

An 'In-Vial' Oxidation Procedure for the Simultaneous Determination of Plutonium alpha-Activity and Plutonium-241 on Smear Samples

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INTRODUCTION

The assessment of radioactive surface contamination is one of the control measures used by operational health physicists in order to maintain safety standards in areas where unsealed radioactive sources are present.

The philosophy and practical problems of surface monitoring have been described in detail by Clayton.¹ In general, when the surface is of suitable geometry and the radioactive material emits high-energy β - or γ -radiation, contamination is detected by direct measurement. The presence of α -activity can also be detected on suitable surfaces by direct measurement, provided the surface is clean. However, in the case of low-energy β -emitters such as tritium or Plutonium-241, or for α -activity on surfaces which are dirty, indirect methods are used. Indirect methods may also be used for high-energy β - or γ -emitters where the surface is unsuitable.

The most common method of indirect surface monitoring is by smearing. A defined area is wiped with a suitable material, usually filter paper, and the activity removed by the smear is measured in the appropriate type of counter. An estimate of the original surface activity is then made assuming some fairly arbitrary removal factor, usually between 10 and 20%.

Of particular interest to the health physicist monitoring for plutonium is the ratio of the β -emitting Plutonium-241 to total α -activity. Plutonium α -activity usually consists of Plutonium-238, -239 and -240, the ratios of these depending on the burn-up of the uranium from which it is produced. The amount of Plutonium-241 present also depends on this factor, a high burn-up producing a high β/α ratio. The age of the plutonium also affects the ratio to a certain extent, as Plutonium-241 ($t_{1/2} = 13.4\text{y}$) decays to α -emitting Americium-241 ($t_{1/2} = 458\text{y}$) which remains as an impurity element. The lowest β/α ratio will therefore be found in aged plutonium produced from low burn-up fuel. A rough knowledge of this ratio can thus give useful information to the health physicist on the source of the

contamination. In addition, the β/α ratio enables Plutonium-241 contamination to be calculated from the direct measurement of the α -activity alone on suitable surfaces, whereas the direct measurement of this nuclide (E_{\max} 21 keV) is extremely difficult.

The usual method of measuring the β/α ratio on a plutonium smear is by a double counting technique. The smear is counted in an internal proportional counter to obtain a measure of the total α - and β -activity, then in an α -scintillation counter to determine the α -activity alone. The β/α ratio can then be calculated if the respective counting efficiencies are known. As surfaces are often dusty or greasy, however, the measurement of α - or low-energy β -activity is complicated by losses due to self absorption.

In selecting a method for the analysis of smear samples for plutonium, two factors should be borne in mind. First, a simple and rapid procedure is necessary as, following a contamination incident, samples may be produced in considerable numbers and the results will be required in a matter of hours. Secondly, samples will generally be taken in areas where separated plutonium is the only radioactive material, so that chemical separation is unnecessary.

Eakins and Lally² have described a technique for the simultaneous determination of plutonium α -activity and Plutonium-241 in biological materials by chemical separation and gel scintillation counting. Although this method, which has subsequently been used by other workers,³ could be applied to smears, a more rapid procedure is required. This paper describes the development of a simple and fairly rapid method for the simultaneous determination of plutonium α - and β -activity in smear samples.

EXPERIMENTAL

Preliminary experiments

A smear sample containing plutonium was analysed according to the method of Eakins and Lally² and the gelled ferri-phosphate source counted in a Packard Tricarb Model 3314 liquid scintillation spectrometer. In Fig. 1 a gain scan at 5V and a window setting of 200–400 illustrates the excellent separation of α - and β -emitting plutonium obtainable by this technique. It is not possible to discriminate between the α -particle energies of Plutonium-238, -239 or -240 so only one α -peak is observed. The following experiments were carried out in an attempt to obtain a similar peak separation with a simpler and more rapid procedure.

Artificial smears were prepared from 3 cm Whatman 42 filter papers. If dirty smears were required, these were obtained by smearing the axles of a laboratory truck, which were covered with a thin layer of black dust and grease. The average weight of the deposit on such smears was 15.4 mg. The smears were spiked by the addition of 0.1 ml aliquots of Plutonium-241 and Plutonium-239 and dried under an infra-red lamp. 'Plutonium-239' is used here for convenience to describe the spike material, as it was known to be low in other plutonium isotopes. In the following work, where the composition is unknown the term 'plutonium α -activity' will be used.

A dirty spiked smear was added directly to a glass liquid scintillation counting vial containing NE 220 liquid scintillator. A gain scan of this, at 5 V and a window setting of 200–400, is shown in Fig. 2a. Virtually no separation of the α - and β -activity was obtained. Another dirty smear was placed in a counting vial which was heated in a muffle furnace at 450°C until completely oxidised. This took about 2 h, due to the restricted supply of air in the vial, and a small bead of brownish ash remained. After cooling, liquid scintillator was added and the vial shaken

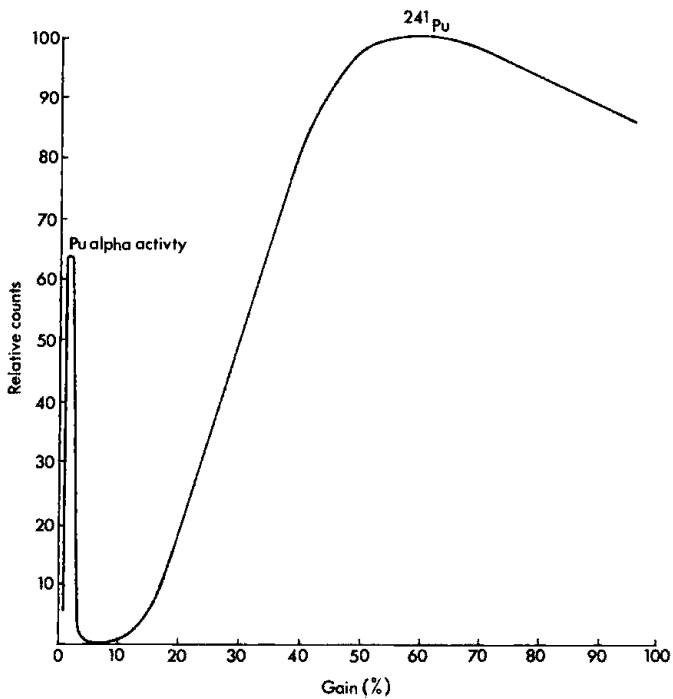


Fig.1. Gain scan of plutonium from a smear analysed by the ferri-phosphate procedure.

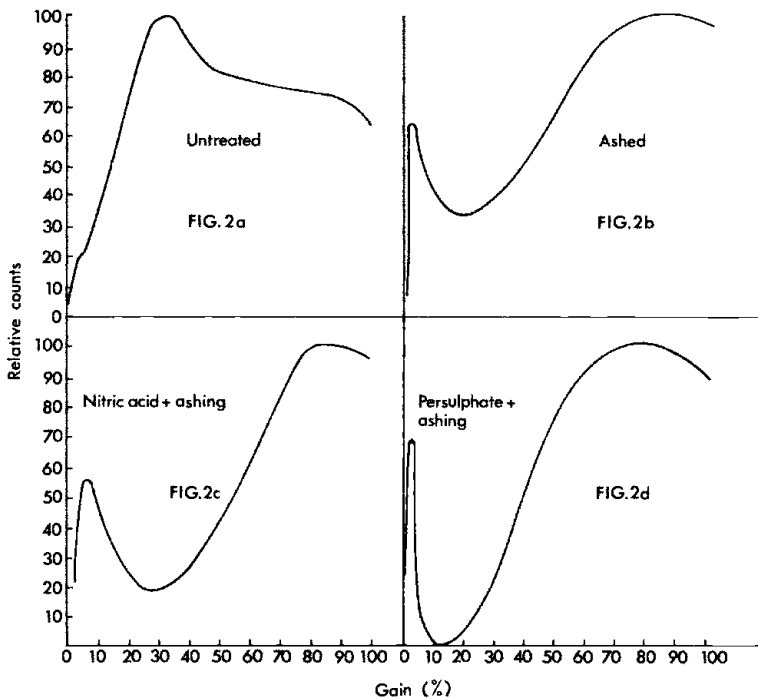


Fig 2. Gain scans of Plutonium-239 and Plutonium-241 on smears after different treatments.

vigorously, but the piece of ash was difficult to disperse. Silica powder was added to the vial to produce a gel and after further shaking the gain scan shown in Fig. 2b was obtained. There is a considerable improvement over that obtained with the untreated smear, but the separation of α - and β -emitting plutonium is still not very good.

A further dirty smear was placed in a counting vial to which 2 ml of nitric acid was added to speed up the oxidation. The vial was heated in the muffle furnace for 30 min, by which time the oxidation was complete, leaving a brownish residue in the bottom. Liquid scintillator was added to the vial, which was shaken up to disperse the residue as much as possible. However, most of it remained stuck to the bottom and sides of the vial. Silica powder was added to gel the source and a gain scan was obtained as before. This is shown in Fig. 2c and indicates a slight improvement on that obtained by ashing without nitric acid.

Ammonium persulphate was then tried as an alternative oxidant. The advantage of this salt is that it has a higher boiling point than nitric acid, completely decomposing into volatile products including oxygen. About 2 g was placed in the bottom of the vial. To prevent the smear ash forming one lump, difficult to disperse, or from adhering to the sides of the vial, silica powder was added to the vial initially. The smear paper was then pushed beneath the powder and a silica wool plug inserted in the neck of the vial to prevent any losses. The vial was placed in the muffle furnace for 30 min, by which time oxidation was complete. Particles of ash, slightly yellow in colour could be observed dispersed in the powder. The silica wool plug was pushed right into the vial and liquid scintillator added. A gel was produced by shaking vigorously and a gain scan carried out which is shown in Fig. 2d. It can be seen that separation of the α - and β -emitting plutonium is very good, similar in fact to that produced by the ferri-phosphate technique. A counting vial prepared for oxidation of a smear sample with ammonium persulphate is shown diagrammatically in Fig. 3.

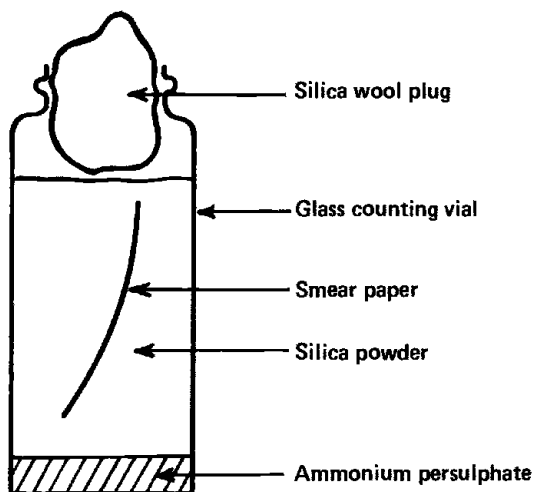


Fig. 3. Counting bottle prepared for 'in-vial' oxidation of smear papers.

Counting efficiencies

Six dirty smears were spiked with Plutonium-239 and a further six with Plutonium-241. All twelve smears were then ashed by the ammonium persulphate

procedure, gelled and counted. The Plutonium-239 smears were counted at 3% and the Plutonium-241 at 80% gain. In each case counts were recorded in a restricted window of 200–400 and also in a full window of 50–1000. The results of these counts are given in Tables 1 and 2.

Table 1. Counting efficiency for dirty Plutonium-239 smears.

Sample no.	Counting efficiency (%)	
	200–400	50–1000
1	70.2	102.9
2	66.7	100.2
3	63.9	101.6
4	68.0	103.3
5	68.2	102.0
6	71.0	99.0
Mean and S.D.	68.0 \pm 4.6	101.5 \pm 3.0

Table 2. Counting efficiency for dirty Plutonium-241 smears.

Sample no.	Counting efficiency (%)	
	200–400	50–1000
1	4.1	11.4
2	3.7	10.0
3	2.9	7.2
4	3.2	8.2
5	4.2	11.7
6	4.2	10.8
Mean and S.D.	3.7 \pm 1.0	9.9 \pm 3.0

From Table 1 it is clear that Plutonium-239 on smears can be counted at 100% efficiency with a full window. A restricted window was used in the initial work because Eakins and Lally² found a better figure of merit when using it with the ferri-phosphate complex. A gain scan of an oxidised dirty Plutonium-241 smear with a full window showed that about 5% of the counts occurred in the Plutonium-239 region, so the restricted window was chosen despite the lower counting efficiency.

The counting efficiency for Plutonium-241 with a full window is higher than that with a restricted window by a factor of almost 3. A gain scan of a Plutonium-239 smear with a full window showed only a 2% contribution to the Plutonium-241 region, so the full window was adopted for Plutonium-241 counting.

In order to assess the average contribution of each nuclide to the other channel, the Plutonium-241 smears were counted at the Plutonium-239 settings and vice versa. The contributions, expressed as a percentage of the counts obtained at the correct gain and window settings, are given in Table 3. These contributions were considered to be negligible, compared with the variations likely to occur in counting efficiencies from one smear to another.

Counting efficiencies for different types of smear

Having established that α - and β -emitting plutonium could be differentiated, even on the worst types of smear, the range of counting efficiencies likely to be

Table 3. Overlap of plutonium α - and β -channels.

Sample no.	Plutonium-241 counts appearing in Plutonium-239 channel (%)	Plutonium-239 counts appearing in Plutonium-241 channel (%)
1	0.11	1.5
2	0.05	1.9
3	0.16	1.8
4	0.11	1.7
5	0.16	2.3
6	0.17	2.4
Mean and S.D.	0.13 \pm 0.08	1.9 \pm 0.6

encountered with smears from a variety of surfaces was investigated. Six smears of different types were prepared. The first consisted of an unused filter paper. The second was prepared by smearing an apparently clean surface and the remaining four by smearing successively dirtier surfaces. The six samples were spiked with both Plutonium-239 and -241 and the counting efficiencies for each smear calculated. In addition, the ratio of the Plutonium-239 was calculated for each sample. The results of these measurements are shown in Table 4.

Table 4. Counting efficiencies for various smears.

Type of smear	Plutonium-241 (%)	Plutonium-239 (%)	Ratio Plutonium-241/ Plutonium-239
Unused paper	14.3	81.4	0.18 : 1
Clean surface	12.9	76.1	0.17 : 1
Dusty surface	11.9	67.8	0.18 : 1
Very dusty surface	9.9	71.2	0.14 : 1
Greasy surface	11.0	69.2	0.16 : 1
Very greasy surface	8.4	65.5	0.13 : 1
Mean and S.D.	11.8 \pm 3.9	71.9 \pm 13.6	0.16 \pm 0.04 : 1

Both the β - and α -counts are quenched with the increase in solid material on the smear. However, the Plutonium-241 is quenched more than the Plutonium-239, as indicated by the relatively greater standard deviation of the mean. For the accurate determination of plutonium activity on smears it would be necessary to determine the counting efficiencies for each smear. However, it is normally more important to determine the β/α ratio with reasonable accuracy than to determine the absolute activity. A qualitative assessment can be made of the category of smear and the appropriate counting efficiencies used. Alternatively, if the mean counting efficiencies for each nuclide are used, the β/α ratio can be determined to $\pm 25\%$, which is normally adequate for this type of work.

A comparison of Plutonium-241/Plutonium-239 ratios determined by two different methods

Three smears were obtained from plutonium areas and each was divided into two halves. One half was analysed by the ferri-phosphate complex method of Eakins and Lally² and the other half by the ammonium persulphate combustion technique. The Plutonium-241/plutonium α -activity ratios obtained by each method are shown in Table 5.

Table 5. Plutonium-241/plutonium α -activity ratios by different methods.

Smear no.	Plutonium-241/plutonium α -activity	
	by ferri-phosphate complex	by 'in-vial' oxidation
1	12 : 1	14 : 1
2	8 : 1	7 : 1
3	23 : 1	20 : 1

The ratios obtained are in reasonable agreement, particularly when it is considered that the combustion method takes less than an hour whereas the other procedure takes about a day.

COMMENT AND CONCLUSIONS

The very good separation of plutonium α - and β -activity obtained by gel scintillation counting, after the 'in-vial' ammonium persulphate oxidation technique, is believed to be due to two factors. The first of these is a reduction in particle size of the smear residue after oxidation. This is because of the support given to the smear paper by the silica powder. When heated in a vial, an unsupported paper curls up and any residue forms a compact lump difficult to disperse. With a supported paper this does not occur and the ash remains distributed in the silica powder. The second factor is related to the composition of the inorganic residue remaining after combustion. This contains a high proportion of iron which normal combustion leaves as a brownish oxide producing considerable colour quenching. Ammonium persulphate converts this iron to a very pale yellow material, presumably ferric sulphate, which produces much less quenching.

No attempt has been made in this work to obtain optimum counting conditions for Plutonium-241 or plutonium α -activity. It seemed pointless to attempt to obtain the maximum figure of merit for a particular smear when individual smears could vary so widely. Instead, counting conditions were used which gave reasonable results for a range of smears.

The procedure described enables Plutonium-241 and plutonium α -activity to be determined on smears in one hour with sufficient accuracy for indirect surface contamination monitoring. The plutonium β/α ratio obtained is good enough for the operational health physicist to estimate Plutonium-241 surface contamination from direct α -counting and also to identify the source of the contamination.

REFERENCES

- 1 R.F. Clayton, 'Monitoring of Radioactive Contamination on Surfaces', Technical Reports Series No. 120, I.A.E.A., Vienna, 1970.
- 2 J.D. Eakins and A.E. Lally in Liquid Scintillation Counting, Vol. 2 (Eds. M.A. Crook, P. Johnson and B. Scales), Heyden, London, 1972, pp.155-65.
- 3 T.H. Bates in Liquid Scintillation Counting, Vol. 2 (Ed. M.A. Crook, P. Johnson and B. Scales), Heyden, London, 1972, p.165.

DISCUSSION

G.A. Sutton: Have you considered the use of combustion via the 'Bomb' technique? If not why not?

J.D. Eakins: No we have not. Mainly because the operational health physicist can put his smears directly into the sample vial literally by the dozen — we believe this to be a more speedy method.