

Technique for Sequential Cerenkov and Liquid Scintillation Counting after Concentration of Emitters on Submilligram Amounts of Carrier

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INTRODUCTION

Since the inception of liquid scintillation counting, there have been descriptions, too numerous to list, of procedures for radioassay of ^{14}C , ^{35}S and ^3H in tracer studies and/or biological and environmental monitoring analyses. A review of preparative methods used up to 1967 is available.¹ Electron capture nuclides and low-energy β -emitters for which this mode of assay has also been employed include ^{51}Cr , ^{54}Mn , ^{65}Zn , ^{88}Yt , ^{125}I ,² ^{129}I ,³ ^{55}Fe and ^{59}Fe ,^{2,4,5} ^{45}Ca ,^{6,7} ^{63}Ni .⁸ Preparative methods usually require specific procedures to (i) eliminate the presence of any other interfering radionuclides and (ii) preclude or reduce quenching arising from both the sample matrix and indigenous or added carrier (usually tens of milligrams).

Assay of α -emitters by liquid scintillation counting has been reported.⁹⁻¹⁷ In the case of plutonium, a frequently used technique is to mix a solution of the carrier-free actinide in specific organic extractant with scintillation cocktail.^{9,13,16} A technique of dispersing plutonium as a colourless ferriphosphate in a gel suspension system has been employed¹⁸ to assay plutonium α (^{238}Pu + ^{239}Pu + ^{240}Pu) and β (^{241}Pu , E_{max} 21 keV) activity simultaneously. Given suitable counting parameters for these isotopes, resolution is sufficient to preclude cross-interference between counting channels.^{19,20} A simple technique for concentrating radiochemically separated plutonium on submilligram quantities of yttrium or ferric hydroxides, collecting the precipitate on a membrane filter, and quantitatively transferring it to scintillant is presented in this paper; the final preparation is homogeneous, and therefore susceptible to quench correction.

Assay of high-energy β -emitters, e.g. ^{89}Sr and ^{90}Yt ,²¹ or β/γ -emitters²² by liquid scintillation counting has received little attention, but assay of high-energy β -emitters by Cerenkov counting in aqueous media using a liquid scintillation counter is becoming an accepted alternative to other forms of β -counting. A wide range of high-energy ($E_{\text{max}} > 500$ keV) β -emitters has been studied,^{7,23-29} and in particular the technique is being applied to the determination of ^{90}Sr in a variety of biological and environmental samples by following grow-in of ^{90}Yt by repetitive counting, and in monitoring of low-level activity in drainage systems.²⁸

It is known that some fission products can be co-precipitated on ferric or yttrium hydroxide, and the above-mentioned preparation technique developed for plutonium was

applied to three different types of fission product (and daughter isotopes), namely (i) ^{90}Yt , a pure β -emitter, $E_{\text{max}} = 2.27$ MeV, (ii) ^{144}Ce in equilibrium with its daughter ^{144}Pr , both of which have complex β - and γ -decay schemes, and (iii) ^{95}Zr in equilibrium with its daughter ^{95}Nb , which are β ($E_{\text{max}} = 890$ keV (2%), 924 keV (0.1%), rest < 400 keV) and γ -emitters. The membrane and precipitate were first dispersed in pure solvent (dioxan) to study the Čerenkov gain spectrum, followed by addition of dioxan-based scintillant to study the scintillation spectrum. The aim was to assess how specific the spectra characteristics would be with regard to determination of purity of a separated isotope, and by the same token to what extent the dual assay might also permit resolution in a mixture of emitters as compared with either assay alone. Advantages and potential applications of the technique are discussed.

METHODS AND RESULTS

Assay of plutonium

A plutonium residue, separated from a sample by a previously described technique³⁰ using ion-exchange resin, is dissolved in a small beaker in about 5 ml of 3M nitric acid containing one drop of hydrogen peroxide (100 vol.). Ferric iron or yttrium (100 μg) as nitrate in 3M nitric acid solution is added, and the pH adjusted to 10 using phenolphthalein indicator by adding sodium hydroxide solution (50% w/v followed by 1% w/v near the colour change). The solution is warmed to 60–80°C for 10 min, allowed to cool and the precipitate is filtered off on a 20 mm diameter, 0.2 μm pore size, cellulose nitrate membrane filter ('Sartorius' is suitable) supported on a conventional filter stick fabricated with a porosity 3 glass sinter whose effective diameter is not more than 19 mm. The filtration procedure involves mounting the membrane on top of the sinter, wetting it with distilled water and applying suction from a water pump. The filter stick is then inverted and the membrane immersed in the solution in the beaker which is carefully agitated as the supernate passes through the membrane; two additions to the beaker of distilled water (about 5 ml) complete transfer of the precipitate and washing. The filter stick is re-inverted, suction removed and the membrane and precipitate are transferred to a desiccator containing silica gel drying agent. After 15 min, the membrane is transferred to a polyethylene counting vial (20 ml capacity), source upwards, and 100 μl of 1M nitric acid is pipetted on to it. After 5 min, when the source appears to have dissolved, 1 ml of a dioxan-based scintillant (NE220 is suitable) is added; after a further 5 min, to ensure complete dissolution of precipitate, further scintillant (11 ml) is added and the vial carefully agitated to achieve an homogeneous solution of source and membrane. The vial is transferred to a liquid scintillation spectrometer (a Packard Tri-Carb (three-channel) Model 3320 was employed in this work), and counted after a dark adaption time of 1 h, against standards and blanks prepared in the same way.

Three counting channels are employed, and settings and typical counting characteristics are shown in Table 1.

At low levels of activity (less than 5 pCi α), a precise α -determination is not possible because of the high background obtained from a counter set up optimally for tritium. For α -determination only, the background may be reduced to about 2 counts min^{-1} ¹⁶ by adjustment of EHT on photomultipliers, but it is possible by the technique described here to carry out a conventional α -assay, in a low background counter (0.3 counts h^{-1}), of the source mounted on the membrane prior to introduction to scintillant. The activity ratio of ^{241}Pu to Pu- α is not usually less than 5, but at low levels of activity it is not possible to obtain precise internal channels ratios. This can be overcome by carrying out

Table 1. Counting characteristics of plutonium- α and ^{241}Pu .

Assay	Spectrometer channel	Amplifier gain (%)	Window	Background (blank cpm)	Counting efficiency (%) (100 x cpm/dpm)
α	1	0.5	50-210	10	100
β	2	50	50-1000	20	37
Channels ratio	3	50	290-1000	10	-

internal standardisation by transferring 1 ml from the counting vial containing standard to the counted sample vial; counting efficiencies are insensitive to volume changes of ± 1 ml. When using the internal channels ratio method a quench curve may be set up by preparing standards with varying amounts of iron or more simply by the conventional technique of adding increments of acetone to a standard. A quench curve for iron is shown in Fig. 1(a). The line was obtained by least squares analysis of the results.

Within the limits of experimental error the quench curve for acetone fell on this line. At very low energies, there is little difference between quench curves for chemical and colour quenchers.³¹ In the range investigated, no quenching of α -pulses was observed. Addition of a second membrane filter to a vial did not increase quenching, so it may be concluded that any observed quenching arises from iron and nitric acid. Figure 1(b) indicates the relationship between iron concentration and degree of quench. (N.B. Herein lies a potential means for determining low concentrations of iron.)

Pure yttrium did not show quenching in a range from 40 to 200 μg as is evident from the results shown in Table 2. In practice, plutonium separated from a sample and precipitated on yttrium contains a few micrograms of iron arising from reagents and slight quenching is observed.

The optimum amount of 'carrier' iron or yttrium to be employed routinely was chosen as 100 μg to ensure quantitative recovery; serious losses occur when less than 20 μg are used, ascribed to mechanical loss and possibly peptisation.

Table 2. ^{241}Pu counting efficiency as a function of mass of yttrium employed.

Yttrium (μg)	Internal channels ratio	^{241}Pu counting efficiency (%)
40	2.02	36.7
80	2.00	37.1
120	2.01	35.8
160	2.00	38.4
200	2.04	37.7
240	1.99	34.5

Mean of results (1-5) = 37.1 ± 0.4 (I.S.D.).

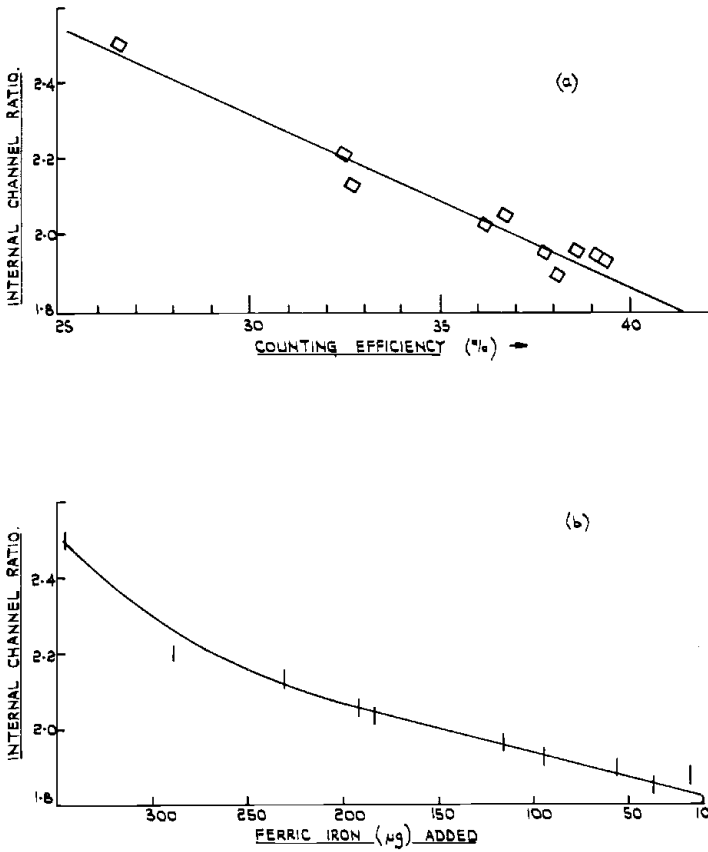


Fig. 1. Liquid scintillation counting of ^{241}Pu using ferric iron. Plot of internal channels ratio versus (a) counting efficiency, (b) mass of iron used.

YTTRIUM-90

Aliquots of ^{90}Yt standard solution (TRC Amersham, 2×10^4 disintegrations min^{-1} per aliquot) were separately subjected to precipitation on $100 \mu\text{g}$ of ferric iron and $100 \mu\text{g}$ of yttrium and the precipitates mounted on membranes as described above. After dissolution of a source in $100 \mu\text{l}$ of 1M nitric acid, 6 ml of dioxan (scintillation grade) was added, and the Čerenkov gain spectrum scanned. Six millilitres of dioxan-based scintillant (NE220) were then added, mixed with the solvent, and the liquid scintillation gain spectrum scanned (window = 50 to 1000 = maximum). The spectra using iron and yttrium are shown in Figs. 2 and 3 respectively, employing a logarithmic gain scale to cover the range; counting efficiency (%) is $100 \times (\text{count rate}/\text{disintegration rate})$. The maximum Čerenkov response in the presence of yttrium carrier is enhanced by a factor of 1.14 as compared with the response in 1M acid solution by virtue of the lower β -energy threshold in a solvent of higher refractive index ($n^{20^\circ}_{\text{D}}(\text{water}) = 1.333$, $n^{20^\circ}_{\text{D}}(\text{dioxan}) = 1.422$). The Čerenkov photons are attenuated by colour quenching in

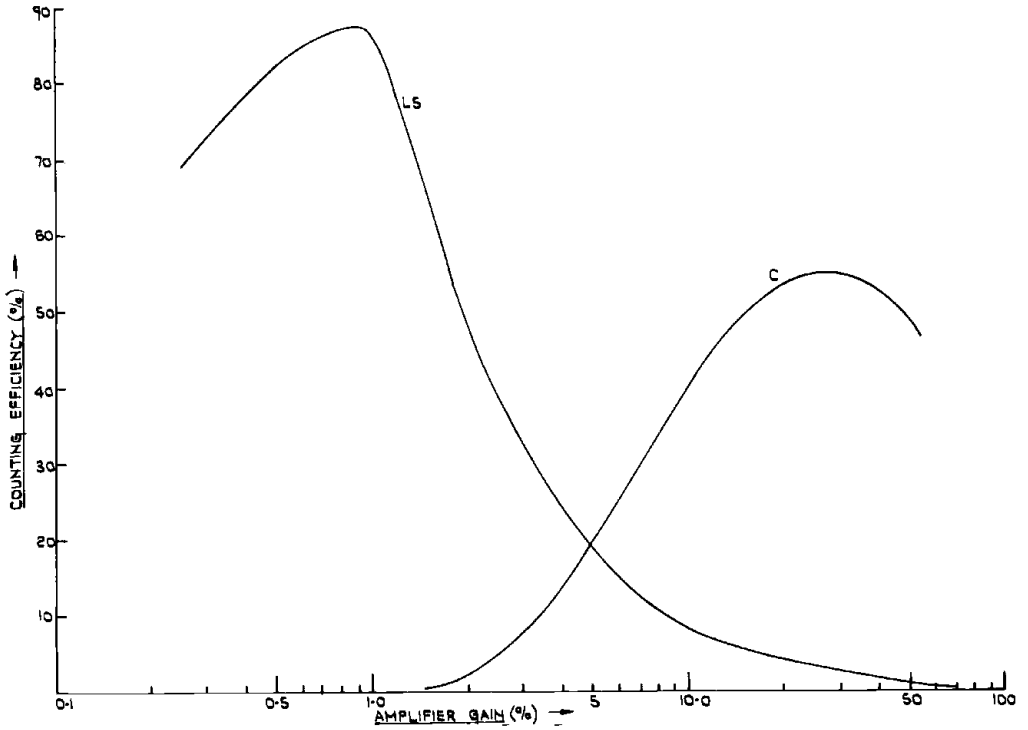


Fig. 2. Gain spectra of ^{90}Yt using ferric iron (100 μg). C = Čerenkov, LS = scintillation.

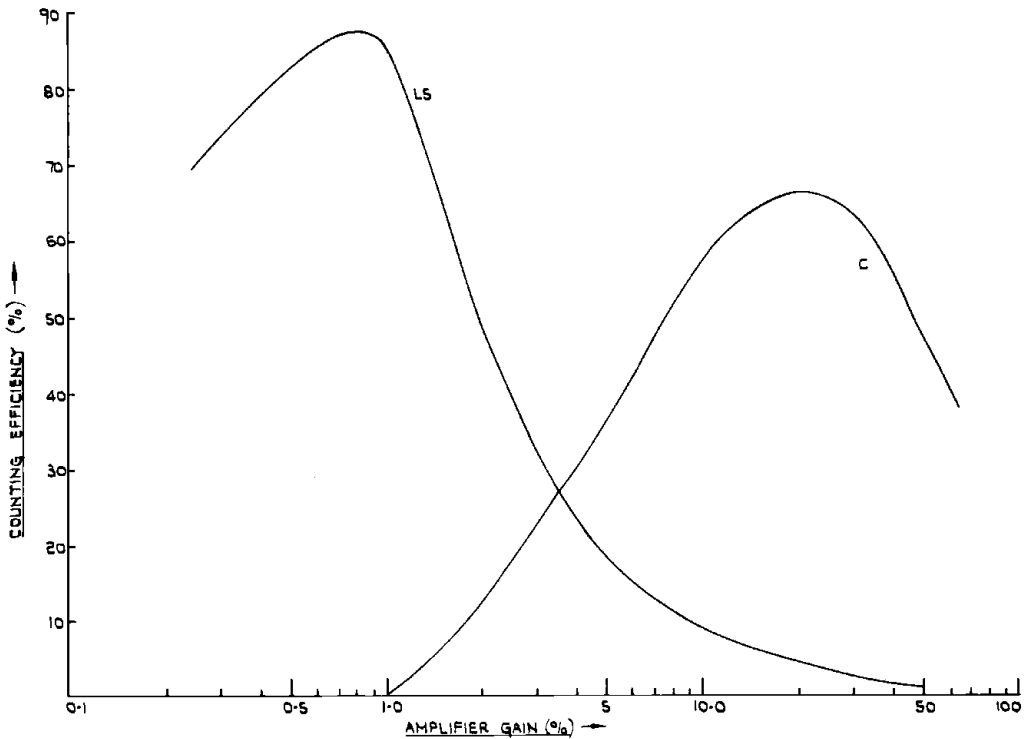


Fig. 3. Gain spectra of ^{90}Yt using yttrium (100 μg). C = Čerenkov, LS = scintillation.

the presence of ferric iron (chemical quenching cannot occur), and at the concentration employed the response is 0.96 of that in a colourless aqueous system. Quench correction in Čerenkov counting is possible.³² On addition of scintillant, the response is at low gain and at the optimum Čerenkov gain setting is reduced by a factor of 16.4, which presumably arises from radiative transfer of photon energy to the solutes in the scintillant; the net result is an enhancement of the ' β '-spectrum produced by energy transfer from ionising particles to the scintillation cocktail.

CERIUM-144 AND PRASEODYMIUM-144

Aliquots of ^{144}Ce (10^4 disintegrations min^{-1}) standard solution (carrier-free) in equilibrium with its daughter ($t_{1/2} = 17.3$ min) were separately subjected to precipitation on 100 μg of ferric iron and 100 μg of yttrium, and the procedure adopted for ^{90}Yt carried out. Recovery was quantitative as determined by γ -assay of the dioxan solution against 6 ml of the standard solution in the same geometry. The gain spectra (Figs. 4 and 5) must be examined in relation to the decay schemes. Cerium-144 emits three types of β -particle, namely $E_{\text{max}} = 309$ keV (70%), 240 keV (ca.5%) and 180 keV (25%) with associated γ -emissions ranging from 34 keV to 134 keV; ^{144}Pr emits β -particles of $E_{\text{max}} = 2.996$ MeV (97.8%), 2.30 MeV (1.2%) and 0.81 MeV (1.0%) with associated γ -emissions ranging from 0.697 to 2.186 MeV. The Čerenkov spectrum may therefore be attributed mainly to the high-energy β -particles of the daughter isotope, which by analogy with ^{90}Yt produce responses in scintillation cocktail in the region of 1% amplifier gain. The responses in the rest of the spectrum can be ascribed to ^{144}Ce β -particles and superimposed pulses arising from γ -photon interactions in the medium. The discernible peaks appearing in the 2 to 8% gain region are tentatively ascribed to the electrons arising from the non-coincident groups of γ -photons of widely different energy range and internal conversions. A theoretical calculation of mean Compton energies has been reported.²²

ZIRCONIUM-95 AND NIOBIUM-95 (IN EQUILIBRIUM)

Quantitative recovery of parent and daughter in equilibrium (3×10^4 disintegrations min^{-1}) was possible using ferric iron (100 μg) and ammonium hydroxide solution as precipitant. In all other respects, the procedures were as described for ^{144}Ce plus ^{144}Pr . Zirconium-95 emits β -particles of $E_{\text{max}} = 890$ keV (ca.2%), 396 keV (55%) and 360 keV (45%) with associated γ -energies of 722 keV and 754 keV. Niobium-95 emits β -particles of $E_{\text{max}} = 160$ keV (100%) and a γ -photon of energy 765 keV. Consequently, very little Čerenkov response can be seen (Fig. 6) since few electrons exceed the energy threshold. The smooth liquid scintillation gain spectrum arises from the β -particles (N.B. for ^{35}S , $E_{\text{max}} = 167$ keV, the optimum gain in NE220 is 5.5%), and the electrons produced by interaction of the almost mono-energetic gammas with the medium.

CONCLUSIONS

The technique is presented as a potentially simple means of source preparation whenever quantitative collection of emitter(s) on a small amount of precipitate, amenable to later dissolution, is possible. The prepared solid source may be submitted to other types of radioassay, e.g. low background α -counting, γ -spectrometry, prior to quantitative transfer to a liquid scintillation counting vial.

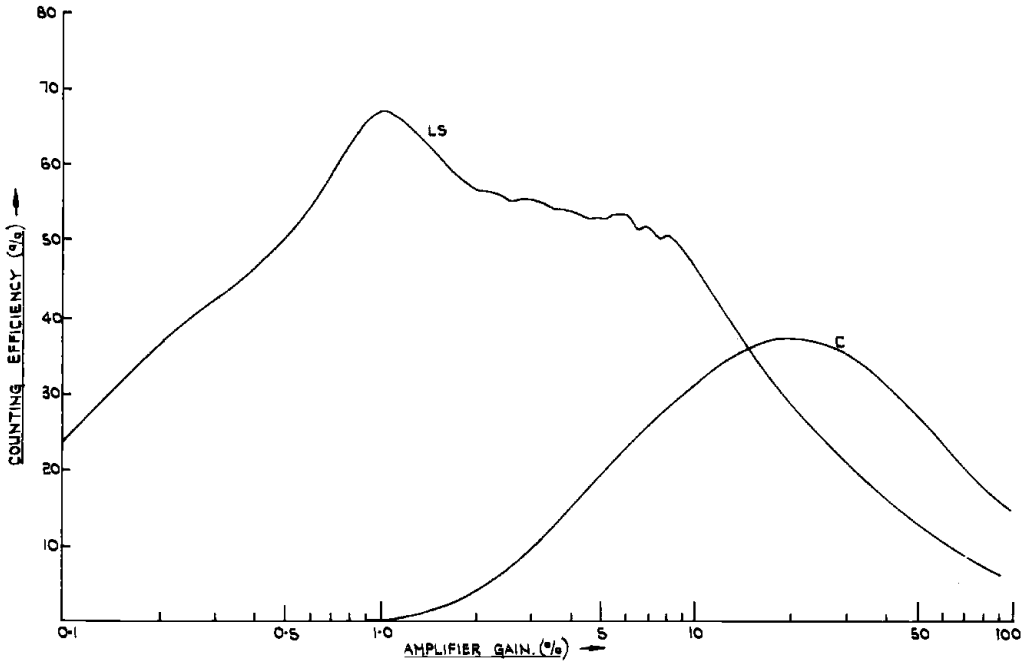


Fig. 4. Gain spectra of ^{144}Ce and ^{144}Pr using ferric iron ($100\ \mu\text{g}$). C = Čerenkov, LS = scintillation.

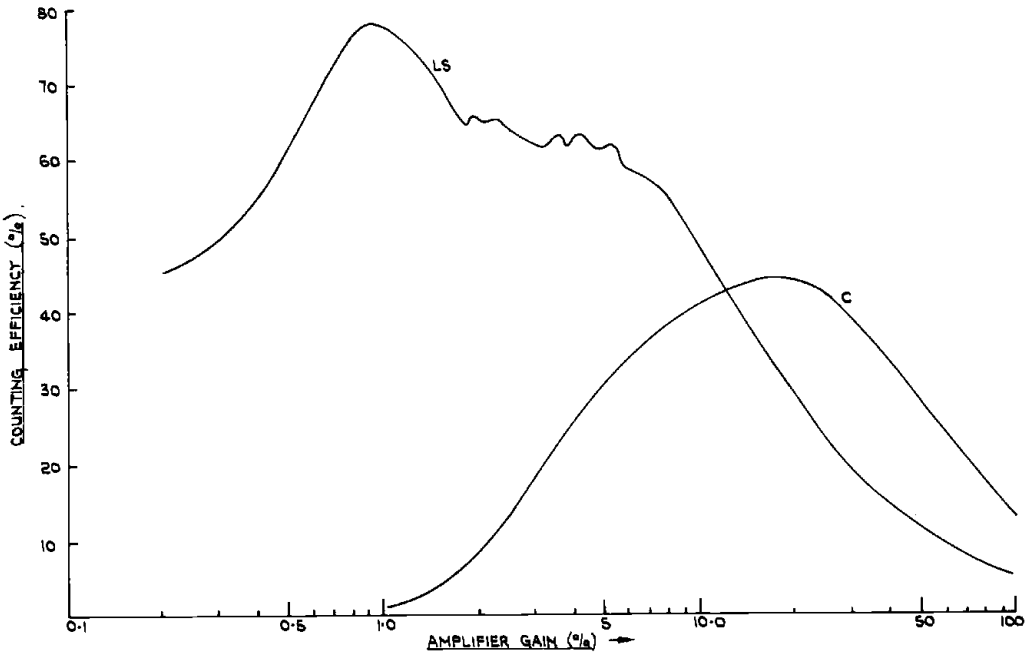


Fig. 5. Gain spectra of ^{144}Ce and ^{144}Pr using yttrium ($100\ \mu\text{g}$). C = Čerenkov, LS = scintillation.

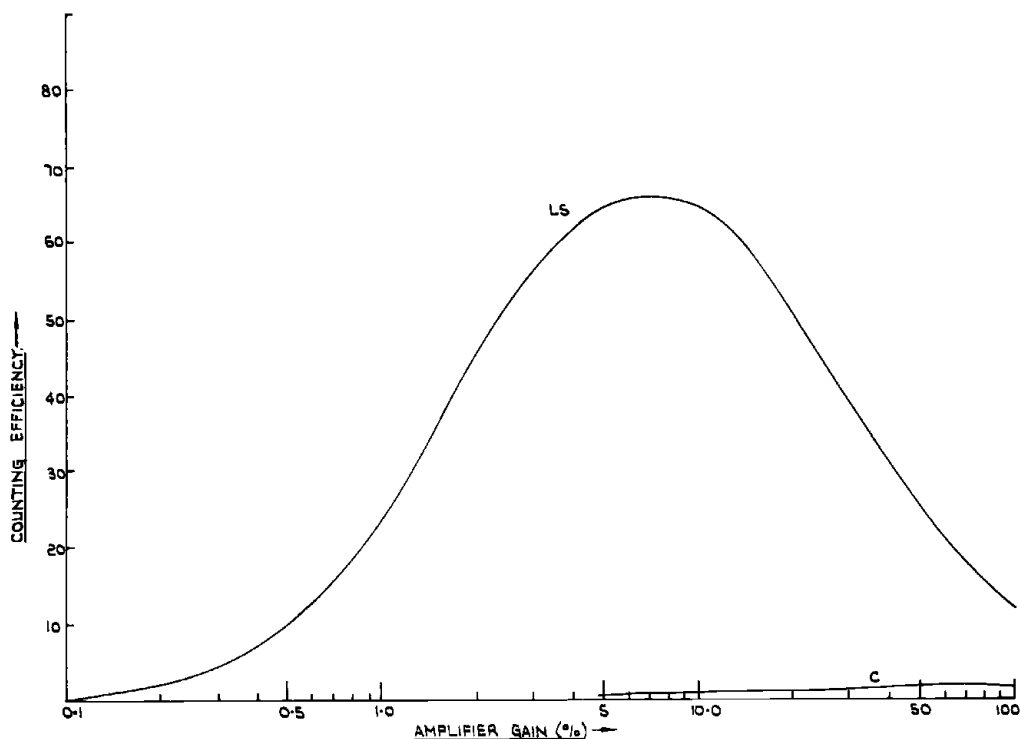


Fig. 6. Gain spectra of ^{95}Zr and ^{95}Nb (at equilibrium) using ferric iron ($100\ \mu\text{g}$). C = \checkmark erenkov, LS = scintillation.

Specific applications of the technique will be described in future publications, but it is worth noting that in addition to use for assay of indigenous ^{241}Pu in a sample, the technique has been used successfully employing pure ^{241}Pu as an added internal spike for recovery determination of plutonium in biological samples as an alternative to the use of spikes of an α -emitting isotope (^{236}Pu or ^{242}Pu) in conjunction with α -spectrometry. Assay of other actinides has not been thoroughly tested, but recent work³³ indicates that quantitative precipitation of actinides on phosphate and assay under similar conditions is possible.

The pairs of gain spectra for the β - and β/γ -emitters give extra information to characterise a radiochemically separated radionuclide in terms of purity as compared with that to be obtained from a single spectrum; the procedures involve little extra operational effort especially if scanning can be carried out with a multi-channel analyser. Alternatively, assay at selected gains, e.g. at maxima and at the intersection points of the spectra, might be useful. Pulse shape discrimination techniques, not available in this work, would permit significantly increased resolution between emissions inducing different ionisation/excitation densities which differently affect the fast and slow components of a pulse,³⁴ e.g. between α -pulses and β -pulses¹⁷ in a mixture.

Determination of emitters in an unknown mixture could never be possible because of inevitable limits in resolution, but in routine control measurements of, say, low levels of activity in water, for which the technique is attractive, any changes in level or

spectra characteristics would prompt closer investigation. The use of the membrane material for obtaining smear samples³⁵ in health physics monitoring is worth considering.

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REFERENCES

1. J. C. Turner, *Sample Preparation for Liquid Scintillation Counting*, Review 6, The Radiochemical Centre, Amersham, 1967.
2. A. Tada and T. Radoszewski, in *Liquid Scintillation Counting*, Vol. 1 (ed. A. Dyer), Heyden, London, 1971, p. 49.
3. J. J. Gabay, C. J. Paperiello, S. Goodyear, J. C. Daly and J. M. Matuszek, *Health Phys.* 26, 89 (1974).
4. J. D. Eakins and D. A. Brown, *Intern. J. Appl. Radn. Isotopes* 17, 391 (1966).
5. A. A. Moghissi, E. L. Whittaker, D. N. McNelis and R. Lieberman, *Anal. Chem.* 46 (9), 1355 (1974).
6. J. Nolan, in *Liquid Scintillation Counting*, Vol. 2 (eds. M. A. Crook, P. Johnson and B. Scales), Heyden, London, 1972, p. 147.
7. C. W. Baker, G. A. Sutton and J. W. R. Dutton, Symposium on the Determination of Radionuclides in Environmental and Biological Materials, CEGB London, AED CONF. 73-085 04, 1973.
8. B. R. Harvey and G. A. Sutton, *Intern. J. Appl. Radn. Isotopes* 21, 519 (1970).
9. D. L. Horrocks and M. H. Studier, *Anal. Chem.* 30, 1747 (1958).
10. D. L. Horrocks, *Rev. Sci. Instrum.* 34, 1035 (1963); *Intern. J. Appl. Radn. Isotopes* 17, 441 (1966).
11. T. Y. Toribara, C. Predmore and P. A. Hargrove, *Talanta* 10, 205 (1963).
12. A. Lindenbaum and C. J. Lund, *Radiation Res.* 37, 131 (1969).
13. R. F. Keough and G. J. Powers, *Anal. Chem.* 42, 419 (1970).
14. A. Seidel and V. Volf, *Intern. J. Appl. Radn. Isotopes* 23, 1 (1972).
15. A. Delle Site, G. Santori and S. Bazzari, *CNEN RT/PROT* (74), 23 (1974).
16. D. L. Bokowski, *J. Amer. Ind. Hyg. Assoc.* 333 (June 1974).
17. J. W. McKlveen and W. Reed Johnson, *Health Phys.* 28, 5 (1975).
18. 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, p. 155.
19. T. H. Bates, see Discussion in above symposium, p. 165
20. T. H. Bates, T. H. Boyd and J. Middlemas, Internal Report, 1971.
21. H. V. Piltingsrud and J. R. Stencel, *Health Phys.* 23, 121 (1972).
22. H. Prochazka and R. Jilek, IAEA Symposium on Rapid Methods for Measuring Radioactivity in the Environment, Neuherberg, July 1971, IAEA-SM-148/52.
23. S. E. H. Rippon, *Nucl. Instrum. Methods* 21, 185 (1963).
24. A. De Volpi and K. G. A. Porges, *Intern. J. Appl. Radn. Isotopes* 16 (8), 496 (1965).
25. K. Haberer and W. Kollé, *Atompraxis* 11, 664 (1965).
26. R. H. Elrick and R. P. Parker, *Intern. J. Appl. Radn. Isotopes* 17, 361 (1966); 19, 263 (1968).
27. A. Lauchli, *Intern. J. Appl. Radn. Isotopes* 20, 265 (1969).
28. T. H. Bates, Symposium on the Determination of Radionuclides in Environmental and Biological Materials, CEGB London, AED CONF. 73-085 14, 1973.
29. A. Dyer, in *Liquid Scintillation Counting*, Vol. 2 (eds. M. A. Crook, P. Johnson and B. Scales), Heyden, London, 1972, p. 121.
30. T. H. Bates, T. H. Boyd and J. P. Clarke, BNFL Report 1(W), 1971.
31. R. J. Herberg, Packard Technical Bulletin No. 15, 1965.
32. A. J. Kemp and F. A. Blanchard, *Anal. Biochem.* 44, 369 (1971).

33. T. H. Bates and J. B. Fardon, publication in preparation.
34. G. W. McBeth, R. A. Winyard and J. E. Lutkin, *Pulse Shape Discrimination with Organic Scintillators*, Koch-Light Laboratories Ltd., 1971.
35. M. J. Slobodien and R. W. Granlund, *Health Phys.* 27, 128 (1974).

DISCUSSION

A. Dyer: You observed that your quench correction curve might be used to estimate concentrations of ions. We have carried out some preliminary investigations into the determination of Ti by developing the pertitanyl ion and observing quench correction and also for Fe as the orthophenanthroline complex. In both cases encouraging results are observed over wide ranges of concentration down to at least 10^{-10} M.