

SOME PROBLEMS IN MEASURING PLUTONIUM IN THE ENVIRONMENT

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Abstract—Excellent analytical procedures are available for measuring plutonium in all kinds of environmental samples. Conditions are discussed under which complete sample decomposition and exchange with isotopic tracers are obtained, thus ensuring accuracy in the measurements. The major problems arise in obtaining sufficient samples to be statistically representative of the populations involved and in obtaining homogeneous samples for analysis.

INTRODUCTION

THE SENSITIVE, accurate, and reliable determination of plutonium in the environment is already of very great interest and concern to knowledgeable people everywhere because of the potential impact of this very singular and important element on the public health. This interest and concern will undoubtedly increase many-fold during the next several decades as the deployment of plutonium is increased to meet the increasing energy needs of the world. In fact, maximum utilization of plutonium might well be limited by the success with which this long-lived alpha emitter can be prevented from contaminating man's environment. Good management of plutonium depends critically on our ability to identify and measure very minute increments added to a wide variety of environmental materials. The present paper discusses some of the problems encountered.

ENVIRONMENTAL SAMPLING

The procurement of enough samples to be truly representative of the populations from which they were taken is undoubtedly the most difficult and limiting aspect of the entire measurement process. It is self-evident that no analysis can be better than the sample on which it is performed. One authority claims "we can do a global inventory for ^{90}Sr by sampling less than one-tenth of a square meter of ground at only 100 sites around the world." Because this is only about 10^{-13} of the total area of all dry land, it does not generate great confidence in the statistical adequacy of sampling the global population. However, when similar numbers keep recurring from

different samples from distant places, one begins to feel that perhaps at least the fundamental conclusions to be derived from the data are not too far off despite the small numbers of samples involved. It will be considerably more difficult to define deposition patterns around a plutonium facility adequately without considerably larger numbers of samples. In the current atmosphere of tight budgets and limited staff, there is a distinct necessity to have to get along with far fewer samples than many of us think necessary to do even a minimal job. The answer to this problem seems to be more administrative than statistical: do the best you can with the support that can be mustered.

ANALYTICAL PROCEDURES

Compared to the problems and uncertainties involved in sampling, analytical problems are relatively minor. In fact, plutonium can probably be determined more accurately than almost any other radionuclide because of the availability of almost perfect isotopic tracers that can be measured simultaneously and with the same detector as the isotopes being determined. Provided complete exchange between tracer and the other isotopes is obtained and contamination and errors in standardizing the tracer are avoided, virtually all other deficiencies in the analytical procedure will be corrected for, and accurate results must be obtained. Errors due to nonuniform electro-deposition, counting efficiencies and times, etc., all cancel out, and losses in the procedure are automatically corrected for. Consequently, sample decomposition becomes the most critical part of the entire determination as far as

accuracy is concerned. If these conditions are met, the accuracy of every plutonium determination made in the world can be guaranteed by simply using a common standardized solution of plutonium tracer.

That the determination of plutonium in the environment is fairly accurate and dependable on a world-wide scale is demonstrated by the results of a recent international interlaboratory comparison program sponsored by the International Atomic Energy Agency (FUKAI, 1974). Eighteen laboratories in nine different countries contributed measurements of both ^{238}Pu and ^{239}Pu in two samples of sea water, one seaweed and one sediment sample. While the results were far from perfect, with ratios of maximum to minimum values as high as 4, there was sufficiently good agreement among most of the laboratories that assessment of the practical impact of plutonium on the environment is not likely to be seriously in error. One of the principal conclusions was that, "in spite of the complicated chemical procedures involved in plutonium analysis, the scatter of the reported results was much smaller than that for fission product radionuclides such as ^{90}Sr , ^{106}Ru , ^{137}Cs , etc." (FUKAI, 1974). Similarly, six out of seven laboratories in the United States analyzing standard soils prepared in this laboratory containing refractory plutonium obtained values that agreed with the known value within the statistics of the measurements (SILL and HINDMAN, 1974). On the other hand, many laboratories are producing numbers that are seriously in error, and more specific identification of the sources of error is desirable.

The two most widely used analytical procedures involve either selective leaching of plutonium with nitric and/or hydrochloric acids or more complete decomposition with hydrofluoric acid, followed by anion exchange. Perhaps the most powerful and highly developed procedure employs total decomposition by potassium fluoride and pyrosulfate fusions, followed by separation of plutonium with barium sulfate and liquid-liquid extractions (SILL *et al.*, 1974). This procedure also possesses the distinct economic advantage over all others that all alpha-emitting radionuclides from radium through californium can be determined simultaneously in a single sample with yields

of each nuclide consistently around 95%. Most procedures finally employ electrodeposition onto either stainless steel or platinum discs, and the plutonium is determined isotopically by alpha spectrometry.

Plutonium tracers

Plutonium-242 has been recommended by several investigators as being superior to the more widely used ^{236}Pu as a tracer in the radiochemical determination of ^{238}Pu and ^{239}Pu . The much longer half-life of ^{242}Pu eliminates need for decay corrections and lessens dependence on its continuing availability. The very long half-life of its ^{238}U daughter virtually eliminates recoil contamination of the detector (SILL and OLSON, 1970) and/or need for repurification from ingrown daughter activities.

More important considerations are cost, availability, and particularly isotopic purity. Plutonium-236 currently is readily available that contains less than 0.01% of either ^{238}Pu or ^{239}Pu activities at a cost of about 0.2 cent per analysis using 10 dis/min. Most ^{242}Pu currently available contains about 1.8% of both ^{238}Pu and ^{239}Pu activities. Plutonium-242 of comparable quality to the best ^{236}Pu is only now becoming available at much higher cost.

The most important consideration is the energy of the alpha radiation emitted. All alpha spectra tail downward from the principal peak to lower energies. This tail becomes larger very rapidly as the quantity of absorbing materials or corrosion of the plate increases. Because ^{242}Pu emits alpha particles of lower energy than those from ^{238}Pu or ^{239}Pu , there is no scattering of the tracer into the energy regions of the other two isotopes being traced. However, this apparent advantage is only superficial. With a properly prepared plate, the tailing amounts to only about 2×10^{-6} count/keV per count in the main peak. If 10 dis/min of ^{236}Pu is used, which is adequate for 10-g samples containing up to at least 1 dis/min/g, the pulses scattered into a 125-keV band at either the ^{238}Pu or ^{239}Pu energies is only 0.7 count in 10^3 min at 28% counting efficiency, while giving a relative S.D. of 1.9% in the determination of the yield. In marked contrast, when samples containing high levels of either ^{238}Pu or ^{239}Pu are encountered, the tailing

from the isotopes being determined into the tracer region will introduce marked errors in the determination of the yield with ^{242}Pu but none at all with ^{236}Pu . This is particularly important because any error in the yield is applied to the entire determination.

Plutonium-242 clearly is an excellent tracer for use with relatively low-level samples, if it can be obtained sufficiently free of the other isotopes being traced, but it is not necessarily markedly better than ^{236}Pu . When higher level samples might be encountered, as in surveillance activities around plutonium facilities, radioactive burial grounds, experimental sites, accident sites, etc., the lower energy of ^{242}Pu will prove markedly disadvantageous.

Leachability

The solubility of plutonium is known to depend on the type of acid used, the particle size, the compound involved, the conditions of treatment, etc., and particularly on whether or not the material had been heated strongly prior to leaching. To determine what success was being achieved with leaching procedures in actual practice, eight residues were obtained from a routine lineup of soils being analyzed in another laboratory as part of an experimental survey following an accidental release of plutonium. In three of the eight samples, more plutonium was found in the residue by the total decomposition procedure (SILL *et al.*, 1974) than the other laboratory found in the acid-soluble portion. The residues from four others contained about one-third of the total plutonium, and even the lowest residue contained about one-fifth of the total. Similarly, standard soils containing exactly known quantities of plutonium (SILL and HINDMAN, 1974) were ignited to render the plutonium refractory and were analyzed by five different laboratories. When only nitric and hydrochloric acids were used in the sample decomposition, only 5–30% recoveries were obtained, even though ^{236}Pu tracer was used in all cases. In no case was ^{236}Pu detectable in the insoluble residues, demonstrating the complete absence of heterogeneous exchange and the consequent inability to correct for undissolved plutonium using tracer. A similar study conducted in the present laboratory (SILL and HINDMAN, 1974) showed losses

of about 3–85% remaining in the residue, depending on the heat treatment used. Clearly, treatment with hydrochloric and/or nitric acids alone is grossly inadequate for dissolution of refractory compounds of plutonium.

On the other hand, experience has shown that plutonium in soil resulting from global fallout can be removed easily and virtually completely with hydrochloric and/or nitric acids. Most particles from nuclear detonations are formed in the stratosphere and are known to have sizes generally in the nanometer range. Such small particles will undoubtedly dissolve more readily than larger ones. Also, plutonium oxide becomes more refractory the more it is heated, but only up to its melting point of about 2400°C. Above that temperature, loss of oxygen occurs, and a lower oxide approximating Pu_2O_3 is formed which is much more readily soluble in acid than quadrivalent plutonium having the RO_2 -type lattice. Certainly, the temperatures of many million degrees generated in the nuclear detonation will not permit the more highly oxygenated and refractory compounds to exist.

Dissolution of soil with hydrofluoric acid

Hydrofluoric acid is best known for its ability to dissolve silica, but even small quantities exert a marked catalytic effect on the nitric acid dissolution of many refractory oxides because of the exceptional stability of the fluoride complexes. Consequently, hydrofluoric acid generally gives much higher and more accurate results. However, several investigators have reported erratic results with its use, probably due either to incomplete dissolution of the plutonium oxide and/or the siliceous matrix or to incomplete elimination of fluoride with consequent deleterious effects on the subsequent separations.

In a previous investigation (SILL and HINDMAN, 1974), standard soils containing two different exactly known concentrations of ^{239}Pu were heated at 1000°C for 4 hr to convert the plutonium to very insoluble and refractory oxide and were then treated with hydrofluoric acid in an attempt to redissolve the plutonium. Plutonium-236 tracer was not added until after the leaching had been completed so that the concentration of plutonium in both the acid-soluble portion and the residue could be

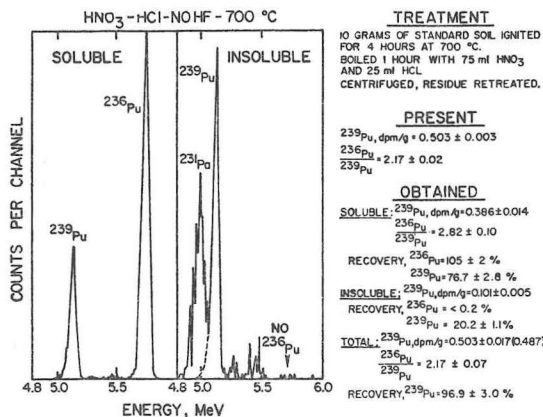


FIG. 1. Dissolution and exchange of plutonium isotopes with nitric and hydrochloric acids after heat treatment at 700°C.

determined accurately. The best one-stage treatment tried without recycling left a large insoluble residue containing both siliceous material and insoluble fluorides that contained about one-third of the total plutonium present.

To determine if even small quantities of plutonium could be recovered with hydrofluoric acid quantitatively, additional tests were made using the lower of the same two standard plutonium soils used in the previous work. The samples were ignited and treated under various conditions given in the legends in Figs. 1-4. The ^{236}Pu tracer was added after ignition, but unlike in the previous work, the

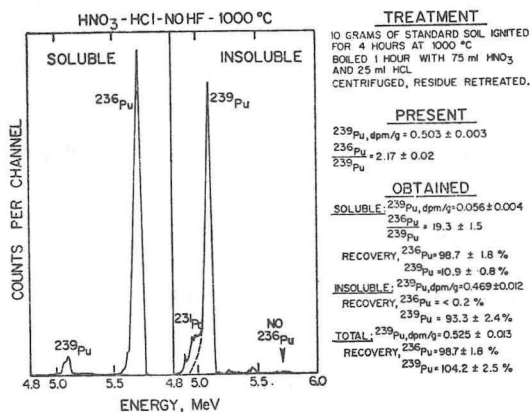


FIG. 2. Dissolution and exchange of plutonium isotopes with nitric and hydrochloric acids after heat treatment at 1000°C.

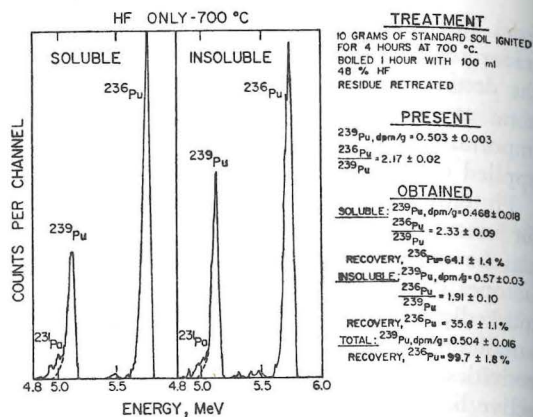


FIG. 3. Dissolution and exchange of plutonium isotopes with hydrofluoric acid alone.

tracer was present during the acid treatment to determine whether or not isotopic exchange occurred under any of the conditions to be used. In any fraction in which a significant quantity of ^{236}Pu was present, the concentration of ^{239}Pu in the *entire sample* was calculated from the ratio of ^{239}Pu to ^{236}Pu recovered in *each fraction*. Consequently, the concentrations shown for the soluble and insoluble portions should not be summed. The distribution between the two fractions can be obtained from the percentage figures under "Recovery." When no ^{236}Pu tracer was recovered in a given fraction, the ^{239}Pu concentration in that fraction was obtained from the known counting efficiency of the alpha spectrometer and an

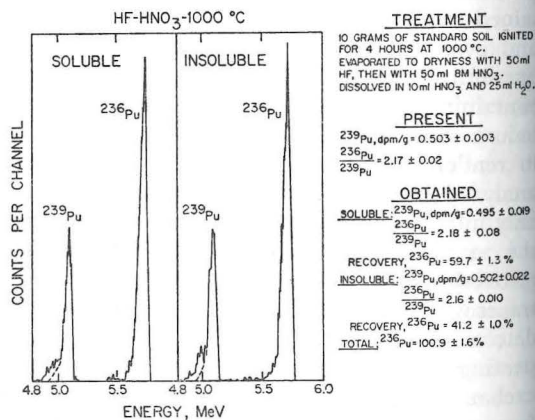


FIG. 4. Dissolution and exchange of plutonium isotopes with hydrofluoric and nitric acids.

assumed chemical yield of 95%, which is obviously less accurate than the ratio method, and should be added to that from the other fraction. The concentrations shown in the totals were always obtained by the ratio of the sums of the counts of ^{239}Pu and ^{236}Pu recovered in both fractions. The ^{231}Pa shown is that present originally in the soil.

As shown in Figs. 1 and 2, about 20 and 93% of the ^{239}Pu but virtually none of the ^{236}Pu tracer remained in the residue after ignition at 700°C and 1000°C , respectively, when only nitric and hydrochloric acids were used. This fact again proves conclusively that heterogeneous exchange does not occur to any significant extent between water-soluble ^{236}Pu tracer and refractory plutonium oxide. Consequently, one may not expect the use of ^{236}Pu tracer to correct for plutonium remaining in insoluble residues in its original insoluble form without having been dissolved. The concentrations of ^{239}Pu obtained by recombination of both fractions in the totals of both figures agree with the known value exactly.

When hydrofluoric acid was used alone, as shown in Fig. 3, the ratio of ^{236}Pu tracer to ^{239}Pu was distinctly too high in the soluble fraction and too low in the residue compared to the ratio known to be present. The value for the reconstituted sample agrees with the known value exactly. About one-third of both the ^{239}Pu and ^{236}Pu is still present in the residue, even though the residue had been retreated, similar to the result obtained previously (SILL and HINDMAN, 1974). However, because a significant fraction of the ^{236}Pu tracer, originally added in water-soluble form, is now present in the insoluble residue and because Figs. 1 and 2 show that heterogeneous exchange with insoluble plutonium oxide does not occur, most of the ^{239}Pu must have dissolved, exchanged with ^{236}Pu , and both isotopes precipitated to about the same extent as insoluble fluorides, probably carried on insoluble calcium fluoride. The fact that exchange was not quite complete indicates that dissolution of plutonium oxide was also not quite complete and could become either better or worse, depending on the exact conditions used.

The relatively large quantity of calcium and other fluorides that remain precipitated when

hydrofluoric acid alone is used is very gelatinous and covers the remaining sample, retarding complete dissolution. Consequently, both sample decomposition and isotopic exchange are incomplete, and at least a third of both ^{236}Pu tracer and ^{239}Pu being determined is discarded with the insoluble residue. Even if exchange were complete so that the accuracy of the determination would not be affected, such a large loss of the total counting rate is certainly undesirable because of a significant loss of both sensitivity and precision. To increase the solubility of the insoluble fluorides, a sample was evaporated to dryness with hydrofluoric and nitric acids to remove as much fluoride as possible, and the residue was dissolved in dilute nitric acid. As shown in Fig. 4, the ratio of tracer to traced and the ^{239}Pu concentrations obtained from both the soluble and insoluble fractions are statistically identical to the values known to be present. Complete exchange—and therefore complete dissolution of the refractory oxide—was obtained, but 40% of both isotopes was still being lost in the insoluble residue. Another experiment in which the residue was reevaporated to dryness with 72% perchloric acid gave almost identically low recovery. Hydrofluoric acid obviously cannot be removed completely by evaporation with either nitric or perchloric acids.

The data of Fig. 5 show the dramatic effect of adding boric acid to complex the fluoride

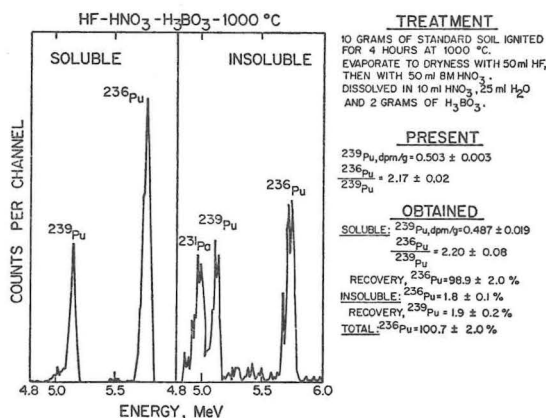


Fig. 5. Effect of boric acid on the recovery of plutonium isotopes after treatment with hydrofluoric acid.

remaining after removal of as much hydrofluoric acid as possible by evaporation. Both sample decomposition and exchange are complete and all but about 2% of the plutonium is available in the acid-soluble fraction, giving accurate results and maximum recovery. However, nitric acid should also be added to the hydrofluoric acid during the initial sample decomposition, and a large volume of the mixed acid should be used to keep as much of the insoluble fluorides dissolved as possible to facilitate complete dissolution.

Hydroxide formation

One of the outstanding characteristics of trivalent and particularly quadrivalent ions is their ability to form extremely insoluble hydroxides at very low hydroxide concentrations. If solutions of plutonium in volatile acids such as hydrochloric, nitric, and perchloric are evaporated to dryness, the plutonium will hydrolyze in its own water of hydration after the volatile acid has been driven off and will not redissolve completely on subsequent treatment with acids. Addition of 100 mg of sodium hydrogen sulfate as an acid buffer and complexing agent before evaporation makes the residue dissolve instantly and completely in water or dilute acid.

An equally troublesome and objectionable practice is to try to adjust the acidity of solutions to relatively high pH values nonhomogeneously in the absence of suitable complexing agents. The hydroxide concentration in the vicinity of each drop of alkali added is high enough to precipitate most trivalent and quadrivalent elements locally, which redissolve less and less readily the closer the final pH approaches that required for incipient hydrolysis. The presence of even μg quantities of heavy metal impurities to serve as carriers causes this effect to be very pronounced even with carrier-free concentrations of radioactive tracers. For example, electrodeposition is used almost universally to prepare plates for alpha spectrometry but is perhaps the biggest single source of loss of plutonium in most procedures for both reasons. It has been shown recently that use of thymol blue (pH 1.2–2.8) in making the preliminary adjustment of pH prior to beginning of electrodeposition instead of the more widely used

methyl red (pH 4.8–6.0) will increase the yield by 20% or more.

The electrodeposition cell and electrodes are the most serious source of contamination encountered because of failure to redissolve hydroxides precipitated when the solution is quenched with ammonium hydroxide at the end of electrodeposition. Before reuse, the cell and electrodes should be boiled for 15 min in conc nitric acid. Blanks should be run to prove the adequacy of decontamination after electrodeposition of samples containing more than a few dis/min.

THE PARTICLE PROBLEM

Inability to obtain reproducible results on separate aliquots of the same prepared sample does not necessarily indicate an inadequate analytical procedure. It can also indicate that the individual aliquots actually do contain the different concentrations indicated (i.e. the sample is inhomogeneous). Inhomogeneity is nowhere more evident than with the transuranium elements in soil. Because transuranium elements do not occur naturally to any significant extent, those present in soil must have been added as high specific activity particles from outside sources. Consequently, homogenization might be expected to be difficult or impossible due to the fundamental impossibility of distributing a few particles uniformly throughout a given mass.

The activity of N spherical particles of pure $^{239}\text{PuO}_2$ is $0.721ND^3$ dis/min, where D is the diameter of the particle in microns. If the activity is low, as is presently true with average soils, the entire activity could have resulted from a very few particles, making reproducible sampling virtually impossible. For example, the present activity of ^{239}Pu from global fallout of about 0.04 dis/min/g would be accounted for by a single 0.82- μm particle in 10 g of soil. Much larger particles can be expected in the vicinity of facilities handling plutonium or in experimental areas. In contrast, the extremely small size of particles containing plutonium from nuclear detonations would require an extremely large number of such particles to produce significant activity, even if the particles were composed of pure plutonium oxide. Plutonium resulting from global fallout

consequently should be homogenizable as well as leachable.

Some typical data are shown in Table 1. The first two samples contain only global fallout. Samples 3-7 were obtained at distances of 2.0, 2.0, 16, 17 and 43 miles, respectively, downwind from a plutonium processing facility known to have released significant quantities of plutonium on more than one occasion. Samples 8 and 9 were taken at distances of about 50 miles and 100 yards, respectively, from two other facilities known to have released plutonium. Sample 10 came from a non-nuclear high-explosive detonation involving plutonium, and sample 11 was taken near ground zero of a nuclear detonation. All analyses were traced with ^{236}Pu , and high and reproducible yields were obtained. Consequently, differences in the replicate values must reflect real differences in the concentration in each aliquot and not variations in the analytical procedure. The statistical uncertainties shown are 1 S.D. of all counting errors propagated to the final result.

Every result obtained on samples 1, 2 and 7 and all but one result each on samples 5, 6 and 8 are well within the statistical uncertainty of the

analyses on 10-g samples. The single high result in samples 5, 6 and 8 are several times the other values for the same sample and undoubtedly reflect the influence of a single larger particle. Contamination can be ruled out unequivocally because blanks were run before and after each analysis, using the identical pieces of apparatus to preclude this very possibility. The results on samples 3 and 9, and possibly 4, clearly show the pronounced inhomogeneity to be expected on samples taken relatively near terrestrial sources where larger particles might be expected. Samples 10 and 11 are surprisingly homogeneous for such relatively high levels of activity, probably indicating very small particle size distributions resulting from the high-temperature detonations. Furthermore, all samples containing only plutonium from very high temperature detonations, including number 11, can be leached almost completely free of plutonium by boiling with concentrated nitric and hydrochloric acids. The particle problem becomes much more severe for $^{238}\text{PuO}_2$, for which the constant in the above size-activity equation is 202. Increasing the sample size decreases the range of values obtained somewhat but does not eliminate the problem.

Table 1. Reproducibility of analyses using 10-g aliquots of prepared soils

Sample Number	^{239}Pu found (dpm/gram)	Sample Number	^{239}Pu found (dpm/gram)
1	0.110 ± 0.009	6	0.079 ± 0.009
	0.116 ± 0.010		0.058 ± 0.008
	0.112 ± 0.012		0.071 ± 0.009
	0.101 ± 0.008		0.290 ± 0.010*
	0.111 ± 0.008		
2	0.060 ± 0.007	7	0.051 ± 0.007
	0.050 ± 0.007		0.066 ± 0.009
	0.054 ± 0.007		0.056 ± 0.006
	0.063 ± 0.007		0.052 ± 0.006
3	1.59 ± 0.04	8	0.071 ± 0.008
	0.56 ± 0.02		0.220 ± 0.020*
	0.94 ± 0.03		0.051 ± 0.007
	0.68 ± 0.03		0.059 ± 0.006
4	0.62 ± 0.02	9	0.35 ± 0.02
	0.56 ± 0.02		0.78 ± 0.04
	0.57 ± 0.02		1.74 ± 0.04
5	0.044 ± 0.006	10	7.10 ± 0.07
	0.077 ± 0.008*		7.30 ± 0.07
	0.042 ± 0.005		7.59 ± 0.08
	0.055 ± 0.010		
	0.047 ± 0.006		
		11	36.0 ± 0.4
			34.9 ± 0.4
			36.2 ± 0.4

* Outside reasonable statistical limits.

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DISCUSSION

KRESSIN, I. K.: Claude, I have two questions, but first, I want to defend ^{242}Pu as a tracer. At present, one can get ^{242}Pu from Livermore with a purity of 10^{-6} , at about $\$10/\mu\text{g}$, which is more material than the ordinary laboratory uses in a year. The advantage of ^{242}Pu , of course, is that you don't have to clean it up.

The two questions I have, Claude, are first, how do you control the samples that are brought into your laboratory, since you have no control over what was done previously with them or how they were collected; and second, how do you control the use of the data after you get an answer?

SILL, C. W.: Perhaps it's a cop-out, but the answer to your first question is that I steadfastly refuse to take any responsibility for what happens to the sample prior to the time it is turned over to me. For example, I will tell you the total dpm on an air sample but not the concentration, because I won't take responsibility for the accuracy with which you know the volume. The second question is a thing that we could talk about for hours. People report activity measurements to six significant figures with a standard deviation to four significant figures when it is well known that a standard deviation is a value which can be expected to be exceeded once out of every three times.

What I was trying to get over is that the type of sample matrix you have will cause some problems peculiar to itself, but the fundamental thing is getting

the sample dissolved. Once you do this and get exchange, it doesn't really make much difference what kind of sample it came from. Your question prompts me to say another thing. I am amazed at how one talks about the plutonium content of tracheobronchial lymph nodes and lungs and what not, without knowing how those data were derived or what they are worth. For example, if your lymph nodes were muffled to reduce them to ash and then just dissolved in some 4 N nitric acid, I will guarantee that you are in trouble, because there is no better way of getting refractory plutonium oxide than to heat it in a muffle at a temperature required to destroy tissue. There are some other problems, but they will essentially succumb once you treat that front end, which is the most important part of the procedure for plutonium where we have this alpha-emitting tracer.

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