

PLUTONIUM ANALYSIS BY LIQUID SCINTILLATION TECHNIQUES

John J. Fardy

Chemical Technology Division, Australian Atomic Energy
Commission, Private Mail Bag, Sutherland, N.S.W. 2232,
Australia

Abstract. Liquid scintillation counting procedures developed during studies of the aqueous complexes of plutonium and having high accuracy and simple sample preparation are discussed. Alpha counting techniques for the assay of plutonium will not discriminate against the natural ^{241}Am content. However, the ^{241}Pu parent is the only beta emitter present in high purity standard plutonium metal and measurement of the beta activity with a commercial liquid scintillation counter effectively differentiates plutonium from americium. This paper examines a variety of scintillator solutions, both commercial and laboratory-prepared mixtures as well as extractive scintillators, for the determination of ^{241}Pu in acid media. Liquid scintillation spectra were repeatedly measured over a 24 hour period, counting efficiencies determined, the maximum solubility of the aqueous phase in each scintillator solution recorded, and the extent of plutonium adsorption on the counting vials examined for a variety of solution conditions including plutonium concentration, valency of the plutonium ions, acidity and acid type. Based on these results suitable counting media are suggested.

Introduction. While liquid scintillation counting is normally associated with the measurement of the weak beta emitters, tritium and ^{14}C , in organic samples, more inorganic chemists are using this technique for counting other beta nuclides and alpha emitters. The determination of the alpha activity associated with the actinides using this technique has been well described in a recent paper by Ihle (1). However, no liquid scintillation methods for the

radiometric assay of plutonium were listed in a recent hand book on plutonium (2). The determination of ^{241}Pu in a mixture of plutonium isotopes was described in 1958 (3) and the liquid scintillation determination of plutonium in biological samples was described recently (4).

While plutonium metal can be purchased as a high purity standard it is not normally isotopically pure. The only important impurity is ^{241}Am from the ^{241}Pu parent. Alpha counting will not discriminate against the ^{241}Am content and many investigators neglect its presence. This study demonstrates the use of beta activity measurements of ^{241}Pu with a liquid scintillation spectrometer to determine the plutonium content of acidic samples. Unfortunately, the low beta energy (18 keV maximum) makes the measurement of ^{241}Pu difficult and this paper examines some of these problems.

Materials and Methods. All chemicals used in these studies were of reagent grade.

A concentrated plutonium solution was prepared from high purity plutonium metal (NBS, Washington) and various plutonium solutions in the +3 and +4 state were prepared as described by Fardy and Pearson (5). These were added to perchloric acid, and mixtures of perchloric/sulphuric, perchloric/hydrochloric and perchloric/nitric acids in which the ionic strengths and total acidity were maintained constant at 1 or 4M and the concentration of added acid (H_2SO_4 , HCl , HNO_3) maintained constant at 0.5M. Since the isotopic composition of the plutonium metal was known the theoretical beta and alpha activity of each solution could be calculated and used as a basis for counting efficiency measurements.

Liquid scintillation counting was performed with an Ansitron liquid spectrometer with a freezer temperature of -5°C . Discriminator circuits permitted manual plotting of the energy spectrum. Alternatively the signal was fed to a 256 Channel Analyser (RCL) and the spectra recorded either as a digital output or on a chart recorder. The operating conditions were selected to obtain maximum counting rate for the beta activity of the ^{241}Pu but with the

LIQUID SCINTILLATION COUNTING

low energy discriminator adjusted so that the preamplifier noise was eliminated. Figure 1 shows typical beta and alpha spectra of a high purity plutonium sample. The alpha particles from ^{239}Pu , ^{240}Pu and ^{242}Pu yield pulses at an energy level of a corresponding 0.7 MeV beta ray.

A number of scintillator mixtures were examined. Two commercially available liquid scintillators, NE-220(NE) and Insta-Gel (IG), were used but later modified by the addition of 4g tri-n-octylphosphine oxide (TOPO) per 100 ml of scintillator (NE/T and IG/T). Another scintillator mixture (O), comprising 5g of 2,5-diphenyloxazol (PPO) and 50 mg of p-bis-2-(5-phenyloxazol)-benzene (POPOP) per litre of 38.5 vol % p-xylene, 38.5 vol % p-dioxane and 23.0 vol % absolute ethanol, and used as a general scintillator at Oak Ridge National Laboratory (ORNL), was also studied. Other alternatives of this mixture involved the addition of TOPO (O/T) and/or naphthalene (O/N and O/N/T). Finally an extractive scintillator recommended by McDowell (6) which was made 0.01 - 0.2M in an organic soluble extractant was tested.

Each scintillator was compared by adding 100 to 500 μl of an acidic solution of plutonium, to 10 ml of the scintillator in a scintillator vial, and measuring the beta and alpha activity as a function of time (0, 4 and 24 hours). Similarly, the energy spectra were recorded over the same time interval. At the conclusion of the 24 hour period the adsorption of the plutonium on the walls of the counting vials was measured. Each sample was removed from the counter, the solution discarded, the vial shaken with 10 ml of the scintillator for one minute, this removed and a fresh aliquot of scintillator added prior to recounting.

Insta-Gel was tested as an emulsion scintillator. The scintillator (10 ml) contained in counting vials were stood in a bath of hot water, 100-500 μl aliquots of Pu III in 0.5M HClO_4 /0.5M H_2SO_4 added to the respective bottles and sufficient demineralised water or acid mixture introduced to give a total aqueous phase of 7 ml. The vials were shaken while being cooled to room temperature with tap water. Each vial was counted after 30 minutes in the freezer of the liquid spectrometer.

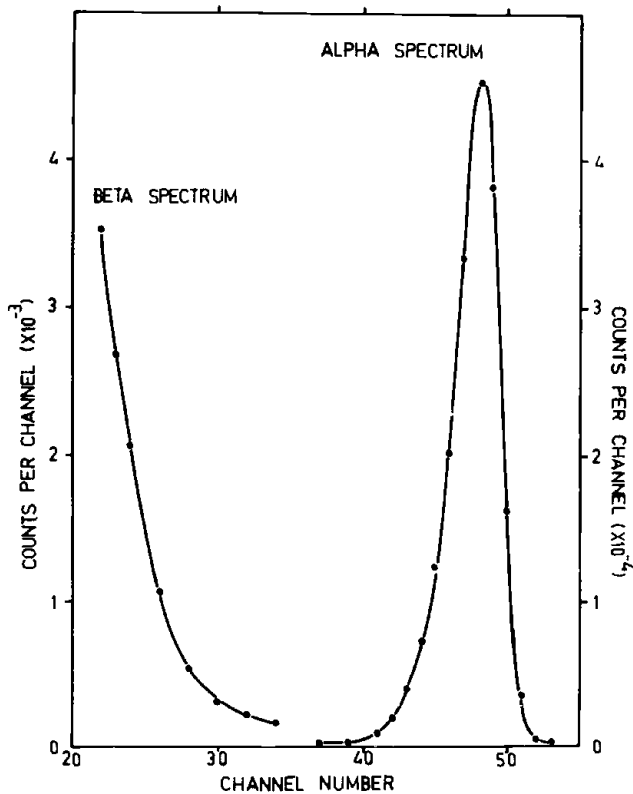


Figure 1 Beta and alpha liquid scintillation spectra of NBS plutonium

LIQUID SCINTILLATION COUNTING

Finally, the maximum volume of water and mineral acid mixture that can be added to 10 ml of each solvent system, without causing cloudiness or separation, was determined at room temperature and -5°C .

Results and Discussion. Initial studies showed that the most marked variation in the scintillation counting occurred when the concentration of the plutonium solutions was low. Therefore, all scouting tests were restricted to 100 μl aliquots of $1.125 \times 10^{-3}\text{M}$ of PuIII solution ($5 \times 10^3 - 10^4$ cpm).

Figure 2 shows a variation observed in some liquid scintillation spectra over 24 hours. It illustrates a marked reduction in the alpha spectrum accompanied by a shift to lower energy of the peak. This change produced a marked shift in the beta spectrum causing an increase of 20% in the total beta activity. The decrease observed in alpha activity opposed this increase. These changes normally occurred through a combination of colour quenching by water and acid, and adsorption of the plutonium on the surface of the counting vial. Another change was observed spasmodically in ORNL type scintillators and which is the opposite of that observed in Figure 2. Initially there was poor resolution of the alpha spectrum while the minimum between the alpha and beta peaks showed an unusually high count rate. However, after a time interval of 24 hours, the plutonium spectrum returned to normal. This change was characterised by an increase of the total alpha activity but a decrease in the beta activity. We have no explanation for this reversal.

Two other forms of spectral changes were observed during the course of this study. A similar reduction in the size of both peaks, which resulted in a decrease of both beta and alpha activity, was attributed to a loss of plutonium from solution either as a precipitate or by surface adsorption. Liquid scintillation counting in 0.5M $\text{HClO}_4/0.5\text{M}$ H_2SO_4 solutions usually yielded this phenomenon. The other change involved an overall increase in the size of the peaks. Under the initial extraction conditions the plutonium was not transferred quantitatively from the aqueous phase to the solvent. On standing, the plutonium

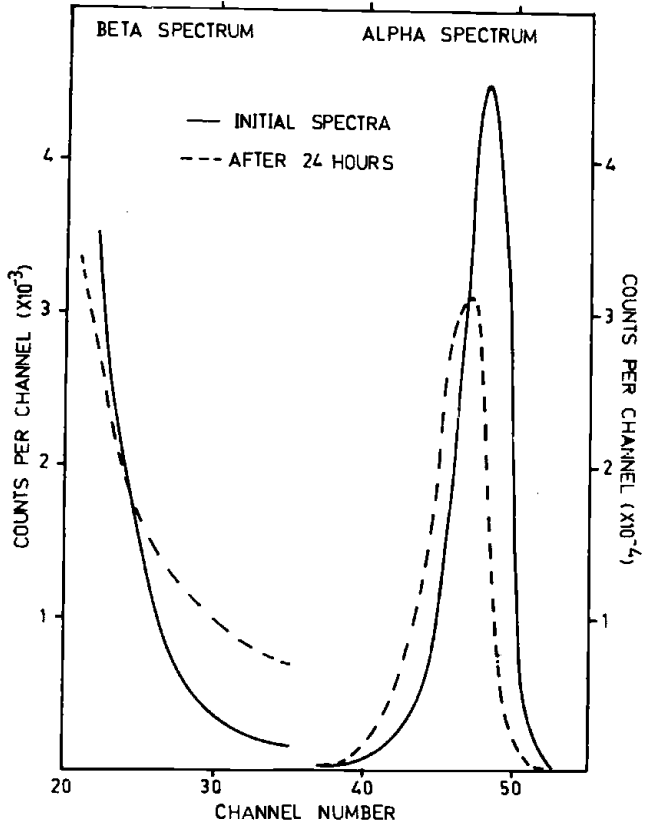


Figure 2 The effect of ageing on the liquid scintillation spectra of plutonium in the scintillator, NE-220

LIQUID SCINTILLATION COUNTING

continued to diffuse slowly into the scintillator.

Tables I - IV summarise the results for the comparative tests on seven scintillator mixtures which gave homogeneous solutions of the plutonium samples.

Table I compares the efficiency of each scintillator for the detection of beta and alpha activity. These are marginally dependent on the acid mixture and most dependent on the scintillator type. Only NE-220 produced coloured solutions but the intensity was reduced when TOPO was added, and led to a large increase in its efficiency for beta detection. Generally $\text{HClO}_4/\text{HNO}_3$ was the preferred acid medium while the presence of H_2SO_4 decreased the efficiency. However, TOPO reduced most acid effects. The more energetic alpha radiation was less susceptible to changes in the aqueous or scintillator media but the small changes observed parallel those obtained for beta detection. Based on these figures the preferred scintillators were placed in the order NE-220/TOPO > Insta-Gel/TOPO > Insta-Gel.

The change in activity recorded over 24 hours for each scintillator mixture is summarised in Table II. The magnitude and sign of these changes can be correlated with spectral changes discussed earlier in this paper. Since the beta activity was about one fifth of the alpha activity the largest changes occurred in the measurement of ^{241}Pu . These figures again showed that NE-220/TOPO was the best counting medium followed by ORNL/TOPO and Insta-Gel/TOPO. The presence of H_2SO_4 caused instability in the latter scintillator which contrasted its extreme stability in other acid mixtures. This follows our initial observation that a 100 μl sample of $\text{HClO}_4/\text{H}_2\text{SO}_4$ produced a slight cloudiness but on further additions of this acid solution the scintillator cleared.

Table III lists the adsorption of plutonium on the surface of each counting vial as a percentage of the original activity. Since the beta activity was more susceptible to the nature of the scintillator all surface adsorption calculations were based on the measured alpha activity. These results explain the difficulty found when

counting plutonium in $\text{HClO}_4/\text{H}_2\text{SO}_4$ solutions. Plutonium losses by adsorption were highest from this acid mixture especially when using the commercial scintillants, NE-220 and Insta-Gel. The addition of TOPO stabilised the plutonium in NE-220 but could not prevent significant adsorption losses from Insta-Gel. Past experiences in the solvent extraction of actinides from sulphate solutions (7) suggested that the addition of a primary amine, Primene JMT (JMT), would correct this situation. Tests with Insta-Gel/TOPO made 0.01M in JMT confirmed this. Adsorption was reduced to less than 4%. The scintillant mixture, ORNL/TOPO, was the best choice, when adsorption losses are required to be minimised, followed closely by NE-220/TOPO and ORNL/N/TOPO. The low rating of scintillator, Insta-Gel/TOPO, was due to its adverse reaction in sulphate systems but the addition of JMT upgraded this scintillator to the level of NE-220/TOPO.

The quantity of aqueous phase that can be maintained as a single phase for each of the scintillators is summarised in Table IV. Both Insta-Gel and Insta-Gel/TOPO mixtures were far superior to the remaining cocktails. An increase in acidity from 1 to 4M did not decrease this capacity. The scintillators not containing TOPO showed a low tolerance for the aqueous phase as its acidity increased. However, TOPO stabilised these scintillants towards highly acid solutions and in combination with some scintillators, particularly NE-220, significantly increased their capacity. For NE-220/TOPO this figure increased from 0.86 ml for 1M HClO_4 to 1.50 ml for 4M HClO_4 . The figures in Table IV were reduced by 0.05 - 0.1 ml when remeasured at -5°C .

Based on the results of the above studies, the scintillator NE-220/TOPO was the obvious choice as the best solvent system for incorporating various acid solution of plutonium into a homogeneous solution for the liquid scintillation counting of ^{241}Pu . Our second choice for continued study was the mixture Insta-Gel/TOPO. Its high capacity for various aqueous media, coupled with its relative high efficiency for the detection of ^{241}Pu suggested it as a useful alternative, despite its poor performance in sulphate systems (which can be corrected by the addition of JMT).

LIQUID SCINTILLATION COUNTING

Both scintillators were re-examined after the volume of $0.5\text{M HClO}_4/0.5\text{M H}_2\text{SO}_4$ added to 10 ml of the scintillator was increased from 100 μl to 500 μl . While the efficiency for ^{241}Pu detection decreased from 19.0% to 9.8% in NE-220/TOPO, the quenching in Insta-Gel/TOPO was less intense and the efficiency decreased from 16.8% to 12.6%. Even more surprising was the reversal in the stability of the activities in these scintillators measured as a function of time. Over 24 hours the total beta count registered in NE/TOPO changed by 0.77% for a 100 μl aliquot size but decreased by 30% for a 500 μl sample. The reverse trend occurred in Insta-Gel/TOPO. The 16.8% loss in the beta activity for a 100 μl sample was totally eliminated when a 500 μl aliquot was used. Changes in the alpha activity were unaffected by aliquot size when using NE-220/TOPO. However, the stability in Insta-Gel/TOPO was similar to that described for the beta activity.

Increasing the total acidity of the plutonium sample from 1 to 4 M reduced the efficiency for ^{241}Pu detection to 15% in both scintillators, yielded no appreciable change in the total alpha efficiency and gave no noticeable change in the measured activities over 24 hours. This suggested that TOPO stabilised the scintillator against acid effects and the changes wrought by increasing aliquot size were largely due to the water.

The valence of the plutonium solutions was increased from +3 to +4 and the above tests repeated. This change did not alter either the efficiencies or stabilities from that recorded for Pu III solutions. The same problems plagued the $\text{HClO}_4/\text{H}_2\text{SO}_4$ system.

We have investigated the use of Insta-Gel as an emulsion scintillator for the detection of ^{241}Pu . The stabilised Insta-Gel/TOPO was also included in this study. The Insta-Gel was superior to Insta-Gel/TOPO. The presence of TOPO led to the formation of clouded or intensely white gels when acid or water was added. This severely quenched the ^{241}Pu activity and to a lesser degree the alpha activity. When TOPO was omitted the alpha activity could be determined with greater than 95% efficiency, independent of water or acid addition. In contrast, the

counting efficiency for ^{241}Pu was reduced from 13.2% to 7.4% when water was added, and to 4.8% with the addition of acid. In all instances the variation in the total beta activity was less than 3% over a 72 hour period.

Finally, we examined some extractive scintillators. Our laboratory experiences with the solvent extraction of plutonium and other actinides (8, 9) suggested a study of the organic extractants, TOPO, di-(2-ethylhexyl) phosphoric acid (HDEHP), JMT and tri-n-octylamine (TNOA). Initial studies were made with 10 ml of the scintillator containing 0.1M extractant and shaken for one minute with 100 μl of Pu III contained in various acid mixtures whose total acidity was one molar. The alpha activity was used to follow the degree of extraction. In no instance did a single extractive scintillator quantitatively extract plutonium from all acid solutions. Both TOPO and HDEHP extracted all the plutonium and give 21% counting efficiencies for ^{241}Pu from 0.5M HClO_4 /0.5M HNO_3 . In 0.5M HClO_4 /0.5M H_2SO_4 solutions JMT quantitatively removed the plutonium but colour quenching reduced the counting efficiency to 13.7% for beta activity. Plutonium was least extracted from 1M HClO_4 but recounting the solution after standing for a day showed a significant increase in the activity of the TOPO scintillator. This suggested that one minute mixing was insufficient for the extraction to reach equilibrium. Several modifications to the above extractive systems were tried. The best results were obtained by adding 100 μl of the Pu III solution to 5 ml 0.05M HNO_3 and shaking for five minutes with 10 ml of the extractive scintillator containing 0.2M TOPO. The hydrolytic reactions of Pu IV precluded its use in such a system.

This study indicates that the scintillator mixture, NE-220/TOPO, is the best counting medium for general use with plutonium in various acid media. Insta-Gel/TOPO is a useful alternative especially when aliquots of 500 μl or more of the plutonium solutions are necessary to obtain reasonable counting statistics. If sulphuric acid is present in the plutonium solutions then this scintillator must be counted within 4 hours of adding the aqueous phase unless it is stabilised with JMT. Suitable extractive

LIQUID SCINTILLATION COUNTING

scintillators can yield counting efficiencies as high as 21% for ^{241}Pu . Emulsion scintillants are practical for alpha measurements on plutonium samples but the necessity of adding large amounts of aqueous solution to stabilise the emulsion detracts from its use for ^{241}Pu detection.

Acknowledgements. The author is indebted to Mrs. J.M. Pearson and Mr. C.H. Randall for their excellent technical assistance.

References.

1. H.R. Ihle, M. Katayannis and A.P. Murrenhoff in Proceedings of a Symposium on Standardisation of Radionuclides, p.485. Vienna, IAEA (1967).
2. R.J. Brouns in Plutonium Handbook, Vol.2, p.707 (O.J. Wick, Ed) New York : Gordon and Breach (1967)
3. D.L. Horrocks and M.H. Studier, Anal. Chem. 30, 1747 (1958).
4. R.F. Keough and G.J. Powers, Anal. Chem. 42, 419 (1970)
5. J.J. Fardy and J.M. Pearson, J. Inorg. Nucl. Chem. 35, 2513 (1973)
6. W.J. McDowell in Proceeding of International Conference on Organic Scintillators and Liquid Scintillation Counting, p.937 (D.L. Horrocks and Chin-Tzu Peng, Ed). New York : Academic Press (1970).
7. J.J. Fardy, D.G. Pinchbeck and M.S. Farrell, AAEC Report AAEC/E189 (1968).
8. J.J. Fardy and J.M. Chilton, J. Inorg. Nucl. Chem., 31, 3247 (1969)
9. J.J. Fardy and J.M. Pearson, J. Inorg. Nucl. Chem., (In Press)

Table I. Efficiency (%) for Beta and Alpha Detection

Solvent	HClO ₄		HClO ₄ / H ₂ SO ₄		HClO ₄ / HCl		HClO ₄ / HNO ₃	
	β	α	β	α	β	α	β	α
NE	9.2	90	8.8	82	10.2	97	11.9	94
NE/T	18.0	98	17.8	96	18.0	98	18.6	99
O/T	7.7	98	7.5	94	7.6	97	7.6	95
O/N	9.5	90	9.8	89	10.0	95	10.6	92
O/N/T	10.7	97	10.6	94	12.9	89	11.4	97
IG	16.0	98	13.2	91	16.8	96	16.1	95
IG/T	16.0	99	16.2	96	16.0	99	16.0	98

Table II. Change in Beta and Alpha Activity (%) over 24 Hours

Solvent	HClO ₄		HClO ₄ / H ₂ SO ₄		HClO ₄ / HCl		HClO ₄ / HNO ₃	
	β	α	β	α	β	α	β	α
NE	-12	-4.1	20	-22	-17	-0.2	-20	-7.8
NE/T	0.1	0.1	-0.8	-2.7	-0.8	0.1	0.1	-0.5
O/T	-0.5	-0.1	3.2	-1.9	-0.9	1.1	-6.8	2.4
O/N	10	-5.7	4.1	-4.5	4.2	-2.3	3.0	-4.2
O/N/T	-0.3	0.3	0.7	-3.9	-25	9.4	-0.3	0.5
IG	-1.5	-2.0	-5.6	-33	-5.4	-4.5	-2.7	-1.1
IG/T	-0.8	-0.4	-15	-6.7	0.4	0.1	-0.7	0.1

LIQUID SCINTILLATION COUNTING

Table III. Surface Adsorption of Plutonium (%)

Solvent	HClO ₄	HClO ₄ / H ₂ SO ₄	HClO ₄ / HCl	HClO ₄ / HNO ₃
NE	8.2	25.5	1.1	9.1
NE/T	0.7	3.3	0.3	0.3
O/T	0.1	2.2	0.1	0.1
O/N	9.4	7.5	2.9	8.6
O/N/T	0.1	4.5	0.1	0.2
IG	3.1	37.7	8.7	2.4
IG/T	0.5	19.1	0.4	0.3

Table IV. Maximum Volume of Aqueous Phase (ml) Miscible
with Solvents at Room Temperature

Solvent	H ₂ O	HClO ₄	HClO ₄ / H ₂ SO ₄	HClO ₄ / HCl	HClO ₄ / HNO ₃
NE	1.09	0.67	0.27	0.64	0.29
NE/T	0.88	0.86	0.50	0.70	0.48
O/T	0.82	0.83	0.75	0.79	0.76
O/N	0.80	0.65	0.65	0.63	0.60
O/N/T	0.70	0.68	0.63	0.60	0.60
IG	2.00	1.75	2.00	1.85	1.95
IG/T	1.95	1.70	1.90	1.80	1.90

