

STUDY OF QUENCHING EFFECTS WHEN MEASURING SOFT β EMITTERS IN ENVIRONMENTAL SAMPLES BY LSC AND ITS APPLICATION TO DETERMINE ^{241}Pu

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ABSTRACT. Using liquid scintillation counting (LSC), ^{241}Pu is usually measured after isolating the Pu isotopes and then electroplating onto planchets via supported-disc LSC (SD-LSC) to minimize quenching problems that might have appeared when dissolving the precipitate deposited on the disc. However, if those quenching problems are carefully controlled or corrected, the measurement of ^{241}Pu activity, once dissolved from the disc, could well be valid. In this paper, we approached the problem of measuring ^{241}Pu directly from the disc in 2 ways: a procedure of Pu dissolution from the planchet is developed in parallel with a study of the chemical quenching in these kinds of environmental samples to obtain the counting efficiency of the measurement of ^{241}Pu by LSC. In relation to the SD-LSC method, an increase in counting efficiency was observed using our radiochemical procedure. Finally, we propose a validation of the LS technique by measuring the ^{241}Pu in electroplated lacustrine sediment samples using an accurate alternative technique consisting of counting the ingrowth of the ^{241}Pu alpha-emitting daughters. To use this technique, the samples must have been electroplated at least 5 yr ago to let the alpha daughters grow in the disc. The activities obtained using both techniques are in good agreement.

INTRODUCTION

Among the plutonium isotopes introduced into the environment as a result of nuclear weapon tests and the Chernobyl accident, ^{241}Pu is one the most important. ^{241}Pu is a soft β emitter, with a maximum energy of 20.8 keV, which decays rather quickly ($T_{1/2} = 14.4$ yr). Although this radioisotope is not as radiotoxic as ^{238}Pu or $^{239+240}\text{Pu}$, its decay daughter, ^{241}Am , with a long half-life and high radiotoxicity ($T_{1/2} = 432.2$ yr), is very important from a radiological point of view. Furthermore, measuring ^{241}Pu provides information about the origin of plutonium in the environmental ecosystem, analyzed using the isotopic ratio $^{241}\text{Pu}/^{239+240}\text{Pu}$.

Given that ^{241}Pu is a soft beta emitter, liquid scintillation counting (LSC) is the most suitable technique to measure it. Several methods based in LSC can be found in the literature. Supported-disc liquid scintillation spectrometry (SD-LSC) consists of a direct measurement of ^{241}Pu placed on a disc after applying a radiochemical procedure for the plutonium isolation and electroplating. The disc is positioned face up, inserted in a vial, and covered with a scintillation cocktail (Condren et al. 1996). Another technique is based on the recovery of the plutonium from the disc; this improves the counting efficiency of the sample because the geometry is 4π in this case. Moreno et al. (1998) used nitric and boric acid to extract the plutonium from the disc that was prepared using micro-coprecipitation.

In this work, the method of measuring ^{241}Pu is based on the recuperation of ^{241}Pu from electroplated discs that have been previously measured to obtain $^{239+240}\text{Pu}$ from environmental samples; subsequently, we measure ^{241}Pu by LSC. Furthermore, $^{239+240}\text{Pu}$ data from PIPS measurement will be used to calculate the radiochemical yield of the process.

To set up the method, 2 parallel lines of work were undertaken to study both the calibration and the radiochemical procedure. Firstly, the quenching effects in the counting efficiency of soft β emitters by LSC have been exhaustively studied, focusing mainly on chemical quenching that might appear when dissolving the disc in acid. The decrease in efficiency due to quenching effects has been evaluated and corrected. Thus, despite the presence of quenching in a sample, it is possible to obtain the

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^{241}Pu activity. Secondly, a radiochemical procedure has been developed to purify the Pu stripped from the supported discs and to measure ^{241}Pu in environmental samples using LSC.

Finally, we present an alternate technique, based on alpha spectrometry, for measuring ^{241}Pu that is applicable to samples that have been already electroplated. Thus, once Pu has been electroplated and $^{239+240}\text{Pu}$ has been measured, if we remeasure the disc a few years later, we will observe an increase in the number of counts due to the ingrowth of the ^{241}Pu daughter ^{241}Am in the disc. From ^{241}Am ingrowth, it is possible to infer ^{241}Pu activity in the discs. This increase of counts can only be observed when at least 5–6 yr have passed since the electroplating; otherwise, it will not be possible apply this technique for ^{241}Pu measurement. As we will see, this technique is suitable to validate results obtained from LSC.

EXPERIMENTAL PROCEDURE

Extraction and Electroplating of Total Plutonium

First, it is necessary to isolate and concentrate the plutonium from the matrix and then electroplate it for measurement via alpha spectrometry. In this work, we define the extraction procedure from sediment samples. This radiochemical procedure is described in full detail in Vioque et al. (2002); a short outline of the procedure is presented in Figure 1.

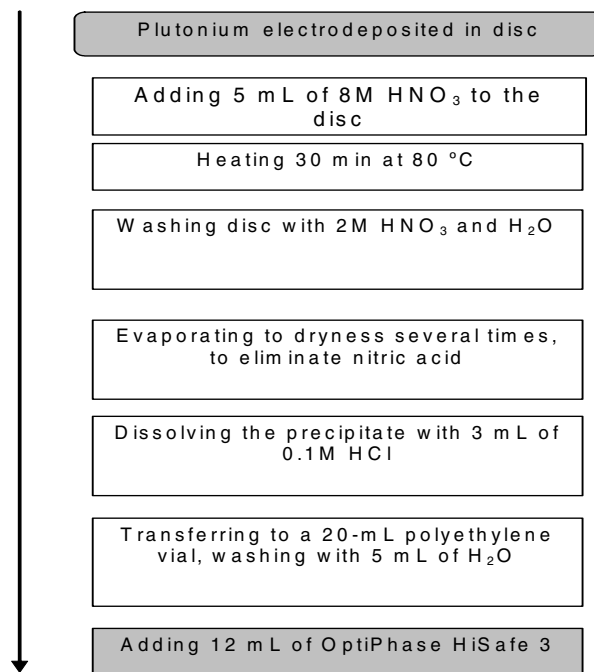


Figure 1 Radiochemical procedure scheme

The sediments are ashed (to remove the organic matter) and then wet-oxidized to dissolve the Pu isotopes and other elements. After filtration, the dissolved sample is passed through an anion exchange resin (AG1-X8 Biorad), and the highly purified Pu isotopes are eluted (to remove interfering elements) after preconditioning. Finally, the Pu isotopes are electroplated from the purified solu-

tion (once it is conditioned) onto stainless steel discs. Once the plutonium has been electroplated, the method described below can be applied to any kind of initial matrix.

Dissolution of Total Plutonium from Supported Discs

To measure ^{241}Pu concentration via LSC, the radiochemical procedure applied aims to extract the plutonium from the disc containing the total plutonium. The recuperation of plutonium from the disc is as follows. The disc containing the total plutonium is transferred to a glass beaker, washed with 5 mL of 8M HNO_3 , and heated for 30 min. The disc is then washed with 2M HNO_3 and H_2O . Next, the solution containing the total plutonium is evaporated to dryness several times to eliminate nitric acid; the precipitate was dissolved with 3 mL of 0.1M HCl . The solution was then transferred to a 20-mL polyethylene vial, washed with 5 mL of H_2O , and mixed with 12 mL of OptiPhase HiSafe 3 scintillation cocktail.

Evaluation of ^{241}Pu through ^{241}Am from α Spectrometry

There is an alternative way to obtain activity concentrations of ^{241}Pu from samples that were already electroplated to determine plutonium through α spectrometry. The beta emitter ^{241}Pu ($T_{1/2} = 14.4$ yr) decays in its alpha-emitter daughter ^{241}Am ($T_{1/2} = 432.2$ yr). Once the plutonium has electrodeposited and after waiting 5–6 yr, ^{241}Am grows in the disc, and it is possible to detect that the number of counts in the alpha spectrum increases due to ^{241}Am ingrowth. Given that ^{241}Am and ^{238}Pu emissions overlap in the spectrum, we must obtain ^{241}Am activity from the increase of counts in the ^{238}Pu peak; furthermore, it is necessary to do ^{238}Pu ($T_{1/2} = 87.7$ yr) decay corrections. This increase must be evaluated using Equation 2, and ^{241}Pu activity is obtained from Equation 1. The expressions used are obtained from the Bateman (1910) equations.

Following the Bateman (1910) equations, the ^{241}Pu activity concentration can be determined by:

$$A_{241Pu} = A_{241Am} \frac{\lambda_B - \lambda_A}{\lambda_B} \cdot \frac{1}{e^{-\lambda_A t} - e^{-\lambda_B t}} \quad (1)$$

where

$$\lambda_A = \frac{\ln 2}{T_{1/2}(^{241}\text{Pu})} = 0.069 \text{ (yr}^{-1}\text{)}$$

and

$$\lambda_B = \frac{\ln 2}{T_{1/2}(^{241}\text{Am})} = 0.00231 \text{ (yr}^{-1}\text{)}$$

A_{241Am} is the ^{241}Am activity concentration determined by:

$$A_{241Am} = A_{241Am + 238Pu} - A_{238Pu_0} e^{-\lambda_C t} \quad (2)$$

where

$$\lambda_C = \frac{\ln 2}{T_{1/2}(^{238}\text{Pu})} = 0.007899 \text{ (yr}^{-1}\text{)} ;$$

t is the time elapsed from A_{238Pu_0} , the initial ^{238}Pu activity concentration, obtained from the first measurement; and $A_{241Am+238Pu}$ is the total current activity concentration of ^{241}Am and ^{238}Pu obtained from the counts of the peak where ^{241}Am and ^{241}Pu emissions overlapped.

Figure 2 shows the ^{241}Am ingrowth versus time as a function of the percentage of initial ^{241}Pu present in the sample.

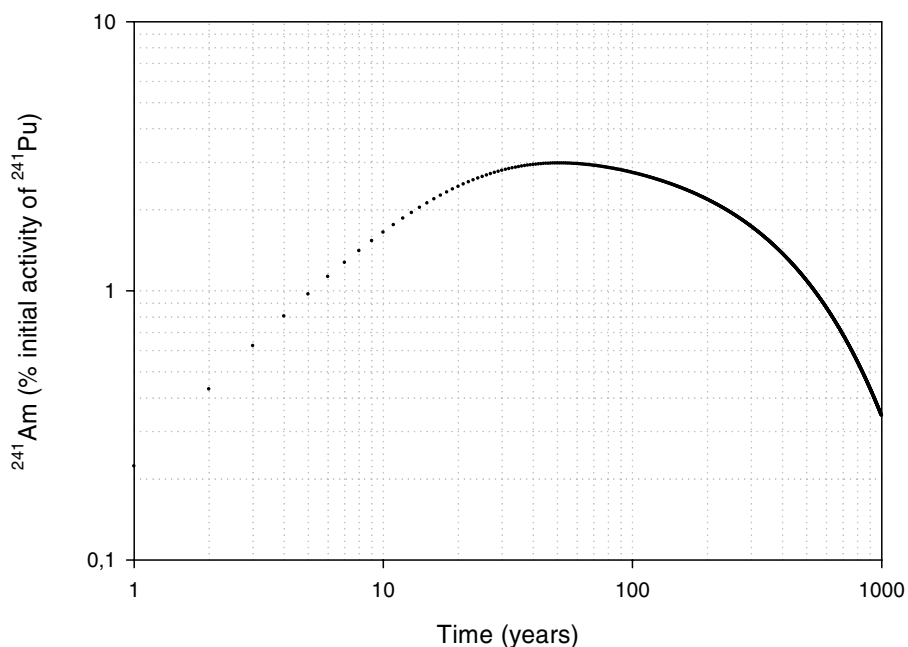


Figure 2 ^{241}Am as a function of the percentage of initial ^{241}Pu present in the sample versus time (yr)

Detection Systems

Scintillation counting is done using a Quantulus 1220™ low-background scintillation spectrometer. The counting time is 800 min. Given that all the isotopes of plutonium are present in the sample, alpha and beta separation must be done to discriminate alpha ($^{239+240}\text{Pu}$ and ^{242}Pu) and beta (^{241}Pu) isotopes. This spectrometer is equipped with a pulse-shape analyzer (PSA) to simultaneously separate and count α and β events. A parameter (PSA threshold level) in a PSA circuit can be adjusted from values 1 to 256 to obtain the best separation between alpha and beta events. ^{239}Pu and tritium are used as pure alpha and beta emitters, respectively, to optimize the PSA parameter. The optimum PSA is set at 50. To evaluate the quenching degree in the sample, we use the SQP(E) parameter obtained from the spectrum provided by the gamma emitter ^{152}Eu .

To measure the activity of the plutonium alpha emitters, an alpha-spectrometry chain (Alpha Analyst, Canberra), with 8 chambers working in parallel, was used for total alpha and alpha plutonium determination. Each chamber held a passivated implanted planar silicon (PIPS) detector with a nominal alpha-peak energy resolution of 18 keV. Alpha Analyst software was used for spectrum analysis.

EFFICIENCY CALCULATIONS AND RADIOCHEMICAL RECOVERY

Efficiency and Quenching Calculations in Environmental Samples

The presence of quenching in a sample always causes a decrease in the number of photons that reach the photomultiplier. This decrease is critical if the radionuclide is a low-energy beta emitter, like ^{241}Pu , and if a small degree of quenching produces significant changes in the counting efficiency (Manjón et al. 2002).

The main disadvantage of dissolving plutonium from the electroplated sample in the discs is that quenching effects might appear during the LS measurement (Liong Wee Kwong et al. 2004). On one hand, quenching is due to the nitric acid used to dissolve the electrodeposited Pu; on the other hand, some quenching might appear if the nitric acid attacks the disc itself. We conducted a study to check if the method described above produces quenching in the samples when measuring by LSC and if a fitting curve using an artificial quencher is suitable to accurately evaluate the decrease of the quenching efficiency.

First, it was necessary to set up the fitting curve to evaluate changes in the counting efficiency (Manjón et al. 2002). We chose ^3H ($E_{\beta\text{max}} = 18.6$ keV) for the calibration because it has a similar beta energy of emission as ^{241}Pu ($E_{\beta\text{max}} = 20.8$ keV). Using ^3H , a calibration curve efficiency versus SQP(E) parameter was done. As an artificial quenching agent we use CCl_4 . The fitting curve that we obtain is:

$$\varepsilon = (3.4 \times 10^{-6} \pm 5 \times 10^{-7})SQP^2 + (3.2 \times 10^{-3} \pm 7 \times 10^{-4})SQP + (0.78 \pm 0.22) \quad (3)$$

Following this fitting curve, we want to test if it is possible to use Equation 1, using CCl_4 as a quench curve to predict the counting efficiency of ^{241}Pu in environmental samples prepared following our radiochemical method. For that, we prepared samples following the procedure described previously and afterwards adding ^3H as an internal standard. Efficiency is calculated by applying the fitting curve (Equation 3), made with CCl_4 , but also from the known tritium added to the sample. Both results are compared in Figure 3.

Two things can be inferred from Figure 3. On one hand, the radiochemical procedure might indeed produce an increase in the quenching degree of the sample. On the other hand, the curve obtained from the artificial quencher predicts, very effectively, the counting efficiency when measuring a real sample. Therefore, we will apply the fitting curve (Equation 3) to correct the counting efficiency in the real samples we prepare.

Evaluation of Total Plutonium and Radiochemical Yield

The accuracy of the method depends on the total recuperation of the ^{241}Pu electroplated on the disc; if that is not possible, an evaluation of the radiochemical procedure will be necessary. The efficiency of the dissolution of plutonium from the disc is evaluated through the alpha-emitting isotopes measured by LS measurement.

The samples are sediments from Härsvatten Lake (Sweden), which were treated and measured in 1998 (Vioque et al. 2002) to obtain $^{239+240}\text{Pu}$ activities. After 6 yr, ^{241}Am from ^{241}Pu has grown in the sample and ^{238}Pu activity has decayed. For that reason, it is necessary to again measure the disc via α spectrometry to know the former total alpha activity in the sample.

After measuring the total activity of the electroplated disk plutonium through α spectrometry, it is dissolved in HNO_3 and prepared for LS counting following the method described in "Dissolution of

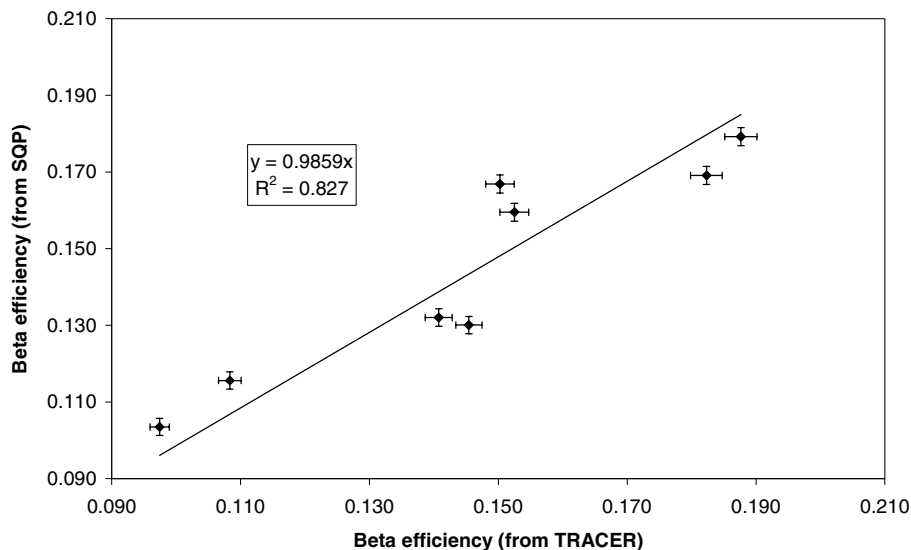


Figure 3 Real samples are prepared following the described method, traced with tritium, and measured. The figure presents the efficiency calculated from the known tritium added to the sample versus the efficiency calculated from SQP(E) and the fitting curve.

Total Plutonium from Supported Discs.” Then, samples are measured and quenching corrections are done when needed.

To evaluate the total alpha plutonium present in the vial, the measurement is done using the PSA α/β discriminator to separate ^{241}Pu (beta emitter) from the remaining plutonium isotopes (alpha emitters). Alpha counting efficiency is calculated using a ^{239}Pu standard. It is not possible to discriminate the isotopes from each other because the LS resolution is quite poor. Yet, we can compare total alpha activity measured via LSC and total alpha activity through α spectrometry and evaluate the yield of plutonium dissolved from the discs.

In Figure 4, we present the total alpha activities measured following both techniques, LSC and α spectrometry (PIPS detectors). From Figure 4, we can see that activities obtained are the same within the uncertainty, proving that the plutonium is completely removed from the disc, and thus, the radiochemical yield associated with the dissolution of plutonium from the disc is 100%.

VALIDATION OF THE METHOD

The method was validated using the group of samples from Hårsvatten Lake, previously prepared and measured in 1998 and measured again after 6 yr of storage. The data from Figure 4 show that it is possible to efficiently dissolve all the plutonium from the electroplated sample. However, it is necessary to check if the radiochemical method employed is suitable for evaluating ^{241}Pu present in the sample, and furthermore, if the quenching degree present in the sample is properly estimated to give an accurate result for ^{241}Pu .

Regarding quenching, the counting efficiency for unquenched samples is ~23% when mixing 8 mL of water and 12 mL of scintillation cocktail, which is the value found in the literature using similar proportions of water/scintillation cocktail (Pujol et al. 1999; Schäfer et al. 2000). For the samples prepared using our method, however, we obtain a mean efficiency of 19.5%, indicating the presence of

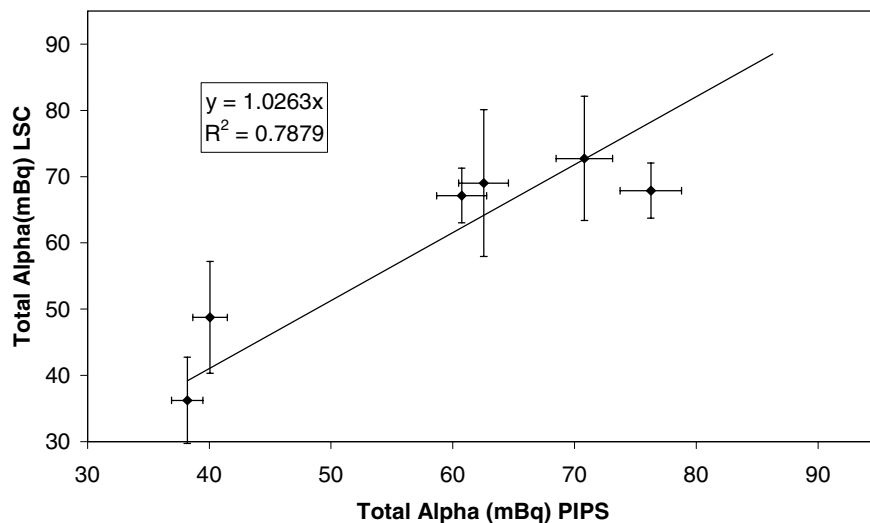


Figure 4 Total alpha activity (mBq) present in electroplated samples measured through alpha spectrometry versus total alpha activity obtained via LSC after extracting plutonium from the planchet.

quenching in some samples and decreasing the counting efficiency in relation to the unquenched samples. Nevertheless, there is a considerable increase of the counting efficiency in relation to the SD-LSC counting efficiency of ~12.5% (Ryan et al. 1993).

After performing the radiochemical procedure on the electroplated disc, ^{241}Pu is measured through LSC, and activity is calculated after correcting the quenching color effect. We described how to calculate the ^{241}Pu present in the sample from a second alpha measurement of the discs (using PIPS detectors) by measuring the ^{241}Am ingrowth in the sample. Both results are compared in Table 1. Clearly, the results are in agreement, within the error, showing the accuracy of the LS method.

Table 1 ^{241}Pu activity concentrations, A (in mBq), from samples from Härsvatten Lake, Sweden, (Vioque 2002) calculated using our method (LSC). Counting efficiencies (ϵ) for the LSC method are included. The results are compared with results obtained via ^{241}Am ingrowth in the planchets (PIPS). The uncertainty corresponds to 1σ .

ID	ϵ (%)	LSC $\pm 1\sigma$	A (mBq)	LSC $\pm 1\sigma$	A (mBq)	PIPS $\pm 1\sigma$
G19	20.33	2.30	17	5	21	7
F67	21.06	2.38	15	5	17	12
F60	19.67	2.23	71	21	66	26
F94	19.16	2.17	19	5	17	5
G39	18.43	2.09	57	16	56	11
G79	17.96	2.03	40	12	47	9

CONCLUSIONS

We set up a method for ^{241}Pu measurement that is based on the direct recuperation of plutonium from electroplating discs and then measuring the plutonium via LSC. Thus, we obtain a mean counting efficiency of 19.5%, pointing to the presence of quenching in some of the samples. The method succeeds in evaluating ^{241}Pu activity concentration from the planchets. Moreover, we argue that a

moderate degree of quenching in the sample is not an obstacle to measuring ^{241}Pu because, using the fitting curve proposed, quenching can be properly estimated and the counting efficiency is accurately corrected.

Furthermore, it is possible to validate the method by comparing the results obtained with an alternative method to evaluate the activity of ^{241}Pu using alpha spectrometry. The method consists of alpha counting of the ^{241}Am ingrowth in plutonium samples electroplated at least 5 yr since the first measurement. Applying both techniques to the measuring of ^{241}Pu in lacustrine sediment samples, we obtain results that are in good agreement.

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