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Preparation of Microspherical Alpha-Radiation Sources

Layton J. Wittenberg

May 7, 1976

Research and Development Report

MOUND LABORATORY
Miamisburg, Ohio
operated by
MONSANTO RESEARCH CORPORATION
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UNITED STATES ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
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Summary

Sodium silicate glass microspheres in the 105-125-μm diameter size range, containing in vitreous solution the radioisotopes plutonium-238 and sodium-22, were prepared in four batches which emitted a nominal 40, 80, 320, and 640 nCi of total alpha radiation and approximately 1 nCi of gamma radiation from the sodium-22 isotope from each sphere. The initial integrity of the glasses was good and no wipeable contamination was detected from the spheres. The alpha particle range in the glass for the 5.5-MeV alpha particle emitted by plutonium-238 was calculated to be 15.2 μm, based upon radiometric analysis of individual spheres from each batch of product.

Introduction

This project was undertaken in order to supply calibrated alpha-radiation sources for use at the U. S. Environmental Protection Agency, National Environmental Research Center, Las Vegas, Nevada. The requirements on these sources were as follows: 1) they should be sufficiently small to be implanted in small animals for times up to 1 yr; 2) there should be minimal solubility of alpha-emitting material during the implantation period; 3) the sources should be prepared in several batches each containing different, but known, external alpha-radiation fluxes; 4) each small source should contain a small quantity (1 nCi) of a gamma-radiation tracer, such as sodium-22.

Microspheres of the 105-125-μm diameter size range were chosen as the desirable geometrical shape in order to achieve uniform small-size sources. High-fired PuO_2 microspheres[1] were known to be sufficiently inert and insoluble for this application; however, such oxide spheres would emit only a single flux. For instance, based upon measurements by Huffman and Kershner,[2] the external alpha radiation for a 120-μm sphere composed of plutonium-238 dioxide was calculated to be 1.5×10^4 nCi, while for a plutonium-239 dioxide sphere the external radiation would be only 54 nCi (1 nCi = 2.22×10^2 dis/min). By contrast, the external alpha radiations desired were in the range from 40 to 800 nCi.

In the search for a suitable diluent for the plutonium dioxide, both thorium dioxide[1] and silicate glasses[3] were suggested because both diluents are known to form solid solutions with plutonium dioxide, based upon extensive previous experience at Mound Laboratory. The dilution with silicate glass was selected as the method to be used for preparation of these sources because the size of the microspheres could be better controlled and the techniques for preparation of the glasses were more easily adapted to the small batch size required. Also, the sodium-22 tracer would be a chemical constituent of the sodium silicate glass, which should retard its dissolution from the glass.

This report describes the preparation and analysis of these required microspheres containing plutonium-238 (half-life 87.40 yr) as the alpha-radiation source and sodium-22 (half-life 2.60 yr) as the gamma-radiation source.

Experimental

Preparation of Radiation Glasses Based upon the measured alpha range in plutonium-238 dioxide microspheres,[2] the effective fraction of alpha particles escaping from the spherical particles was estimated and the required amount of plutonium dioxide in each particle was calculated. Also, from the measured density values[3] of glasses containing various dilute amounts of plutonium dioxide, the weight fractions of plutonium dioxide and silicate glass were calculated so that each batch of microspheres contained the required amount of plutonium dioxide.

The isotopic composition and other actinide impurities in the type of plutonium-238 dioxide used in this work are given in Table 1. Because of its short half-life, plutonium-238 makes the only significant contribution to the alpha radioactivity. The silicate glass, composition X-1211, given in Table 2 and supplied by Owens-Corning Fiberglas was used because previous experience indicated good durability and high solubility for plutonium dioxide.[3] Both the glass and the plutonium dioxide were ground to pass through a 250-μm sieve. All work with the plutonium dioxide was performed in an alpha-type glovebox.

The homogenization of the various glasses was accomplished in a platinum crucible heated by radiofrequency induction heating and followed closely the previously described work.[3] Preparations of the 800-nCi batch, containing approximately 21 wt % PuO_2, were not successfully homogenized; consequently, compositions containing approximately 16, 8, 2, and 1 wt % PuO_2 were selected for preparation. Initially, 2-g batches of compositions containing 16 and 2 wt % PuO_2 were prepared. Then, one-half of each homogenized composition was crushed and diluted with an equal weight of ground glass to form the 8 and 1 wt % compositions, respectively.

Because a small amount of glass remained in the crucible at the completion of each preparation, an accurate weight determination of each composition was not possible.

The heating times and temperatures required for the homogenization of each composition are given (Table 3). At the conclusion of each homogenization procedure two glass beads, approximately 1 g each, were poured from the platinum crucible. Each bead was examined visually by use of a stereo microscope set at 20X magnification. The beads were transparent and uniformly dark green. No undissolved plutonium dioxide particles were observed in transmitted light. These beads were crushed and the particles were held for the incorporation of the sodium-22 isotope.

Two millicuries of sodium-22, supplied by New England Nuclear Corporation, was obtained in approximately 0.9 cm^3 of 0.5N HCl solution. By use of a transfer pipette this solution was divided equally into five 1-dram glass vials. The shipping vial was rinsed repeatedly with 0.5N HCl solution and the rinse liquid was divided among the five vials until each vial contained approximately 1 cm^3 of liquid. Small amounts of these solutions were transferred between vials until each vial emitted nearly the same radiation flux, as determined by a gamma survey meter.

As required, the entire contents of each vial containing the sodium-22 solution (approximately 400 μCi) were placed in a clean, small platinum crucible, which was then transferred into the glovebox. A weighed quantity (0.5 g) of crushed plutonium-bearing glass was added to this crucible. The crucible was heated slowly, for approximately 1 hr, by use of the radiofrequency induction heating coil in the glovebox so that the HCl solution evaporated without splattering. When all of the liquid had evaporated, the contents of the crucible were homogenized by heating for 0.5 hr at 1200°C. After cooling, the glass, which was visually transparent and uniformly green, was ground in a porcelain mortar and pestle and passed through standard-mesh stainless steel sieves. The size fraction from 149 to 105 μm (estimated to weigh 0.2 to 0.3 g) was collected, placed in a vial, and carefully transferred out of the glovebox into a fumehood.

Preparation of Microspheres The glass particles were spheroidized by melting during transit through a propane gas-oxygen flame. The spheroidization apparatus consisted of a cylindrical stainless steel powder-feeder, a stainless steel delivery

Table 1

TYPICAL COMPOSITION OF PLUTONIUM-238

Plutonium Isotopes	Concentration (wt %)
238	80.75
239	15.01
240	2.66
241	1.07
242	0.51
236	0.9 ppm
Other Actinides	**Concentration (wt % PuO_2)**
^{241}Am	0.03
Np	0.14
Th	0.2
U	0.02

Table 2

PARENT GLASS COMPOSITION

Constituent	Composition (wt %)
SiO_2	66.6
Na_2O	16.6
K_2O	5.6
Al_2O_3	5.6
CaO	5.6

Table 3

HOMOGENIZATION PARAMETERS FOR PREPARATION OF GLASSES

Composition (wt % PuO_2)	Time (hr)	Temperature (°C)
1	2	1260
2	4	1325
8	8	1200
8	5	1225
8	2.5	1525
16	3	1400
16	3	1475

tube, the gas-oxygen torch head located in a 3-in. (7.6-cm) diameter silica glass tube, and a stainless steel receiving pan. The ground glass particles were washed with water and ethyl alcohol to remove loosely adhering dust and placed in the powder-feeder. A mechanical vibrator attached to the feeder was energized, and a low-velocity (2-ft^3/hr) stream of helium was passed through the feeder and carried the particles into the gas flame. The particles were allowed to free-fall into the receiver. The product was recycled through the flame two or three times in order to increase the yield of spherical particles.

Following the spheroidization step, the particles were passed through stainless steel standard sieves and the 105-125-μm fraction was recovered. Microscopical examination of this product indicated nearly 80-90% spherical particles with a yield of about 10^3 particles (approximately 1 mg). The spheres appeared transparent, with a slight green color evident in the highest concentrations of plutonium-bearing glasses.

Radiometric Analysis From each batch of spheres approximately ten spheres were selected for analysis. Each sphere was placed in an individual 25-ml polyethylene vial to which was added 5 ml of liquid scintillator solution prepared from 2,5-diphenyloxazole (PPO), naphthalene, and 1,4-bis [2-(5-phenyloxazolyl)] benzene (POPOP) diluted with 1,4-dioxane. The external alpha radiation from each sphere was determined when each vial was assayed by use of an automated liquid scintillation counter manufactured by Packard Instrument Company.

In a preliminary experiment, the effect of the placement of the sphere in the vial was determined when gel was added to the liquid scintillation solution so that the sphere was suspended in the solution. The counting rate for the same sphere which contained no sodium-22 was nearly identical, whether it was suspended in the gel or in solution without the gel so that it rested on the bottom of the vial; consequently, the gel was not used in further work. Also, the efficiency of the technique for the detection of alpha particles was determined to be nearly 100% when a solution containing a known quantity of plutonium-238 was diluted with the scintillator fluid and the disintegrations were counted with the instrument. This calibration did not mimic, however, the geometry during the sphere counting nor the proportion of alpha particles with degraded energies caused by self-absorption in the sphere. One difference noted was that the spheres emitted more very-low-energy radiation (approximately 20 keV) than did the plutonium solution. This radiation was not included in the total alpha radiation from the spheres as given in Table 4.

For determination of the total plutonium-238 content of each sphere, the spheres were assayed in their individual vials by use of a 3-in. (7.6-cm)-diameter, 2-mm-thick NaI(Tl) crystal and phototube. Output of the phototube was amplified and directed into a 200-channel pulse height analyzer. All counts associated with the 17-keV x-ray from the decay product of plutonium-238 were accumulated for 10 min. This detection method was standardized when a small aliquot of a calibrated solution of plutonium-238 was counted in the same geometry as the sphere so that the total plutonium-238 content of each sphere could be calculated. Experimentation showed that for this detector the gamma rays from sodium-22 were undetectable above the system background.

The sodium-22 content of each sphere was determined by use of a 2-in. x 2-in. (5.1-cm x 5.1-cm) NaI(Tl) crystal and phototube. Pulses were amplified and directed into a 200-channel analyzer so that counts associated with the 1.27-MeV gamma ray and the 0.511-MeV annihilation radiation associated with sodium-22 were recorded for 10-min periods. This detection system was standardized when a calibrated solution of sodium-22 was placed in a vial so that the system geometry was approximately that of the sphere. The sodium-22 solution was standardized both by detection of its positive beta emissions by use of the liquid scintillation counter and also by comparison of its gamma-ray flux with a foil containing a known amount of sodium-22. Because the 0.511-MeV peak was the predominant peak, the counts from each sphere associated with this energy peak were compared with the standard and the sodium-22 content of each sphere was calculated.

Table 4

ASSAY OF PLUTONIUM-238/SODIUM-22 SPHERES

Bottle No.	External Alpha (nCi)	Total Plutonium (nCi)	Ratio: External / Total	^{22}Na Gamma (nCi)
		40-nCi (Nominal) Batch		
3	40.9	210	0.195	1.12
4	67.1	329	0.204	1.27
5	34.3	168	0.204	0.97
6	37.8	198	0.191	0.52
7	40.8	196	0.208	1.21
8	30.5	141	0.216	1.03
9	38.2	217	0.176	2.14
10	40.5	196	0.207	1.46
	Total plutonium (avg) = 207 nCi; standard deviation = ±52 nCi = ±25% of total plutonium (avg).			
		80-nCi (Nominal) Batch		
20	84	451	0.185	2.2
21	85	460	0.186	0.7
22	63	346	0.183	4.6
23	63	314	0.200	1.6
24	99	496	0.200	1.8
25	77	386	0.200	2.3
26	65	287	0.225	0.7
27	62	353	0.176	1.8
28	72	378	0.190	1.5
29	53	282	0.189	2.5
	Total plutonium (avg) = 375 nCi; standard deviation = ±70 nCi = ±19% of total plutonium (avg).			
		320-nCi (Nominal) Batch		
30	345	1653	0.208	1.2
31	388	1928	0.201	1.3
32	355	1721	0.206	0.6
33	329	1617	0.203	0.4
34	378	2113	0.179	1.5
35	366	1698	0.216	0.7
36	366	2000	0.183	0.8
37	324	1595	0.203	0.7
38	305	1595	0.191	1.1
39	301	1333	0.226	0.6
	Total plutonium (avg) = 1725 nCi; standard deviation = ±217 nCi = ±13% of total plutonium (avg).			
		640-nCi (Nominal) Batch		
40	851	4775	0.178	2.1
41	467	2333	0.200	1.1
42	602	2878	0.209	1.8
43	430	2230	0.193	1.6
44	539	2667	0.202	1.1
45	633	3333	0.190	0.9
46	464	2311	0.201	0.9
47	525	2478	0.212	1.4
48	613	3243	0.189	2.8
49	573	2982	0.192	1.6
50	830	4595	0.181	1.7
	Total plutonium (avg) = 3075 nCi; standard deviation = ±837 nCi = ±27% of total plutonium (avg).			

Results and Discussion

Four batches of microspheres containing plutonium-238 and sodium-22 (Table 4) and one batch of spheres containing only sodium-22 (Table 5) were prepared. As a result of the radiometric assay technique, the total quantity of plutonium-238, the external alpha and gamma radiations, and the ratio between external and total alpha radioactivity of the representative spheres from each batch were determined (Table 4).

The microspheres in each batch of product met the required specifications for various external alpha radiations and a constant gamma flux. The total plutonium content of individual spheres within each batch (column 3 of Table 4) varied with the standard deviations shown. Calculations showed that the difference in volume among spheres of 105 to 125-μm diameter contributes an apparent variation in plutonium content of ±26%. Because the largest standard deviation was only slightly larger (1%) than this possible error, it was concluded that the spheres in each batch were homogeneous and a distribution of sphere sizes existed between 105 and 125 μm. Some spheres outside of this size range might be expected in each batch because the spheres were only given one pass through the sieves, which could account for the few large deviations in each batch of spheres.

The ratio of external to total alpha radiation (column 4, Table 4) remained remarkably constant at approximately 0.198 for all batches of spheres while the total plutonium content varied by a factor of 16. Also, within each batch the spheres with the lowest plutonium content, and presumably the smallest in diameter, had the highest external-to-total alpha ratio. These results confirmed the optical observations that the glasses were homogeneous and contained no minute particles of undissolved plutonium dioxide.

Table 5

RADIOASSAY OF ^{22}Na SPHERES

Bottle No.	^{22}Na Gamma (nCi)
80	0.7
81	0.6
82	0.7
83	1.0
84	0.3
85	0.5
86	0.6
87	0.6
88	0.7
89	0.6

Because the fraction of alpha particles escaping from the microspheres (all of the same size) was constant at approximately 0.2 over the range of compositions, the alpha particle range in the glass could be estimated for the 5.5-MeV alpha particles emitted by plutonium-238. In a similar determination of the alpha particle range in plutonium dioxide microspheres, Huffman and Kershner[2] measured the energy distribution of the alpha particles which escaped from the spheres and fitted the experimental results to a theoretical intensity-versus-energy curve. This technique increased the accuracy of their determinations and showed that an apparently large intensity of low-energy alpha particles was an anomaly caused by the counting apparatus. In the present work, the energy distribution of the alpha particles was not determined; however, the very-low-energy radiation (≤20 keV) detected by the liquid scintillation counter was not included as part of the total alpha radiation, for the same reasons as given by Huffman and Kershner. Based upon the total number of alpha particles detected by the liquid scintillation counter, the range of the alpha particles was calculated by the relationship:

$$f_e = \frac{R}{r}\left[\frac{3}{4} - \frac{(R/r)^2}{16}\right]$$

where: f_e = fraction of particles escaping the surface ≈ 0.2
R = alpha particle range in the glass
r = radius of the microsphere ≈ 57.5 μm

The calculated range for the 5.5-MeV alpha particles in the glass was 15.2 μm. This value is comparable to the range of 11.7 to 11.8 μm measured by two investigators[2,4] for alpha particles of the same energy in plutonium dioxide, but slightly less than the 21 μm (±20%) calculated by the Bragg-Kleeman Rule[5] for a glass of the composition $Na_2O{\cdot}4SiO_2$. The fact that the experimental range was lower than the calculated value may indicate that either the glass was more complex (in terms of stopping power) than the simple formula assumed for the glass or the counting technique was not capable of integrating the complete spectrum of alpha-particle energies so that some alpha particles were not counted.

The initial integrity of the glasses appeared to be very good. The most concentrated microspheres were handled individually without any detectable spread of plutonium dust, and no alpha contamination was detected in the liquid scintillator fluid which had been in contact with the spheres for up to 2 weeks. No degradation has been detected for plutonium-239-bearing glasses of nearly the same concentrations after nearly 10 yr; however, because of the differences in half-lives, the alpha-radiation flux of the present glasses is nearly 300 times greater.

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