

The Simultaneous Determination of Plutonium Alpha Activity and Plutonium-241 in Biological Materials by Gel Scintillation Counting

J. D. Eakins and A. E. Lally

*Health Physics & Medical Division, UKAEA Research Group,
Atomic Energy Research Establishment, Harwell, England*

INTRODUCTION

Plutonium-241 is produced from plutonium-239 in nuclear reactors by successive neutron captures. It has a physical half-life of 13.2 years and decays predominately by β -emission to americium-241, an α -emitter with a half-life of 458 years. A very small proportion, about $2.3 \times 10^{-3} \%$, decays by α -emission to uranium-237.

The maximum permissible body burden (MPBB) recommended by the International Commission on Radiological Protection¹ is $0.9 \mu\text{Ci}$, compared with $0.04 \mu\text{Ci}$ for plutonium-239. However, the determination of plutonium-241 in biological materials is becoming increasingly important as the burn-up level of uranium in power reactors increases. As Dalton *et al.*² have pointed out, the advent of the advanced gas-cooled reactor with proposed fuel irradiations of the order of 12000 MW days/metric ton will result in each MPBB of α -active plutonium being associated with 5.2 MPBB's of plutonium-241. In addition, the use of plutonium-239 as a nuclear fuel will greatly increase the relative hazard of plutonium-241.

Because of the low energy of its β -emission ($E_{\text{max}} = 21 \text{ keV}$), plutonium-241 is usually detected either by internal proportional or liquid scintillation counting. Gale and People³ have reported the use of both internal proportional and plastic scintillation counters for the measurement of plutonium-241 surface contamination on smears. Dalton *et al.*² have described a small volume low background internal proportional counter for the determination of low levels of plutonium-241 electrodeposited on stainless steel. However, difficulties have been experienced with this method due to variations of source thickness causing changes in the counting efficiency.

The use of liquid scintillation for the determination of plutonium-241 was first reported by Horrocks and Studier.⁴ These workers modified a Packard Tricarb liquid scintillation spectrometer to improve the light collection efficiency and incorporated plutonium-241 into a xylene-based liquid scintillator as the dibutyl phosphate complex. Ludwick⁵ used this procedure for the determination of plutonium-241 in urine, after measuring the plutonium α -activity of an electrodeposited source by nuclear track counting. The plutonium was removed from the stainless steel backing by an acid treatment and after several chemical steps it was extracted into dibutyl phosphate for incorporation

into a toluene-based scintillator. A minimum detectable level of 2.2 pCi of plutonium-241 was reported, with a counting time of 24 h.

Several workers have reported the use of liquid scintillation counting for the determination of plutonium α -activity in urine. Toribara *et al.*⁶ used a toluene-based scintillator and after the addition of an aqueous solution of plutonium, added absolute alcohol to obtain a single-phase system. Because of the presence of trace quantities of iron in the plutonium, phosphoric acid was also added to produce a colourless solution. Lindenbaum and Lund⁷ described the analysis of small samples of animal tissue in which the oxidation of the samples was carried out directly in the counting vial prior to the addition of liquid scintillator. Keough and Powers⁸ dry-ashed tissue samples and added a nitric acid solution of the ash to a counting vial containing di(2-ethylhexyl) phosphoric acid dissolved in a toluene-based scintillator. The plutonium was extracted into the organic phase and liquid scintillation counting performed with both phases present in the vial. In all these methods the counting efficiency for plutonium α -activity was almost 100 %.

The method described in this chapter utilizes a simple gel scintillation counting technique simultaneously to determine both plutonium α -activity and plutonium-241 in a two-channel Packard Tricarb Model 3214 liquid scintillation spectrometer.

PREPARATION OF SOURCE FOR COUNTING

Chemical separation of plutonium

Any method can be used to extract the plutonium from the biological material, provided the end product is an acidic aqueous solution of ionic plutonium containing little or no iron. The present authors use the methods described in AERE-AM 103⁹ to separate plutonium from urine and faeces. In the final stage of both methods the plutonium is eluted from an anion exchange column with concentrated hydrochloric acid containing a small amount of hydriodic acid. This solution is evaporated to near dryness under an infrared lamp and 1 ml of nitric acid is added to oxidize any residual hydriodic acid. The solution is again evaporated almost to dryness and transferred with water washings to a 10 ml centrifuge tube.

Preparation of gel source of ferriphosphate complex

Eakins and Brown¹⁰ described the preparation of a white iron complex of diphosphatoferrous acid which was used to determine iron-55 and iron-59 in blood by gel scintillation counting. It was found that this complex will coprecipitate the actinide elements quantitatively and is thus a useful method of introducing them into a scintillation system for gel counting. 2 mg of iron carrier are added to the acid aqueous solution of plutonium and ferric hydroxide is precipitated by the addition of ammonia. The precipitate is washed with water and dissolved in 0.25 ml of orthophosphoric acid. Absolute ethanol containing ammonium chloride is added to precipitate the ferriphosphate complex, which is centrifuged and washed with methylated spirit. The complex is slurried with 4 ml of NE 220* liquid scintillator and transferred to a counting vial containing Cab-O-Sil† silica powder as a gelling agent. The centrifuge tube is washed out twice with 4 ml volumes of scintillator, the washings being transferred to the counting vial which is mechanically shaken to produce a uniform gel for scintillation counting. The procedure is shown in outline in Fig. 1.

* NE 220 liquid scintillator is a dioxan-based scintillator manufactured by Nuclear Enterprises (G.B.) Ltd., Sighthill, Edinburgh 11, Scotland.

† Cab-O-Sil silica powder is supplied by the Packard Instrument Company Inc., York House, Empire Way, Wembley, Middlesex, England.

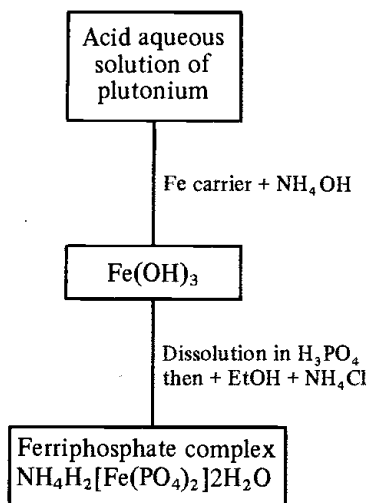


Fig. 1. The preparation of the ferriphosphate complex from a solution of plutonium.

SELECTION OF OPTIMAL COUNTING CONDITIONS

The term 'plutonium α -activity' is used in this chapter because plutonium-239 contains variable amounts of plutonium-240 and plutonium-238, depending on its source. The α energies of plutonium-239 and -240 are almost identical at 5.15 and 5.16 MeV respectively. The energy of the plutonium-238 α -particle is 5.49 MeV but this causes little shift of the gain spectrum compared with plutonium-239. Plutonium-239/240 containing only a few per cent of plutonium-238 was used for all the experiments described in this report and this is referred to as plutonium-239. Where the plutonium is of unknown isotopic composition the term plutonium α -activity is used.

Gain scans of plutonium-239 and plutonium-241

In order to obtain the optimum gain settings for α - and β -emitting plutonium a source of each was prepared as described above. Several gain scans were carried out at different high voltage settings at the full instrument window of 50–1000. The maximum count rate and peak separation were obtained with a high voltage setting of 4.3 on the instrument in use. These gain scans are shown in Fig. 2 where it can be seen that the optimum gain for plutonium-239 is about 3% and that for plutonium-241 is 60%.

Optimum window settings for plutonium-239

With the lower window or bias level at 50 and the gain at 3%, the upper level was reduced successively and the count rate at each setting recorded. In Fig. 3, curve A is a plot of count rate versus upper window setting and it can be seen that few counts are lost until the upper level is reduced to 500. The upper bias level was therefore fixed at 600 and the lower level raised as shown in Fig. 3, curve B. The count rate does not begin to drop appreciably until the lower level reaches 350 and the counting window was therefore taken initially as 300–600.

If E is the counting efficiency and B is the background, the sensitivity of the counter

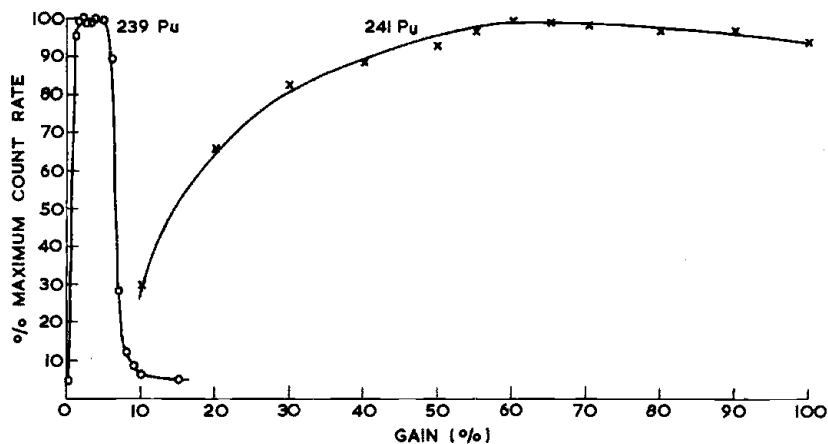


Fig. 2. Gain scans of plutonium-239 and plutonium-241.

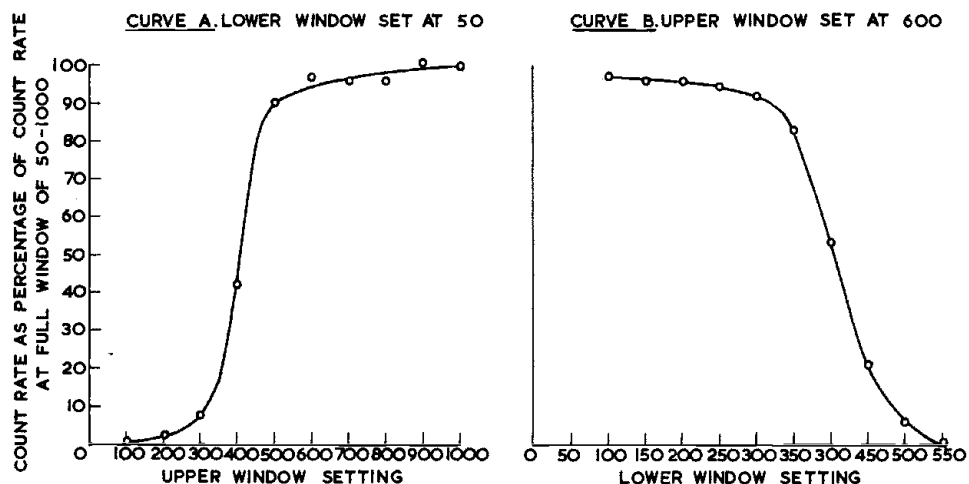


Fig. 3. Effect of window closure on count rate of plutonium-239.

is greatest when E^2/B is a maximum. The counting efficiency of the plutonium-239 source at a gain of 3% with a window width of 300–600 was 92.5%. The background count rate at these settings from a gel containing no added plutonium was 6.7 c.p.m. and hence E^2/B was 1277. Closing the window still further reduced both the counting efficiency and background as shown in Table 1. The maximum counting sensitivity was with a window of 300–500 and this was adopted as the optimum setting for plutonium-239.

Optimum window settings for plutonium-241

The background count rate of a gel containing no plutonium was 16.3 c.p.m. at the optimum gain of 60% with the full instrument window of 50–1000. The counting efficiency

Table 1. Window settings for counting plutonium-239 at maximum sensitivity.

Window	Counting efficiency (%)	Background (c.p.m.)	E^2/B
300–600	92.5	6.7	1277
300–550	89.7	5.6	1437
300–500	86.4	4.4	1696
350–500	69.0	3.2	1490
350–450	55.3	2.2	1274

for the plutonium-241 source was 21% and no reduction of the window was possible without a considerable loss in counting efficiency with little reduction in background. E^2/B was therefore at a maximum of 27.6 for plutonium-241 with a full window of 50–1000.

BACKGROUND MEASUREMENTS AND COUNTING EFFICIENCIES

Background measurements on urine samples from unexposed persons

In order to determine the mean background from urine, six 1400 ml (nominal 24 h) urine samples from people not occupationally exposed to plutonium were analysed by the method for plutonium in urine described in AERE—AM 103.⁹ The sources were prepared for gel scintillation counting as described on p. 156. The gain and window settings were adjusted to count plutonium α -activity in the red channel of the scintillation spectrometer and plutonium-241 in the green channel. The sources were counted for 100 min and the results are shown in Table 2.

These backgrounds compare favourably with the figures of 4.4 and 16.3 c.p.m. previously obtained by counting ferriphosphate gels prepared directly from iron carrier solution.

Table 2. Background count rates obtained from 1400 ml urine samples.

Sample number	Red channel (c.p.m.)	Green channel (c.p.m.)
1	4.9	16.8
2	4.4	16.4
3	4.5	16.8
4	4.5	16.6
5	5.0	16.8
6	4.4	16.8
Mean and SD	4.6±0.3	16.7±0.2

Counting efficiency of plutonium-239 coprecipitated with ferriphosphate complex

To obtain a mean counting efficiency for plutonium-239 coprecipitated on the ferriphosphate complex, six samples of 2 mg of iron carrier in acid solution were spiked with

Table 3. Counting efficiency for plutonium-239.

Sample number	Counting efficiency (%)	
	Red channel	Green channel
1	87.7	99.1
2	90.5	99.2
3	85.2	98.2
4	86.9	98.6
5	91.7	102.6
6	88.2	100.7
Mean and SD	88.4±2.2	99.9±1.5

53.3 pCi of plutonium-239 and prepared for gel scintillation counting. Both channels of the counter were set at 3% gain, with a reduced window of 300–500 in the red channel but with a full window of 50–1000 in the green channel. The red channel counts therefore gave the counting efficiency for plutonium-239 at maximum sensitivity and the green channel gave the maximum counting efficiency obtainable. The results of this experiment are shown in Table 3. The counting efficiency in the green channel is virtually 100%, indicating that the coprecipitation of plutonium with the ferriphosphate complex is quantitative.

The above sources were then recounted with the red channel on the same gain and window settings, but with the green channel set for plutonium-241 with a gain of 60% and a full window of 50–1000. The mean count rate above background observed in this channel was 4% of the count rate in the plutonium-239 channel. This could be a genuine contribution of the α -activity in the plutonium-241 region or it could possibly be due to a small amount of plutonium-241 in the plutonium-239 spike solution.

Counting efficiency of plutonium-241 coprecipitated with ferriphosphate complex

Six samples were prepared containing 253 pCi of plutonium-241 with 2 mg of iron as the ferriphosphate complex. These were counted in the liquid scintillation counter for 100 min with the red channel set for counting plutonium α -activity and the green channel

Table 4. Counting efficiency for plutonium-241.

Sample number	c.p.m.	Efficiency (%)
1	117.0	20.8
2	116.1	20.7
3	121.0	21.6
4	118.0	21.0
5	118.7	21.2
6	118.2	21.1
Mean and SD		21.1±0.3

for plutonium-241. There were no significant counts in the red channel above background, showing that the plutonium-241 was not contributing any counts to this channel. The counts obtained in the green channel and the counting efficiency for plutonium-241 are shown in Table 4.

RADIOCHEMICAL RECOVERIES FROM URINE

Plutonium-239 spikes

Six 1400 ml urine samples from unexposed persons were spiked with 10.66 pCi of plutonium-239 and analysed according to the procedure described. The gelled sources of ferriphosphate complex were counted for 50 min and the amounts of plutonium-239 detected and the radiochemical recoveries are shown in Table 5.

Table 5. Radiochemical recovery of plutonium-239 from 1400 ml urine samples.

Sample number	Plutonium-239 found (pCi)	Radiochemical yield (%)
1	10.00	93.8
2	9.05	84.9
3	9.86	92.5
4	9.10	85.4
5	9.82	92.1
6	9.19	86.2
Mean and SD		89.2±3.8

Plutonium-241 spikes

The above experiment was repeated with six 1400 ml urine samples spiked with 253 pCi of plutonium-241 and the sources were counted for 50 min. The results are shown in Table 6.

Table 6. Radiochemical recovery of plutonium-241 from 1400 ml urine samples.

Sample number	Plutonium-241 found (pCi)	Radiochemical yield (%)
1	211	83.6
2	214	84.7
3	208	82.4
4	224	88.4
5	202	80.7
6	210	82.9
Mean and SD		83.8±2.4

High level mixed spikes

Six 1400 ml urine samples were spiked with 10.66 pCi of plutonium-239 and 127 pCi of plutonium-241 and analysed. It was assumed that 4% of the plutonium-239 counts in the red channel of the liquid scintillation spectrometer would appear in the green channel with the plutonium-241 counts and this was allowed for in calculating the results shown in Table 7.

Table 7. Recovery of plutonium from high level plutonium-239 and plutonium-241 spiked urine samples.

Sample number	Plutonium-239 recovery (%)	Plutonium-241 recovery (%)
1	84.9	92.8
2	81.1	81.1
3	86.6	90.4
4	84.9	84.3
5	89.6	93.9
6	81.5	81.5
Mean and SD	84.8±2.9	87.3±5.2

Low level mixed spikes

The previous experiment was repeated with six 1400 ml urine samples spiked with 2.13 pCi of plutonium-239 and 12.7 pCi of plutonium-241. The results are given in Table 8.

Table 8. Recovery of plutonium from low level plutonium-239 and plutonium-241 spiked urine samples.

Sample number	Plutonium-239 recovery (%)	Plutonium-241 recovery (%)
1	95.2	80.4
2	76.8	81.2
3	100.0	95.3
4	87.2	82.8
5	102.3	91.4
6	96.6	96.8
Mean and SD	93.0±8.3	88.0±6.2

ANALYSIS OF URINE SAMPLES FOR PLUTONIUM α -ACTIVITY AND PLUTONIUM-241 FOLLOWING AN INCIDENT

Urine samples were received from six subjects following acute exposure to plutonium. As the subjects had been treated with DTPA it was necessary to oxidize the urine to break down complexed plutonium. The samples were evaporated to dryness with nitric acid and the residue heated at 500°C for 30 min. The ash was dissolved in nitric acid and calcium

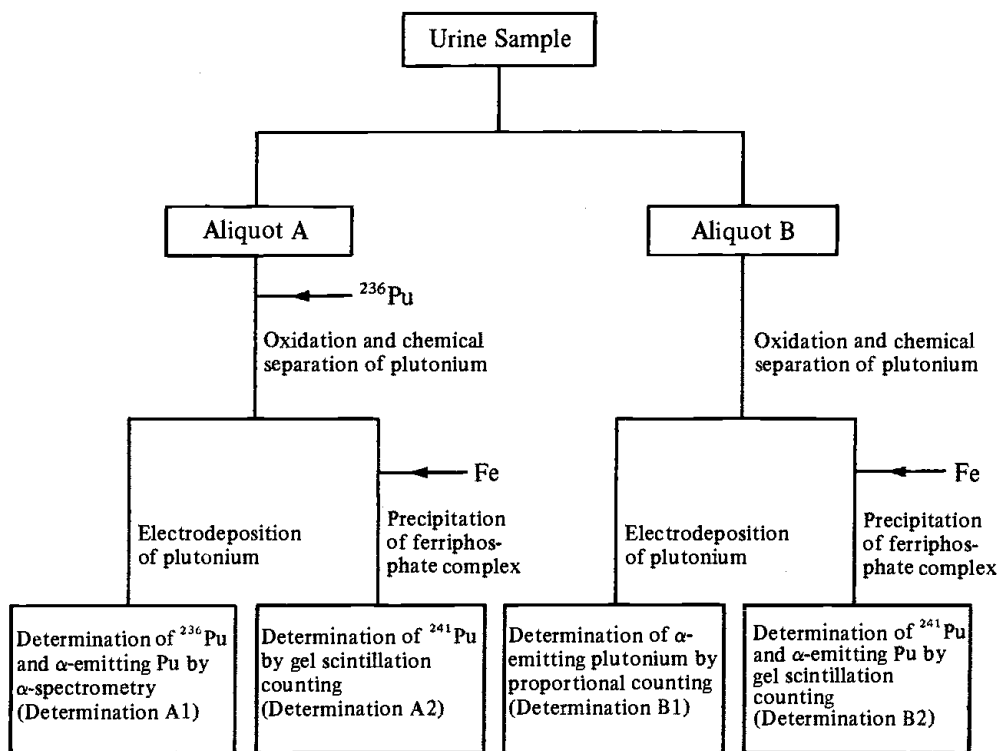


Fig. 4. Procedure used to analyse urine samples following acute exposure to plutonium and subsequent treatment with DTPA.

phosphate precipitated by the addition of ammonia. The analyses were then completed as described in AERE-AM 103⁹ and in this chapter.

The urine samples were split into two equal aliquots. The first aliquot was spiked with plutonium-236 as an internal standard. After chemical separation but prior to the addition of iron to prepare the ferriphosphate complex, half of this aliquot was taken and the plutonium electrodeposited for α -spectrometry. The radiochemical recovery of plutonium α -activity in the urine was determined from the yield of plutonium-236. The mean radiochemical recovery obtained by this method was 79.5%. The other half of this aliquot was prepared as the ferriphosphate complex and the plutonium-241 determined by gel scintillation counting. The second aliquot was analysed in exactly the same way but without the addition of plutonium-236. In this case the plutonium α -activity on the electrodeposited source was determined by proportional counting. It was also determined simultaneously with the plutonium-241 by scintillation counting of the gelled source. Three results were thus obtained for the plutonium α -activity and two for the plutonium-241. The analysis is shown diagrammatically in Fig. 4 and the results are shown in Tables 9 and 10.

The errors quoted in Tables 9 and 10 are 2σ and refer only to the counting statistics. Although the results are quoted in pCi/l, it should be noted that the volumes of urine

Table 9. Plutonium α -activity in urine.

Sample number	Determination A1 by plutonium-236 and α -spectrometry (pCi/l)	Determination B1 by proportional counting (pCi/l)	Determination B2 by gel scintillation counting (pCi/l)	Mean (pCi)
1	28.6 \pm 1.1	29.7 \pm 1.8	33.7 \pm 1.4	30.7
2	38.7 \pm 1.2	36.9 \pm 2.2	42.4 \pm 1.5	39.3
3	21.9 \pm 1.8	14.4 \pm 0.9	14.1 \pm 3.9	16.8
4	25.3 \pm 1.3	24.4 \pm 1.5	27.1 \pm 2.3	25.6
5	14.2 \pm 1.2	15.4 \pm 0.9	14.1 \pm 2.2	14.6
6	28.7 \pm 1.7	26.4 \pm 1.6	27.1 \pm 4.1	27.4

Table 10. Plutonium-241 in urine.

Sample number	Determination A2 (pCi/l)	Determination B2 (pCi/l)	Mean (pCi/l)
1	692 \pm 13	648 \pm 12	670
2	844 \pm 14	912 \pm 15	878
3	339 \pm 34	406 \pm 41	372
4	590 \pm 20	543 \pm 18	567
5	364 \pm 18	321 \pm 16	343
6	598 \pm 25	518 \pm 22	558

received ranged from 0.25 to 1.0 l and that because of the subdivision of the samples, the final counting sources in each case represented the plutonium in urine volumes of from 62.5 to 250 ml. This accounts in some measure for the relatively large errors obtained. The mean recovery of 79.5% is lower than that found with spiked urine samples but this is probably due to losses occurring during the complete oxidation of the urine samples prior to analysis.

COMMENTS

The procedure described can adequately detect α -emitting plutonium at the 1 pCi level and plutonium-241 at the 10 pCi level of activity. The minimum detectable level (equivalent to a count rate equal to two standard deviations of the background of the counter) for plutonium α -activity is 0.3 pCi with a counting period of 100 min and 0.15 pCi for 300 min. The corresponding figures for plutonium-241 are 1.8 and 1.0 pCi respectively. It should be stressed that these limits can only be obtained with a stable background. The most likely cause of variable background is the liquid scintillator and it is important to process blank samples with the active specimens to establish the background for each batch. Dioxan-based scintillators are particularly prone to variations in background due to oxygen absorption and such scintillators should be thoroughly purged by bubbling with nitrogen both before and after use.

For routine urine analysis the procedure is not sufficiently sensitive for the detection

of plutonium-239 at the levels suggested by Dolphin *et al.*¹¹ i.e. taking a reference level of 0.2 pCi/24 h. However, as the MPBB for plutonium-241 is about 22 times greater than that for plutonium-239, a corresponding reference level of 4.4 pCi could be detected with a 2σ error of $\pm 30\%$ using a counting period of 300 min. If necessary, prior to the formation of the ferriphosphate complex, an aliquot of the solution can be taken for electrodeposition and detection of plutonium-239 by solid state α -counting, when a minimum detectable level of 0.02 pCi is readily obtainable.¹² However the gel scintillation procedure is sufficiently sensitive for the analysis of faecal and nose blow samples, where much higher levels of activity may be expected, and also for the analysis of urine samples following an acute exposure.

Although other workers^{4,5} have claimed counting efficiencies of 30% for plutonium-241 compared with the gel scintillation counting efficiency of 21%, the use of gel counting eliminates the necessity for quench corrections and simplifies the chemistry involved in the preparation of the source.

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DISCUSSION

T. H. Bates: Comment: At Windscale we are employing this technique satisfactorily in the bioanalytical laboratory using a more recent Packard Tricarb Model and we obtain a counting efficiency of 37% for plutonium-241 and 95% for plutonium- α . By use of a set of accurately calibrated standard solutions of plutonium-239 and plutonium-241 blended so as to give β/α ratios ranging from 5 to 40 we found no statistical bias to suggest that there was any detectable contribution in the β -counting channel from the α -emitting isotope. Apparent counts in the β -counting channel from americium-241 and plutonium-238 standards could also be entirely accounted for by the presence of trace amounts of contaminating plutonium-241 determined by mass spectrometry.