

TABLE 1. Influence of HNO₃ concentration on counting efficiency for ²⁴¹Am in 10 ml Optiphase HiSafe™ 2 scintillator. Mass of the sample was 0.2 g.

HNO ₃ concentration (M)	Relative counting efficiency (%)
0.5	100
1.0	100
2.0	100
3.0	98
4.0	94
5.0	93

TABLE 2. The additional correction for α counting rate losses estimated from 24 samples of the count rate from 20,000–600,000 cpm prepared from Pu CRM-126 and RIWRM-009-238-89

Count rate (cpm)	Correction (%)
up to 150,000	–
150,000 – 300,000	0.17
300,000 – 400,000	0.33
400,000 – 500,000	0.41
500,000 – 600,000	0.55

are software-selected in the 0–256 range. To select the PSA level correctly, we chose the ³H standard source (sealed in a glass vial) and ²⁴¹Am (a prepared source in a PE vial). We changed the PSA level and observed the influence of β counts in the α channel; we also observed α counts in the β channel. From these, we chose PSA = 50; for this value, the influence in each “channel” was equal, ~0.1%. There was no effect on α count rate for PAC values <200, but β count rate began to decrease at PAC = 80, so this parameter was also fixed at 50. We monitored sample quenching by using the external ²²⁶Ra source. We calculated the sample quenching parameter (SQP(E)) for each measurement and related it to the detection efficiency.

RESULTS

Tables 3 and 4 summarize α and β counting efficiency; Table 5 gives results of intercomparison measurements. The quenching effect was tested by adding CCl₄ to the counting vial. SQP(E) was related to the counting efficiency for variable degree of quenching for ²⁴¹Pu (CRM-126). The results given in Figure 1 are rather surprising, at least for β counting. The α counting rate was stable at the beginning, with decreasing SQP(E), but we observed a sharp decrease as a result of increasing the amount of quenching (complexing) agent. For β counting, efficiency decreased slowly, at first simultaneously with SQP(E), then decreased significantly. With the addition of quenching agent, the counting efficiency rose quickly. This efficiency increase can be explained as a “degradation” of α pulses to β pulses. This effect is confirmed by the spectrum shown in Figure 2, where the α peak can only originate from α particles affected by the quenching agent; they interact with the scintillator solution in a similar way to β particles of the same energy. The quenching agent makes the light pulses from α particles shorter and the PSA electronics count them as β particles.

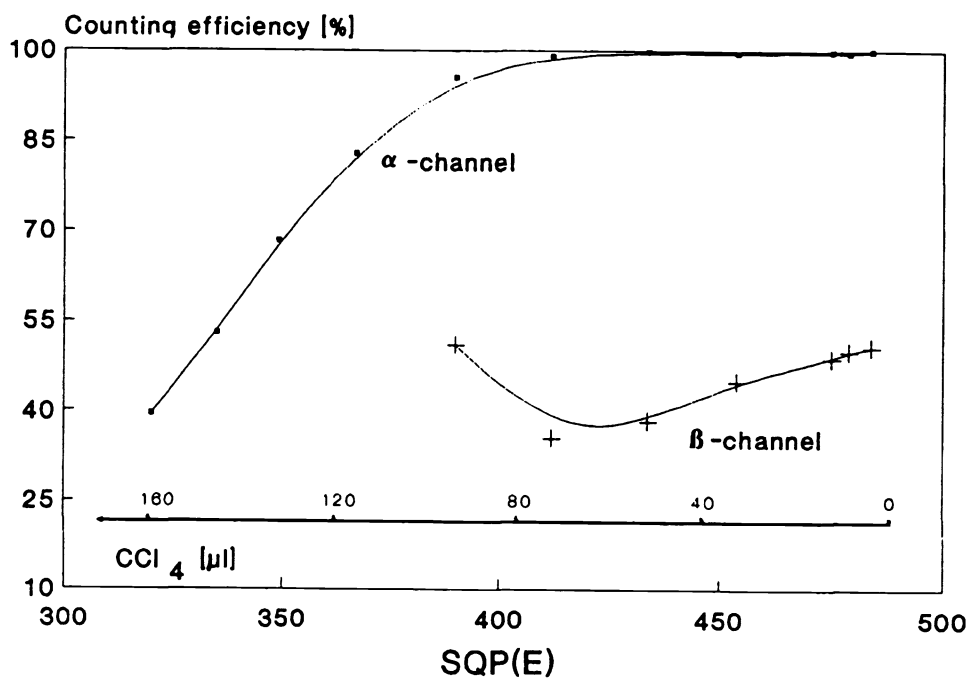


Fig. 1. Quenching effect for Pu CRM-126. CCl₄ added (2 μl–160 μl)

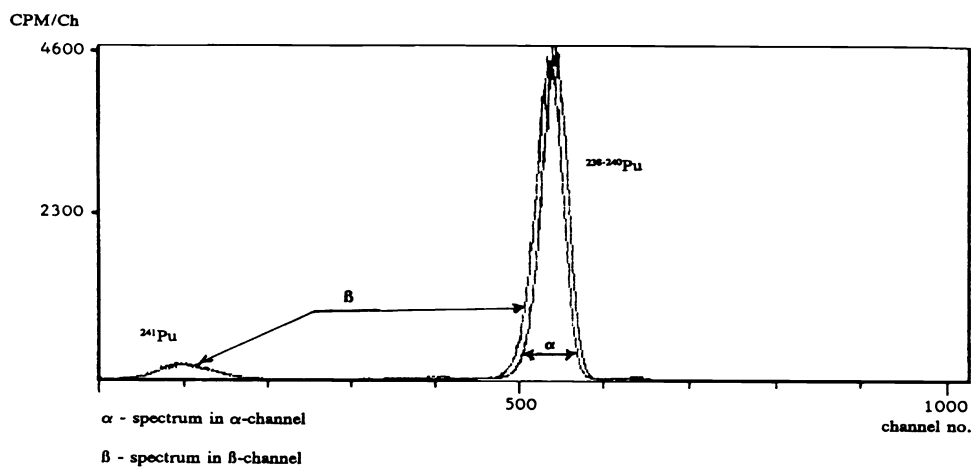


Fig. 2. Degradation of α spectrum to β spectrum for “deep” quenching effect (SQP(E)~330) Pu CRM-126

TABLE 3. Alpha Counting Efficiency

CRM	No. of aliquots	Certificate accuracy (%)	Counting efficiency (%)	Experimental uncertainty RSD (%)
126 (Pu)	12	± 0.2	100.08	0.06
²⁴¹ Am (F)	6	± 0.8	99.56	0.17
²⁴¹ Am (P)	6	± 0.35	99.92	0.06

TABLE 4. Beta Counting Efficiency

CRM	No. of aliquots	Certificate accuracy (%)	Counting efficiency (%)	Experimental uncertainty RSD (%)
126 (Pu)	12	± 1.0	50.14	0.41
³ H (F)	5	± 1.1	51.69	0.20
³ H (with ²⁴¹ Am added)	5	± 1.1	50.58	0.16

TABLE 5. Alpha-Activity Measurements of ²³⁸Pu and ²³⁹Pu Spike Solutions in Three Laboratories

Laboratory	Activity and uncertainty (kBq g ⁻¹)	Difference to the mean (%)
<i>RIWRM-009-238-89</i>		
1	156.8 ± 0.30	+ 0.141
2	156.4 ± 0.5	- 0.115
SAL*	156.55 ± 0.04	- 0.019
	Mean value = 156.58 kBq g ⁻¹	
	Standard deviation = 0.20 kBq g ⁻¹	
<i>RIWRM-009-239-89</i>		
1	201.17 ± 0.38	- 0.109
2	201.8 ± 0.3	+ 0.204
SAL	201.19 ± 0.04	- 0.099
	Mean value = 201.39 kBq g ⁻¹	
	Standard deviation = 0.36 kBq g ⁻¹	

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SUMMARY

Alpha-counting efficiency in 0–2 M nitric acid solutions is very close to 100%. Accurate determination of this value depends on the quality of standard reference materials used. To fulfill the accuracy requirements for Pu measurements, the standards should be certified with ± 0.1% uncertainty. The results from interlaboratory comparison show that an accuracy of ± 0.1 to ± 0.2% is attainable. The β-counting efficiency of ²⁴¹Pu is very sensitive to sample composition, which must be kept stable; SQP(E) must be monitored closely and counting efficiency adjusted. The ³H standard can be used for calibration but the certification uncertainty (± 1% or more) is inadequate. ²⁴¹Pu concentration can be measured to an uncertainty of ± 1 to ± 2%.

REFERENCES

- McDowell, W.J. 1986 Alpha counting and spectrometry using liquid scintillation methods. *National Academy of Sciences-National Research Council: Nuclear Science Series, Radiochemistry Techniques*. Office of Scientific and Technical Information, U.S. Department of Energy, Oak Ridge, Tennessee.
- Oikari, T., Kojola, H., Nurmi, J. and Kaihola, L. 1987 Simultaneous counting of low alpha-and beta-particle activities with liquid scintillation spectrometry and pulse-shape analysis. *International Journal of Applied Radiation and Isotopes* 38A(10): 875–878.

LIQUID SCINTILLATION COUNTING OF PLUTONIUM AND/OR AMERICIUM CONCENTRATIONS

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ABSTRACT. We determined americium (as ^{241}Am) and plutonium in solutions using liquid scintillation counting (LSC). We used a Rackbeta 1219 commercial spectrometer, which can distinguish alpha (^{241}Am and/or $^{238-240}\text{Pu}$) and beta (^{241}Pu) particles according to their pulse shapes. We studied the effect of count rate, nitric acid concentration and the addition of complexing and quenching reagents on the counting efficiency. The α counting efficiency is $100\% \pm 0.2\%$, defined by the uncertainty of the best available standard reference material; this was fairly stable in all measurements. Based on this efficiency, two solutions of Pu were measured and the results were compared with measurements of two other laboratories; the agreement was within $\pm 0.2\%$. We found that tritium is suitable for counting efficiency calibration of ^{241}Pu . The counting efficiency, which, in this case, is quite sensitive to the presence of other chemicals, is about 50% and is corrected by an external ^{226}Ra standard source.

INTRODUCTION

Liquid scintillation counting (LSC) has the potential for highly accurate determination of plutonium concentration in solutions, for which several possible applications are:

1. Accurate determination of Pu concentration when its isotopic composition, determined by other methods, is known and ^{241}Am concentration is negligible or known.
2. In the presence of a significant amount of ^{241}Am , the total alpha activity is measured and the ^{241}Am content is determined by gamma spectrometry.
3. In the presence of ^{241}Am , the Pu concentration is determined by a beta activity measurement of ^{241}Pu provided that the isotopic composition is known.
4. Determination of a total content of α emitters in the presence of β and γ radiation, particularly in radioactive wastes.

In these applications, the radionuclide concentration is usually high, and high precision and accuracy of measurements are required. To show LSC capabilities, we made measurements on well-characterized reference materials. The possibility of simultaneous separate measurement of α and β radiation is a very important feature, because the ^{241}Pu is practically a pure β emitter, and this enables measurement of Pu concentrations in the absence of other β emitters.

METHODS

The following standard reference materials were used for calibration:

- CRM-126, Pu certified for isotopic composition and content, in metallic form, New Brunswick Laboratory (NBL), Argonne, Illinois, USA (0.2% uncertainty for α , 1% for β emission). The isotopic composition (in atom %) as of 1 October 1990 was as follows: $^{238}\text{Pu} = 0.0015$, $^{239}\text{Pu} = 97.929$, $^{240}\text{Pu} = 2.0563$, $^{241}\text{Pu} = 0.0122$, $^{242}\text{Pu} = 0.0010$. It had α radioactivity of $2.42 \times 10^9 \text{ Bq g}^{-1}$ and β activity of $0.46 \times 10^9 \text{ Bq g}^{-1}$.

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- ^{241}Am , Laboratoire de Metrologie des Rayonnements Ionisants (LMRI), Gif-sur-Yvette, France, in nitric acid solution (0.8% uncertainty).
- ^{241}Am , Radioisotope Centre (RC), Otwock/Świerk, Poland, in nitric acid solution (0.35% uncertainty).
- ^3H -tritiated water, LMRI (1.1% uncertainty).

The following materials were analyzed:

- ^{238}Pu spike solution (^{241}Am -free), Khlopin Radium Institute (KRI), St. Petersburg, Russia
- ^{239}Pu spike solution (^{241}Am -free), KRI.

Sample Preparation

All samples were prepared by double weighing (with a Mettler analytical balance) using pycnometers individually prepared from 1.5 ml polyethylene (PE) disposable pipettes. Pu and Am were in the form of HNO_3 solutions of 0.5–5.0 molarity. We used 25 ml PE counting vials or glass vials with 15 ml of scintillator and ~0.2 g active solution. Table 1 gives the results of varying the HNO_3 concentration. We observed a small recovery in counting efficiency with time (measured on the day after the initial experiment). The concentrated HNO_3 added to the counting vial almost completely destroyed the ability of the sample to be counted. We investigated the stability of the count rate of samples as a function of time. We had already observed that Pu samples are stable in α -counting rate, but unstable in β -counting rate (decreasing count rate over time). We observed this effect over the duration of the experiment (several weeks), which may have been due to an optical or chemical instability occurring in the scintillation cocktail/radioactive sample solution. Instability would first affect β emitters, because, in continuous spectrum, some β particles had energies just above the zero level, and the ^{241}Pu maximum β particle energy is only 20.81 keV.

To eliminate the counting rate instability, we introduced complexing agents to the solution:

1. bis(2-ethylhexyl)phosphoric acid (HDEHP)
2. octylphenyl-n, n-di-isobutyl carbamoylmethylphosphine oxide (CMPO)
3. tri-n-octylphosphine oxide (TOPO).

Only TOPO was effective. For HDEHP, recounting of samples after 24 days showed higher instability in β counting than for a Pu solution without any additional agent. Similar results for CMPO showed that only 2 counting vials from the set of 10 were unstable. For TOPO, the stability was better, but not perfect. In 24 days, the mean decrease in β -counting efficiency for 10 counting vials was 0.4%.

COUNTING EQUIPMENT

We used a Wallac Rackbeta 1219–016 LS spectrometer and an Optiphase HiSafe™ 2 scintillator. The counter can distinguish β particles from α particles using a pulse-shape analyzer and record β and α spectra of the counted radionuclides. McDowell (1986) and Oikari *et al.* (1987) described the pulse-shape analysis (PSA) technique in detail; it is now used widely with LS spectrometers. We checked the automatic compensation of dead-time losses by counter circuitry, and prepared and measured 24 sources (Pu CRM-126 and WRM-009-238-89). Counting rate ranged from 20,000 to 600,000 cpm. Our results allowed for only a rough estimate of the additional correction given in Table 2; we conclude that the count rate of the measured samples should not exceed 100,000 cpm. The Rackbeta spectrometer has two built-in software-controlled variables that allow for optimizing counting conditions in α and β channels: PSA and pulse-amplitude comparator (PAC) levels. Both