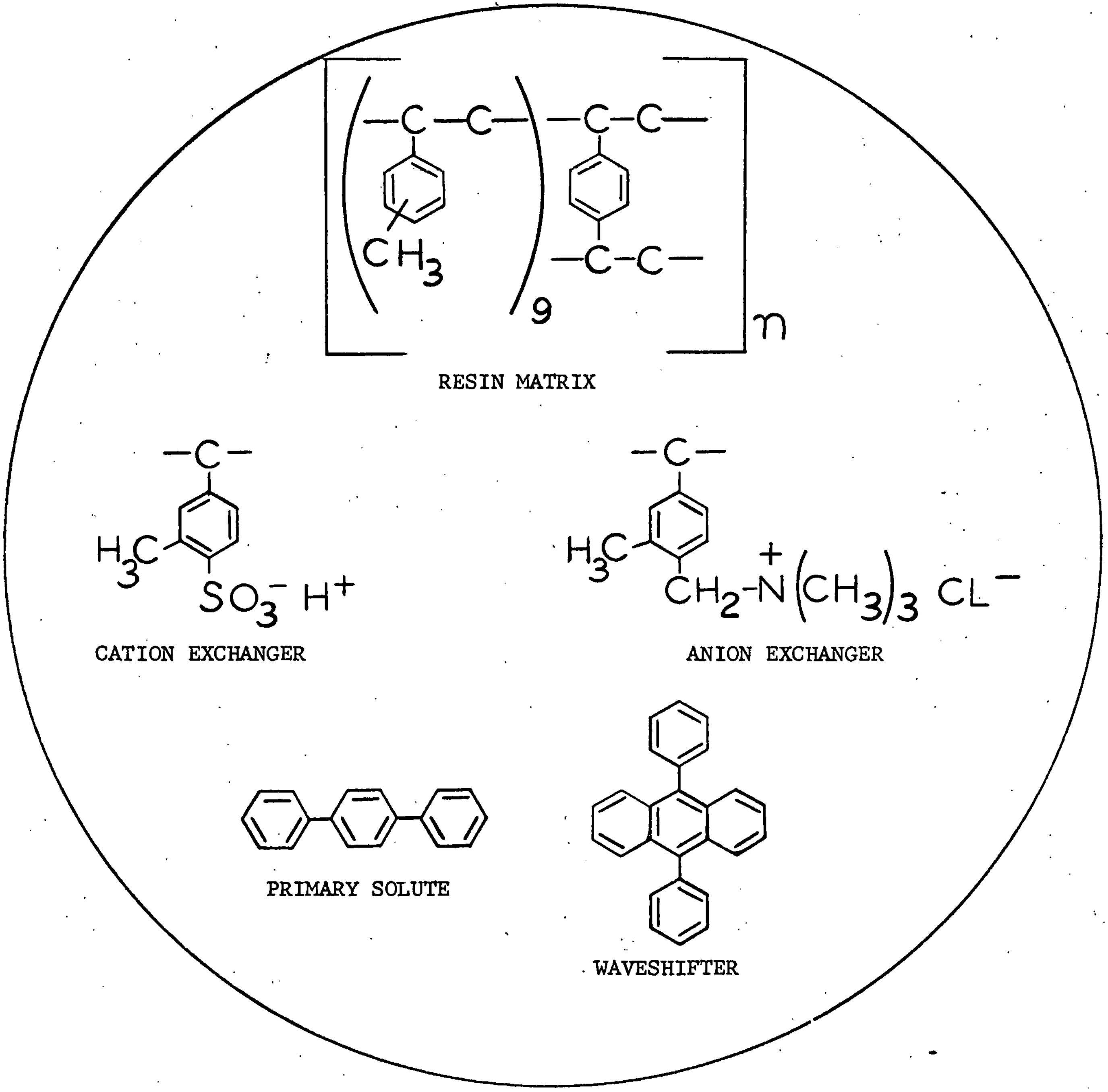

FIGURE 1. BFAD COMPOSITION

media necessary for anion resin preparation. The light output of resin containing diphenylanthracene was nearly the same as that with POPOP, and it had the advantage of containing no functional groups such as the tertiary ring nitrogen in POPOP which could enter into ion exchange reactions.

The second step in the synthesis of the ion exchange resin was the chemical treatment of the fluorescent bead with the appropriate reagents to introduce the ion exchange groups. The bead was not swelled with organic solvents before introducing the ionizing groups as is done in the preparation of commercial resins.(4) There were two main reasons for this: (1) The sulfonating medium would destroy or greatly reduce the light output by reaction with the phosphor, and (2) A porous bead would contain many solid-liquid interfaces which would tend to trap the light. Thus, the ion exchange groups were introduced on the bead surface and sub-surface to a depth of about 10 microns for a 0.5 mm diameter bead (based on calculations from ion exchange capacity).

The cation resin was made by using a common sulfonation medium, 5% fuming sulfuric acid containing 1% Ag_2SO_4 by weight as a catalyst. The reaction temperature was kept at 5°C for 48 hours and then allowed to rise to and remain at room temperature for several hours--depending upon bead stability with respect to light pulse height. Exchange capacities of 0.01 to 0.05 milliequivalents per gram of resin were attained by this method. The pulse height decreased as exchange capacity increased, and so one is limited to the exchange capacity that can be attained by this method of sulfonation.

The anion resin was prepared by chloromethylation of the bead followed by amination. A modified procedure of those found in the literature (5,6) was used. Chloromethyl methyl ether, with $AlCl_3$ or $SnCl_4$ as catalyst, was employed as the chloromethylating agent. The chloromethylated beads were then treated with 25% methanolic trimethylamine to yield the quaternary ammonium derivative. Anion exchange capacities of 0.10 milliequivalents per gram were obtained with only slight reduction in pulse height. Details of this procedure have been described.(7)

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(4) Boyd, G. E., Ann. Rev. Phys. Chem. 2, 312 (1951).
(5) McBurney, C. H., U. S. Patent 2,591,573 (April, 1952).
(6) Pepper, K. W., Paisley, H. and Young, M., J. Chem. Soc. 4097 (1953).
(7) Heimbuch, A. H., U. S. Atomic Energy Commission, Third Progress Report on Contract No. AT(30-1)-2885, November, 1962.

The ion exchange capacities of the resins were measured using radioisotope dilution techniques. A solution of Co^{60} of a standardized specific activity (dpm Co^{60}/mg Co carrier) was used to determine the exchange capacities of both anion and cation exchange resins. For the cation resin, the Co was adsorbed from a nitrate solution at pH 3. The chloride anion complex of Co was adsorbed from concentrated HCl solution on the anion resin. The activated resin was then counted in a NaI (Tl) well-type crystal, and the exchange capacity was calculated from the Co^{60} count rate and the specific activity of the standard solution.

A standardized solution of Cl^{36} was also employed to determine the anion exchange capacity. Cl^{36} was adsorbed from a NaCl solution with the resin in the hydroxyl form. The activated resin was then transferred to a transparent plastic cup which was optically coupled to a photomultiplier tube in a light-tight system connected to a pulse counter. Further details on these methods have been reported.(2)

Scintillation measurements

The relative pulse height of each resin preparation was measured to determine the effects of various synthesis parameters and to make comparisons between batches. An optically clear container for the resin was machined from acrylic plastic rod to fit snugly over the face of a 2 inch diameter, photomultiplier tube as shown in Figure 2. The plastic cup was coupled to the photomultiplier tube, in a vertical position, with optical grease (Dow-Corning QC-2-0057).

A one gram quantity of resin was placed in the cup and covered with 5 ml of water. The beads were evenly dispersed on the bottom of the cup to a depth of about 2mm by gently rotating the cup, in place, on the phototube. A 1-inch metal disc, gamma source of Cs^{137} (Ba^{137}) was centered on a plastic lid which fit over the cup to maintain geometric reproducibility. This was used as a constant source of excitation for the scintillating resin samples.

The signal from the photomultiplier tube was passed through a linear amplifier into a single channel, pulse-height analyzer. The lower level of the energy spectrum was started just above the phototube noise since most of the pulses were near this level. Curves of the integral pulse height distribution were made on semi-log paper. Relative comparisons were then made at that voltage (channel) which contained 10 counts per minute. This is illustrated in Figure 3 where several waveshifters have been compared.

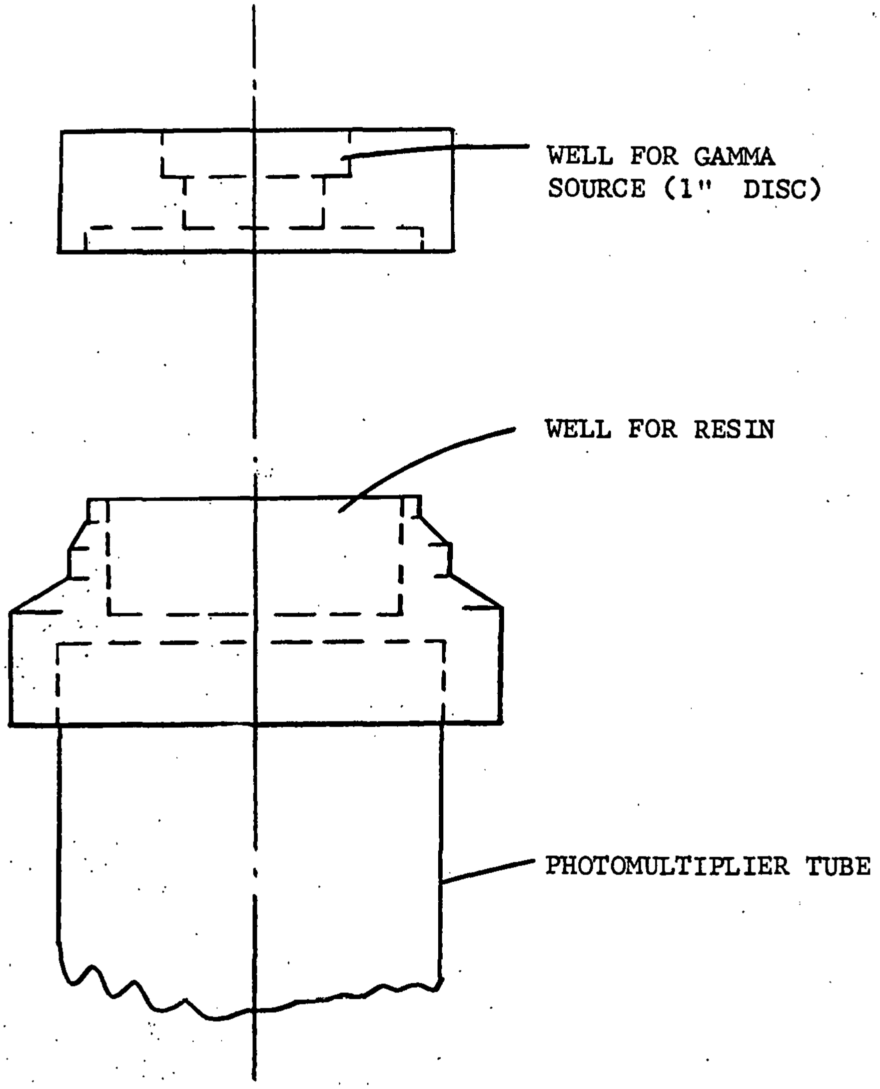

FIGURE: 2 TRANSPARENT PLASTIC CONTAINER FOR SCINTILLATING, ION EXCHANGE RESIN

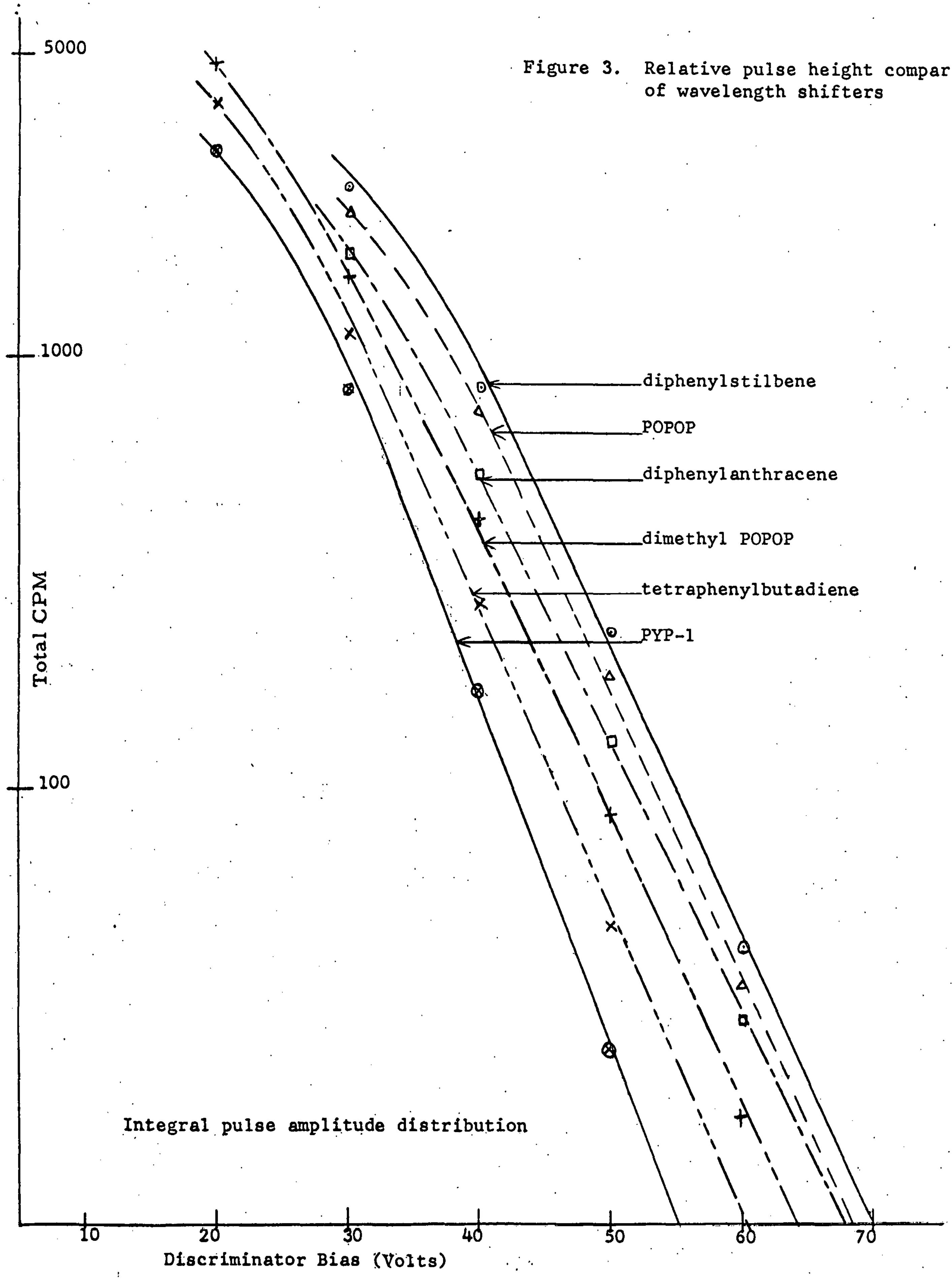

Figure 3. Relative pulse height comparisons of wavelength shifters

The term " pulse height" as used in this report is not the same as the pulse height one obtains from a NaI or anthracene crystal. The beads are coupled to the photomultiplier tube through water, plastic and optical grease; whereas a NaI crystal is coupled directly by optical grease. Another important distinction is that the beads do not respond as a single crystal. A third difference lies in the geometrical shape of the bead which captures more of its own light by internal reflection. Even though these differences existed, the response of the beads in this system provided convenient and reproducible pulses for relative comparisons.

A fluorescence spectrum was not taken since the relative pulse height of the resin containing 9,10-diphenylanthracene compared favorably with other resin preparations containing POPOP or p,p'-diphenylstilbene. Also, the work by Basile and Weinreb(8) showed that a 0.07% concentration of 9,10-diphenylanthracene in polystyrene gave a fluorescence spectrum with maximum light output at a wavelength of 430 mμ. In addition, their work showed the fluorescent decay time to be of the order of 10^{-8} seconds; although this may not necessarily be the same for the scintillating resins.

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(8) Basile, L. J. and Weinreb, A. J., J. Chem. Phys. 33, 1028 (1960).

RESULTS AND DISCUSSION

Alpha and beta response spectra

There was no resolution of the Cs^{137} gamma ray energy with respect to a "peak" of pulses in a given energy range when a differential spectrum was taken. Instead, a curve was obtained which showed a high number of pulses in the lower energy range which monotonically diminished in the higher energy levels.

When a differential spectrum was taken of the resin response to a beta emitter, the curve slightly approached the semblance of a falling "Compton" edge. This is shown in Figure 4. However, the differential spectrum for an alpha emitter showed a definite peak with a hill to valley ratio of 5:1 which is shown in Figure 5. These spectra were taken using a 256 channel analyzer.

Counting efficiencies for alpha and beta emitters

The chemical conditions of ion exchange which apply for the strongly basic, quaternary ammonium exchangers and for the strongly acidic, aryl sulfonic exchangers also apply to the fluorescent, anion and cation exchangers respectively. Therefore, the voluminous literature on uses of the commercially available ion exchange resins can be of great value in predicting uses for the scintillating resins.

Counting efficiencies of both the anion and cation resins were determined for several radioisotopes. Two counting systems were used: (1) the plastic cup-photomultiplier tube with a single channel analyzer as described above, and (2) a 1.5 dram (6 ml), screw-cap, glass vial (Figure 6) which was counted in a refrigerated liquid scintillation counter (Tracerlab LSC-20), schematic in Figure 7. The resin samples counted in the plastic cup were covered with aqueous solutions. The resin counted in the glass vial was immersed in toluene, or occasionally in 50% aqueous methanol.

The radioactivity was adsorbed on 1 gram samples of resin in small ion exchange columns (tubulated test tube 15 x 75 mm). A small dacron plug was used to hold the resin in the column and was inserted from the bottom of the column. This dacron plug was easily removed with a forceps when transferring

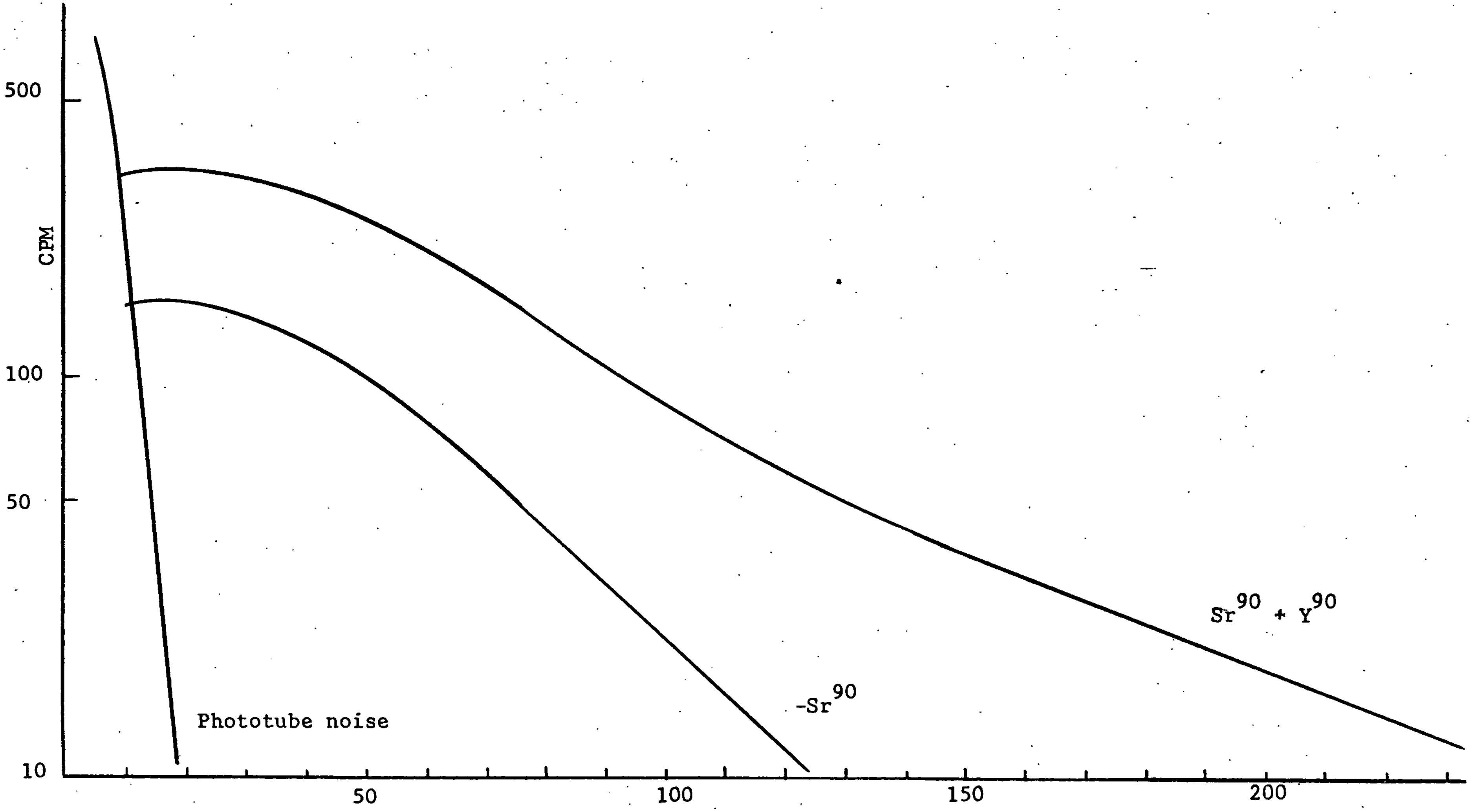


FIGURE 4

BETA RESPONSE CURVES OF SCINTILLATING, CATION RESIN

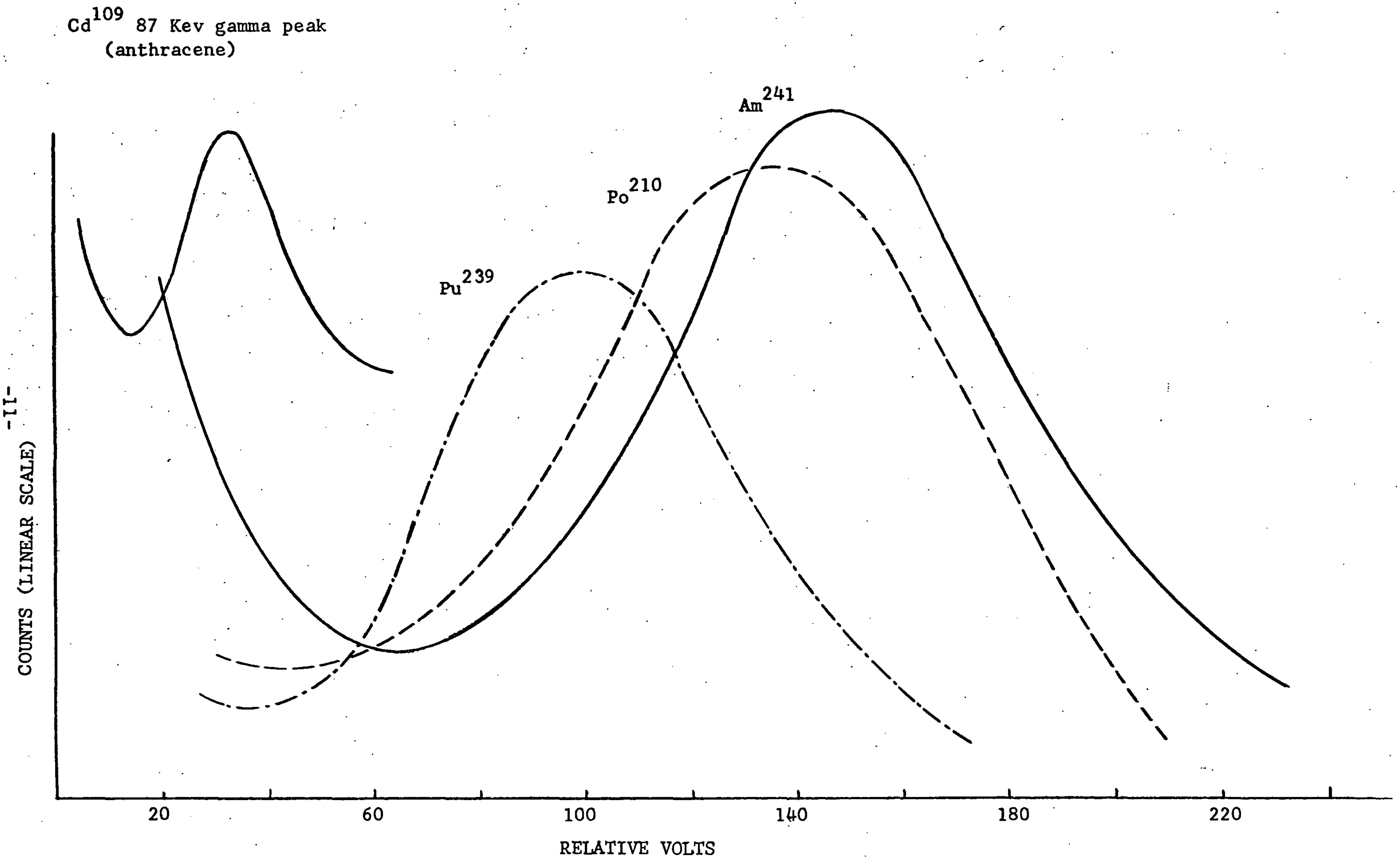
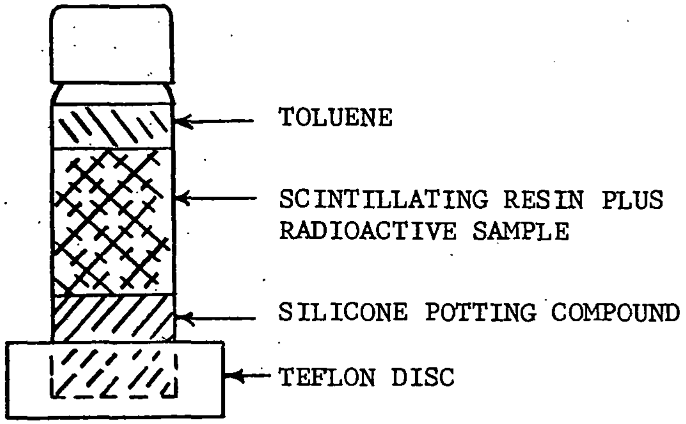


FIGURE 5

ALPHA RESPONSE CURVES OF SCINTILLATING, CATION RESIN

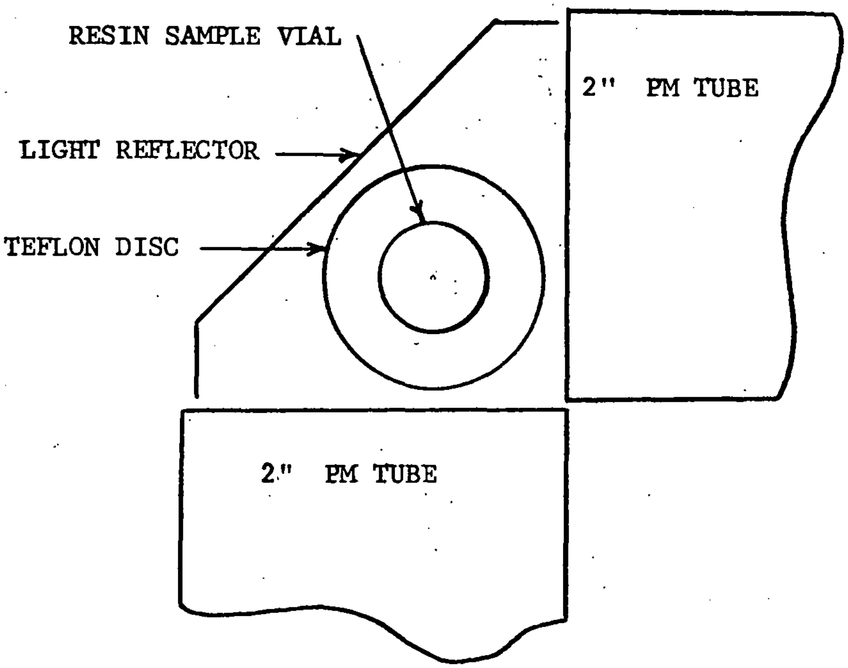
(Total counts in peaks are not to be compared)

FIGURE 6



SAMPLE PREPARED FOR LIQUID SCINTILLATION COUNTER IN 1-1/2 DRAM SCREW-CAP, GLASS VIAL

FIGURE 7



COUNTING ARRANGEMENT IN TRACERLAB LSC-20 LIQUID SCINTILLATION COUNTER (TOP VIEW) the resin to the plastic cup or glass vial. When transferring the resin to the plastic cup, the excess liquid was drained off, the dacron plug removed and the resin washed into the cup with 5 ml of an aqueous solution which would not remove the activity from the beads. The plastic cup was covered with aluminum foil, shiny side down, for improved light collection after coupling to the photomultiplier tube.

Before transferring the resin to the glass vial, the resin was washed with absolute methanol followed with toluene, and then transferred to the vial with toluene. If the radionuclide had been adsorbed by the resin from concentrated HCl solutions, then dry methanolic-HCl was used to wash the resin before washing with toluene.

The counting efficiencies for several alpha and beta emitters are listed in Table 1. The method of counting and particle energies are also given so that comparisons can be made in this respect.

Adsorption of I^{131} from milk

A practical experiment was performed to determine the efficiency with which the scintillating anion resin could remove I^{131} from milk. Raw milk was obtained from a cow which had been fed I^{131}. The collection efficiency of the scintillating resin was compared with a commercial anion exchange resin, Dowex 1 x 8, containing the trimethyl benzyl ammonium group.

Three grams of scintillating resin of 32-60 mesh size and containing 0.10 meq. per gram exchange capacity was compared with 2.5 grams of commercial resin of 100-200 mesh size containing 3.2 meq. per gram of resin. The flow rate of milk through the columns was maintained at about 2 $ml/cm^2/min$. The resins were first put in the chloride form with HCl and then washed with distilled water until nearly neutral. Nothing was added to the milk except toluene, as a preservative, to half of the samples. It was found that the scintillating resin with less than one-tenth the exchange capacity of the commercial resin removed the iodine from milk with equal efficiency. Furthermore, over seven times the volume of milk was passed through the fluorescent resin as was passed through the commercial resin. Table 2 gives a more detailed description of the experiment and the results. All resin samples were compared by transferring the activated resin to a 15 x 75 mm test tube and counting in a gamma well counter (NaI crystal).

TABLE 1. ISOTOPE COUNTING EFFICIENCIES USING SCINTILLATING ION EXCHANGE RESINS

ISOTOPE	MAXIMUM PARTICLE ENERGY	IONIC SPECIES ADSORBED	METHOD OF COUNTING	COUNTING EFFICIENCY
	(KeV)			
C^{14}	158	CO_3^{-2}	LSC*	35**
S^{35}	167	SO_4^{-2}	LSC	39**
Cl^{36}	714	Cl^-	LSC	85
		Cl^-	PC***	50
I^{131}	610	I^-	LSC	74
Sr^{90}	540	Sr^{+2}	PC	50
Y^{90}	2270	Y^{+3}	PC	71
	(MeV)			
Pu^{239}	5.15	$PuCl_6^{-2}$	LSC	77
		Pu^{+4}	PC	35-40
Np^{237}	4.79	$NpCl_6^{-2}$	LSC	70
Am^{241}	5.48	Am^{+3}	PC	40
Po^{210}	5.30	Po^{+4}	PC	40

*LSC glass vial in liquid scintillation counter.

**Some data has been obtained which indicates that the counting efficiency is over 50%.

***PC plastic cup with single channel analyzer.

TABLE 2. REMOVAL OF I^{131} FROM MILK

RESIN SAMPLE	VOLUME OF MILK (Ml)	TOTAL I^{131} ADSORBED (DPM)	I^{131} ADSORBED PER Ml OF MILK (DPM)
Commercial			
Dowex 1-a	100 at 25°C	404	4.0
Dowex 1-b	100 (+toluene) at 25°C	450	4.5
Dowex 1-c*			
Scintillation			
1-A	750 at 5°C	3444	4.5
1-B	740 of a ten-fold dilution at 5°C	341	0.46
1-C	500 +toluene at 5°C	2146	4.3

*Effluent from 1-C passed over commercial resin but no significant activity adsorbed <1%.

Stability of the resin

Effect of solvents. The resin has good stability toward alcohols and aromatic solvents such as benzene, toluene or xylene. However, the aromatic compounds do swell the bead and leach some of the fluor near the surface. The halogenated hydrocarbons also swell the bead as does acetone. Figure 8 shows the degree of swelling as effected by several solvents.

Toluene swells the resin more than the lower alcohols and acetone, but this does not have an adverse effect on the light output. The count rates for several samples have remained fairly constant for 30 to 60 day periods in toluene, as is illustrated in Table 3. A point of caution about organic liquids is the possibility of using a compound which not only swells the bead but also quenches the fluorescence, such as pyridine or nitrobenzene. However, even the use of trimethylamine, which is a strong liquid scintillation quencher(9), had little effect on pulse height reduction in the preparation of the anion resin.

Toluene-methanol. Anion and cation resin samples were loaded into columns and washed with toluene and absolute methanol in sequence. The resin was allowed to stand in toluene for 10 minutes and then rinsed with methanol. After 10 wash cycles the pulse height of each sample was measured. There was a slight reduction (~5%) in the pulse height of the anion resin, but none was observed in the cation resin. This treatment should simulate the " drying" of aqueous beads preparatory to their counting in toluene.

Regeneration studies. Samples of both the anion and cation resins were put through 50-cycle regeneration tests. The resin was loaded into an ion exchange column and treated sequentially with acid and base washes. The reagents used were 5% NaOH and 5% HCl which were employed alternatively with distilled water washes between each treatment. The anion resin did not show any decrease in pulse height, however, there was a 10% reduction in the pulse height of the cation resin. The cation resin contained POPOP, but it has not been determined if this was a contributing factor.

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(9) Kerr, V. N., Ott, D. G., Hayes, F. N., Int. J. Appl Rad. Isotopes, 1, 284 (1957).

FIGURE 8. SOLVENT SWELLING EFFECTS

Scintillating, anion resin

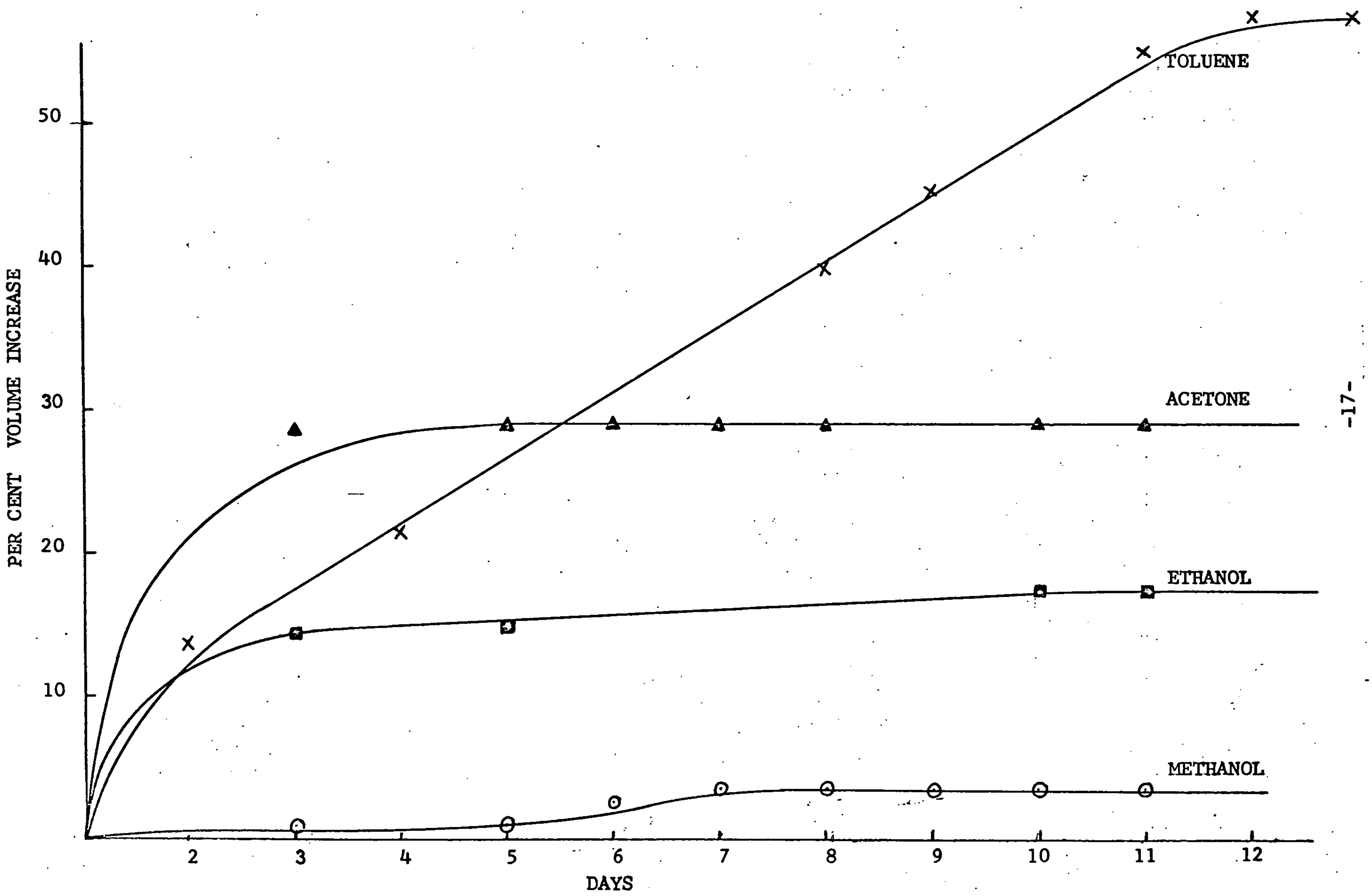

TABLE 3. ANION RESIN FLUORESCENCE STABILITY IN TOLUENE

ADSORBED ISOTOPE	COUNTING EFFICIENCY Initial (%)	Time Elapse (days)	Final (%)
Cl^{36} *	85.6	63	83.3
Cl^{36} *	84.6	63	83.2
Pu^{239} **	71.4	55	77.8

* Duplicate samples

** Single Sample

Inorganic reagents. The anion resin was not stable to concentrated HNO_3 for 10 minutes at room temperature. The resulting beads were yellow to amber in color with 50% loss in pulse height. When treated with 6N (25%) HNO_3 in a similar manner, the pulse height of the anion resin was reduced slightly, 5 to 10%.*

Anion resin was mechanically shaken with 10% aqueous hydrogen peroxide for 90 minutes at 25°C. The loss in pulse height was 5% or less. It is expected that the cation resin would show similar results toward the peroxide and nitric acid treatments. However, the aryl sulfonic group would be more stable than the trimethyl benzyl ammonium group to nitric acid, and in fact the cation resin has shown considerably more stability to 6N HNO_3. A 6N HNO_3 wash was one of the steps used to remove Ag_2SO_4 sulfonation catalyst.

Both resins have shown good stability to concentrated HCl and NH_4OH solutions. The stability to 5% NaOH has already been noted. The resin was also stable to boiling aqueous solutions which did not contain strong oxidants. The beads do not deform at 100°C, but they should not be heated to this temperature in the presence of oxygen.

Specific gravity

The resins have a specific gravity slightly greater than water. Beads with a diameter range of 0.3 to 0.5 mm were tested in distilled water with respect to settling rate. Over ninety per cent of the beads settled at a rate of 5 to 7 inches per minute at 25°C. This was an average rate for most batches - anion or cation resin.

Applications

Fluorescent, ion exchange resins were made to complement, not supplant, other methods of radioisotope detection and counting. For example, the resin does not approach the absolute sensitivity of low level beta or alpha counters which detect samples with activities less than 1 dpm. This is because a relatively high " noise level" photomultiplier tube must be used to transform the weak light pulses from the resin into strong electrical signals. However, the resin can indirectly achieve this sensitivity by counting, " looking at", a

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*Note: Commercial anion resins of similar chemical structure are not stable to warm solutions of 15% HNO_3.

much larger sample. This can be done since the activity, in a large aqueous volume, of less than 1 dpm per ml can be concentrated into a small volume of resin which can be efficiently counted.

In addition to its ability to concentrate ionic radionuclides from aqueous solutions, the resin transmits a signal of visible light which can be used to advantage. The use of alpha and beta emitters can now be extended into those areas of tracer application where direct transmission of the alpha or beta ray is restricted. Thus, the energy of a weak beta emitting tracer, which might be used in an aqueous process stream, can be transformed into light energy which readily passes through a transparent window such as glass or plastic. By placing the resin in-line or in a loop which is optically coupled to a photomultiplier tube, the process stream can be monitored by either integration or loss of activity.

An extension of the above principle can be applied to monitoring of ion exchange and chromatographic columns. With the insertion of a scintillating resin " sandwich" at a specific position in the column, the detection of a radiotracer could indicate the resolution of a desired constituent(s), exhaustion of the column capacity or the time to collect a given fraction.

Scintillating resins offer a definite complement to liquid scintillation counting. Liquid scintillators yield somewhat higher counting efficiencies and will dissolve many tagged organic compounds which have no ionizing groups. However, oxygen and sample quenching as well as sample incompatibility are sometimes serious problems in liquid scintillation counting. The resins are not affected by oxygen and many of the quenchers attendant in biological samples. Furthermore, the concentration of ionic constituents on the resin might well eliminate the problem of sample incompatibility due to large volumes necessary for counting or due to sample insolubility.

The ease of sample preparation using fluorescent ion exchange resin is a distinct advantage. Radiochemistry will be shortened for those isotopes which can be adsorbed and counted directly on the bead. The electroplating of alpha emitters is unnecessary for those samples containing about 20 dpm or over. The property of ion exchange also allows for the preparation of a " weightless" sample so that self-absorption of emitted particle energy is not a problem.

The "resin sample" allows for immediate counting with carrier yield to be determined later. This would be important where daughter growth complicates counting and calculations. Rapid sample preparation is important for short-lived alpha and beta emitters needing fast decontamination and counting times. The screening of aqueous solutions containing unknown levels of activity can be done with an economy of time, labor and materials.

Another area of counting techniques that can be aided by the resin is that of gas counting. The apparatus is complex, and the methods can become tedious for sample preparation. Both C^{14} as CO_2 and S^{35} as SO_2 are determined by gas counting techniques. It has been demonstrated that the anion resin will efficiently adsorb and count C^{14} as carbonate and S^{35} as sulfate. The resin thus provides another method of counting for inorganic C^{14} and S^{35}.

Inorganic and organic phosphates tagged with P^{32} are also readily and efficiently counted on the anion resin. The resins should find utility in fields of research concerned with nucleic acids and phospholipids and carbohydrates.

Other features of the resins to be mentioned briefly are (a) ease of recovery of sample, (b) the counting of beta emitters in the presence of gamma rays, (c) non-destruction of biological acids or amines and (d) conforming to any desired shape of the counting vessel used.