



Uncertainty and detection limits of ^{241}Pu determination by liquid scintillation counting (LSC)

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ABSTRACT

Determination of ^{241}Pu is an essential issue for radiation protection, as it is the precursor of some nuclides with high radiotoxicity. ^{241}Pu is a low energy beta emitter, which makes its measurement more challenging than that of Pu alpha emitters. The most widely used method for the measurement of ^{241}Pu is liquid scintillation counting (LSC). In this method, the assessment of Pu radiochemical yield is done by measuring the sample by alpha spectrometry before being lixiviated and measured by LSC. This double measurement affects uncertainty analysis, as well as decision threshold and detection limit, considering that both components of the total yield (radiochemical and lixiviation) should be contemplated.

In this paper, and for quality assurance (QA) purposes, in-depth uncertainty and detection limit formulae for the proposed method, controlling correlations and considering all the parameters involved including chemical and lixiviation yields, have been developed. A sensitivity analysis of the uncertainty budget together with an assessment of ^{242}Pu tracer quantity to be used, ensuring a total yield of at least 50% and a relative uncertainty of the leaching yield of at most 5%, have been carried out. In addition, an analysis of the impact of the real lixiviation yield value and its uncertainty on the results has been done.

As a general conclusion, and considering the values of the parameters chosen for this work (samples of 1 g measured for 24 h by LSC), the ^{241}Pu uncertainties range from 5% to 30% depending on the activity concentration values and the detection limits range from 14 to 30 Bq kg⁻¹, depending on yield values. The main components of the uncertainty budget are the net ^{241}Pu and background counts obtained in the LSC measurement for low contaminated samples while this is the case for the alpha gross count rate in LSC measurement of the alpha calibration source for highly contaminated samples.

In addition, an analysis of possible interference by Pu alpha emitters in the ^{241}Pu signal and a comparison of quench standard curves of ^3H and ^{241}Pu are also performed.

1. Introduction

Determination of ^{241}Pu in materials from nuclear facilities and environmental samples, such as soils, sediments, water, air, and terrestrial and aquatic organisms, is an essential issue for radiation protection of workers and members of the public. Indeed, ^{241}Pu is the precursor of other transuranium nuclides, for example ^{241}Am , with longer half-life, higher mobility between environmental components (Thakur and Ward, 2018) and higher radiotoxicity and chemical toxicity (Coughtrey et al., 1984; Thakur and Ward, 2018).

Like the other isotopes of plutonium (Table 1), ^{241}Pu is formed in nuclear fission reactors through neutron capture reactions. However, unlike them, ^{241}Pu is a short-lived radionuclide (14.33 (4) y (LNHB,

2017)) and a low energy beta emitter of 20.8 keV (LNHB, 2017), which makes its measurement more challenging than that of plutonium alpha emitters.

^{241}Pu can appear in the environment as a result of accidents involving nuclear reactors and critical assemblies, and radioactive materials are in turn released to the site and its surroundings. For example, when a reactor core such as RBMK type in Chernobyl is affected and damaged, 3% of ^{241}Pu core inventory could be released into the atmosphere (IAEA, 1973; Tykva and Sabol, 1995; UNSCEAR, 2000). This leads to an activity ratio of $^{241}\text{Pu}/^{239+240}\text{Pu}$ of about 70–100 being released soon after the accident (Corcho Alvarado et al., 2011). Moreover, according to Jian Zheng et al. (MEXT, 2012; Zheng et al., 2012), in the Fukushima DNPP accident, where the reactor type was BWR, there

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Table 1

Main radiological characteristics of the most usual Pu radionuclides (LNHB, 2017).

Pu radioisotope	Half-life (y)	Main α energy (keV)	Intensity (%)	Maximum β energy (keV)	Intensity (%)
^{238}Pu	87.74 (3)	5499.03 (20)	71.04 (6)	–	–
^{239}Pu	24.100 (11) 10^3	5156.59 (14)	70.79 (10)	–	–
^{240}Pu	6.561 (7) 10^3	5168.13 (15)	72.74 (18)	–	–
^{241}Pu	14.33 (4)	–	–	20.8	99.99
^{242}Pu	373 (3) 10^3	4902.3 (10)	76.53 (17)	–	–

was a high activity ratio of $^{241}\text{Pu}/^{239+240}\text{Pu}$ (>100) in the 20–30 km zones, due to the release of plutonium into the atmosphere and deposition on the ground.

^{241}Pu should also appear in spent fuel, where $^{241}\text{Pu}/^{239+240}\text{Pu}$ activity ratio increases with the burn-up grade (IAEA, 2007; CNRS, 2020), and thus in wastes and decommissioned materials from nuclear power reactors. Therefore, releases from nuclear facilities and nuclear waste disposal repositories could be sources of ^{241}Pu in the environment.

At present, a variety of methods exists for the measurement of ^{241}Pu in environmental samples and materials from nuclear facilities. Among them, the most widely used are liquid scintillation spectrometry (LSC) and mass spectrometry (ICP-MS), but it is also possible to determine ^{241}Pu by measuring the ingrown ^{241}Am from ^{241}Pu by alpha spectrometry (Hou, 2018), which requires much more time for its determination.

Both methods, LSC and ICP-MS, require plutonium isolation from other elements (to avoid their interference) and plutonium concentration, as ^{241}Pu activity concentration in samples, not originating from D&D or waste management activities, is usually very low (Hou, 2018; Thakur and Ward, 2018).

In general, plutonium is first released from the solid sample matrix by acid digestion, lixiviation or alkaline fusion followed by acid dissolution (Hou, 2018). Subsequently, the sample solution obtained or liquid sample is pre-concentrated by co-precipitation of hydroxide, fluoride or phosphate, and loaded to an anion exchange column or TEVA, UTEVA or DGA extraction chromatographic column, where plutonium isotopes are absorbed by the column and eluted using $\text{NH}_2\text{-OH-Cl}$, HCl or HF (Qiao et al., 2009; Hou, 2018). Usually, ^{242}Pu is used as a tracer before sample treatment.

Next, if the LSC method is used, there are two options for the eluate. In the first, the eluate is evaporated to dryness and then dissolved by using HCl before mixing with a liquid scintillator and measured by LSC. In the second, after some preparation, the eluate is electrodeposited on a metal disc or micro-precipitated on a membrane filter and alpha spectrometry (Hou, 2018) measurement is carried out followed by LSC. In both options, the yield is calculated through the measurement of plutonium alpha emitters.

The first option is faster than the second and entails more simple equations for the uncertainty of activity, decision threshold and detection limit; but the low spectral resolution of LSC prevents deconvolution of ^{238}Pu , ^{239}Pu , ^{240}Pu and ^{242}Pu alpha emissions. As a result, it is impossible to calculate chemical yield if the sample contains ^{238}Pu or $^{239+240}\text{Pu}$. Therefore, this method is only valid when the sample only contains ^{241}Pu ; in practice, this is almost impossible in any real sample.

The second option allows determination of all plutonium alpha emitters, by alpha spectrometry, and hence, calculation of accurate chemical yield by ^{242}Pu tracer. However, this means that after alpha spectrometry, the metal disc or the membrane filter should be lixiviated and the obtained solution measured by LSC. This method necessitates that the yield of metal disc lixiviation must be calculated, complicating equations for activity uncertainty, decision threshold and detection

limit. The direct measurement of the membrane filter by LSC is also possible, in which case, the filter must be carefully placed inside the vial, although an accurate calculation of the efficiency is relatively difficult.

In some studies, an additional solvent extraction or ion exchange step is carried out after metal disc lixiviation, in order to avoid traces of Fe, Ni, Cu and Pt, which could cause quench effect in LSC (L'Annunziata, 2012; Hou, 2018).

In ICP-MS method, the eluate is evaporated to dryness and the residue is dissolved in aqua regia and heated to dryness again. Then, the sample is dissolved in HNO_3 solution and measured by ICP-MS (Ayranov et al., 2009).

In using LSC, detection limits for ^{241}Pu are of the order of 30–100 mBq kg^{-1} for counting times of 100–600 min and mass of 1 kg (L'Annunziata, 2012; Hou, 2018); while, in using ICP-MS those limits are of the order of 1–10 mBq per kg, and counting times being a few minutes (Hou, 2018; Thakur and Ward, 2018). In this sense, ICP-MS can be qualified as a fast, multi-element technique with high sensitivity (Ayranov et al., 2009). However, it requires more maintenance and is more expensive than LSC (Ayranov et al., 2009). In addition, it presents relatively high measurement uncertainties (up to 60%) for this isotope, due to the instability of ICP-MS signal for low level samples during the measurement process and it is hampered by polyatomic interference peaks from possible matrix constituents (Hou and Roos, 2008; Xu et al., 2014; Thakur and Ward, 2018).

In this work, a method for ^{241}Pu activity determination consisting on the chemical isolation of plutonium, from any kind of sample matrix, its electro-deposition followed by alpha spectrometry, metal disc lixiviation and liquid scintillation spectrometry, was chosen to be implemented in the laboratory. Electro-deposition is chosen instead of micro-precipitation because the second causes a loss of spectral resolution in alpha spectrometry and some sample instability, as it sometimes warps, therefore metal disc lixiviation is chosen.

In this method, the calibration of the alpha spectrometer as well as the alpha calibration of LSC can be done by using the same radionuclide (i.e. ^{242}Pu). The beta calibration of the LSC is usually done by using ^3H , as its beta spectrum is like that from ^{241}Pu (L'Annunziata, 2012). In this paper, ^{241}Pu and ^3H are analysed as standards to calibrate the LSC, and a comparison between calibration curves obtained by using both radionuclides is provided.

Additionally, an analysis of the possible interferences by Pu alpha emitters in the ^{241}Pu signal and also of the lixiviation performance has been done.

It should be pointed out that in the available literature nowadays, there is no work that clarifies and deeps into the analysis of uncertainties and detection limits for this ^{241}Pu activity determination method.

Thus, and for QA purposes, uncertainty and detection limit formulae for the proposed method, considering all the parameters involved including chemical and lixiviation yields, have been developed. A sensitivity analysis of uncertainties together with an assessment of ^{242}Pu tracer activity to be used, ensuring a total yield of at least 50% and a relative uncertainty of the leaching yield of at most 5%, have carried out. In addition, an analysis of the impact of the value of the true lixiviation yield and its uncertainty on the results has been done.

2. Material and methods

2.1. Equipment, reactive and tracers

Two different pieces of equipment were used for this study. For alpha measurements, an alpha spectrometer Alpha-Analyst, from Canberra, provided with 4.5 cm^2 passivated implanted planar silicon detectors (PIPS), was used. Alpha measurements were carried out at a 0.5 cm sample-detector distance, with a typical detection efficiency of approximately 25% and background count rate of around $5.8 \cdot 10^{-5}$ cps.

The other equipment used was an ultra-low background liquid scintillation spectrometer 1220 QUANTULUS TM, from Perkin Elmer.

This spectrometer is able to distinguish between events from alpha and beta particles, by analysing the different de-excitation time of the states in solvent caused by both particles due to their differences in linear energy transfer (Perkin ElmerInc., 2000). Moreover, it allows for sample quench monitoring via SQP (standard quench parameter) in a reduced time period, taking into account the quench effect by measuring the effect of a low activity external ^{152}Eu standard on the sample (Perkin ElmerInc., 2000).

All the chemical reactivities used in the analyses carried out were of pro-analytical grade. ^{242}Pu certified reference material (CRM) was provided by the NIST, ^{241}Pu CRM was provided by the NPL and ^3H CRM was provided by the IPL (Isotope Products Laboratory). The liquid scintillation cocktail (Ultima Gold LLT) and 20 mL glass vials for LSC (liquid scintillation counting) were provided by Perkin Elmer; and AG® 1-X8 Anion Exchange Resin, analytical grade, 100–200 mesh, chloride form by BIO-RAD.

2.2. Method

The complete method used in this work for ^{241}Pu determination in samples using liquid scintillation counting is summarised in Fig. 1. The method covers, in total, 6 steps: sample digestion, chemical isolation of Pu, electro-deposition, alpha spectrometry, planchet lixiviation and test sample preparation, and LSC measurement. In the different steps, the parameters needed to calculate ^{241}Pu activity and its uncertainty, decision threshold and detection limit are obtained, as explained in the following sections.

In addition, and due to the large number of symbols and definitions used in this paper, a summary is shown in Table 2. More detailed descriptions appear in the corresponding sections.

2.2.1. Sample digestion, chemical isolation of Pu, electro-deposition, and alpha spectrometry measurement

Any sample is usually traced with around 0.01 Bq of ^{242}Pu , as a chemical yield tracer, before undergoing sample digestion process. In general, Pu is first released from the solid sample matrix by acid digestion, lixiviation or alkaline fusion, depending on the complexity of the sample, followed by acid dissolution (Hou, 2018). The obtained sample solution, or liquid sample, is then prepared and loaded to an anion exchange column. There, Pu isotopes are absorbed on the column and eluted using $(\text{NH}_3\text{OH})\text{Cl}$.

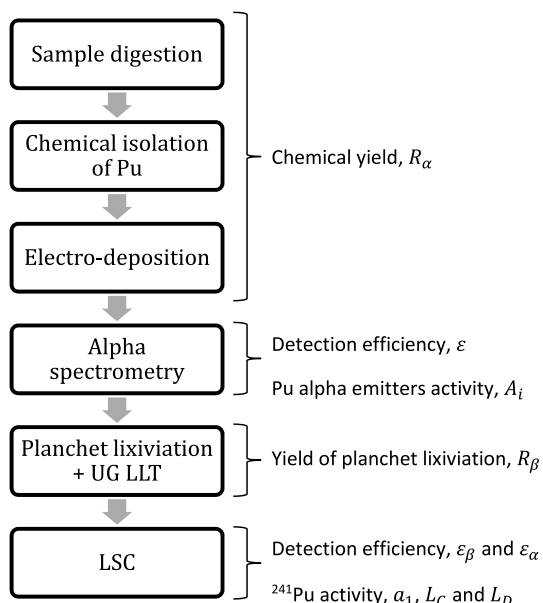


Fig. 1. Summary of the method.

Table 2

Summary of symbols and definitions used in this work.

In alpha spectrometry measurement		In LSC measurement	
A_i	Radionuclide activity i in planchet	a_1	^{241}Pu activity concentration
r_i	Gross count rate radionuclide i	r_1	^{241}Pu gross count rate
r_{0i}	Background count rate radionuclide i	r_{01}	^{241}Pu background count rate
t	Counting time	A_α	Total alpha activity
A_t	Tracer activity added	r_α	Total alpha gross count rate
r_t	Gross count rate of the tracer	$r_{0\alpha}$	Total alpha background count rate
r_{0t}	Background count rate of the tracer	t_t	Counting time
A_s	Calibration planchet (CP) activity	A_{pa}	Alpha calibration source (CS) activity
r_s	Gross count rate of the CP	r_{pa}	CS alpha gross count rate
r_{0s}	Background count rate of the CP	r_{0pa}	CS alpha background count rate
t_s	CP counting time	ϵ_α	Alpha efficiency
ϵ	Efficiency	ϵ_β	Beta efficiency
R_α	Chemical yield	t_p	CS counting time
R	Total yield	R_β	Lixiviation yield
		m	Sample mass

Finally, Pu isotopes contained in the eluate are electro-deposited on a stainless steel planchet, according to the Hallstadius method (Hallstadius, 1984). This way, the sample to be measured in the alpha spectrometer is obtained. For the measurement, the sample-detector distance is set at 0.5 cm and the measuring time is 600,000 s.

In all the following expressions, gross and background count rates refer to the counts in the ROI (region of interest); background counts are always obtained in the same ROI as the nuclide under evaluation and relative uncertainty of X , $u_{rel}(X)$ refers to $u(X)/X$.

The background spectrum is obtained by using a clean planchet, measured in the same conditions as the sample.

The same counting time for blanks and samples in alpha spectrometry (t) is taken. Only counting times for the measurement of the calibration source are different to those devoted to blanks and samples.

^{238}Pu , $^{239+240}\text{Pu}$ and ^{242}Pu activities in the planchet (A_i) are obtained from the spectrum and following Eq. (1):

$$A_i = \frac{r_i - r_{0i}}{\epsilon} \quad (1)$$

Where:

A_i is the activity of nuclide i , in Bq, nuclide i being ^{238}Pu , $^{239+240}\text{Pu}$ or ^{242}Pu ; r_i is the gross count rate of nuclide i , in s^{-1} ; r_{0i} is the background count rate of nuclide i , and in s^{-1} ; ϵ is the detection efficiency.

Detection efficiency (ϵ) and its relative uncertainty ($u_{rel}(\epsilon)$) are calculated after measuring a calibration planchet, s , (certified reference planchet, CP), following Eqs. (2) and (3):

$$\epsilon = \frac{r_s - r_{0s}}{A_s} \quad (2)$$

$$u_{rel}^2(\epsilon) = \frac{(r_s + r_{0s})}{t_s (r_s - r_{0s})^2} + u_{rel}^2(A_s) \quad (3)$$

Where:

r_s is the gross count rate of the calibration source, in s^{-1} ; r_{0s} is the background count rate, in s^{-1} ; A_s is the activity of s , in Bq; and t_s is the s counting time for calibration, in seconds. Usually, r_s is much greater than r_{0s} , and then r_{0s} can be neglected. This relative uncertainty will be used later.

Chemical yield (R_α) is calculated by Eq. (4):

$$R_{\alpha} = \frac{r_t - r_{0t}}{A_t \varepsilon} \quad (4)$$

Where:

A_t is the activity, in Bq, of the chemical yield tracer Pu – 242; r_t is its gross count rate in s^{-1} ; r_{0t} is the background count rate in s^{-1} . Usually r_t is much greater than r_{0t} so r_{0t} can be neglected.

The knowledge of the content of alpha emitting Pu isotopes in the planchet is a key aspect of this method because it permits the evaluation of the total yield of the method (R), as explained in section 2.2.4.

2.2.2. Planchet lixiviation and test sample preparation for LSC

After alpha measurement, the planchet is treated with of 8 M HNO_3 to lixiviate the maximum amount possible of Pu electro-deposited on it. The obtained solution is concentrated by evaporation to near dryness in a 20 mL glass vial, adding some drops of water. Then, 15 mL of Ultima Gold LLT (Perkin Elmer) scintillation cocktail are added before shaking the vial well before measurement. This is the test sample for LSC measurement.

Ultima Gold LLT scintillation cocktail was chosen, among others, due to its extremely low background contribution, high counting efficiency and long-term stability (Thomson, 2003). Although it was primarily designed for low-level tritium (LLT) monitoring (Thomson, 2003), it is suitable for other low energy beta emitters like ^{241}Pu . Moreover, Ultima Gold LLT can accept mineral acid species normally encountered in alpha/beta counting applications (Thomson, 2003), even in concentrations >2 M (L'Annunziata, 2012), and avoid chemiluminescence induced by them (L'Annunziata, 2012).

The scintillation cocktail volume was set at 15 mL following the results of Te-Yen, Su and Tsuey-Lin, Tsai (Te-Yen and Tsuey-Lin, 2019).

Finally, test samples are stored in the dark, inside the scintillation chamber at least for 6 h before measurement.

Blank samples, to obtain background signal, were prepared following the same process, by using a Millipore water as a sample and stored in the same way and for the same time as real samples.

2.2.3. Liquid scintillation spectrometry (LSC) parameters

Before carrying out liquid scintillation spectrometry some QUANTULUS equipment parameters were chosen. We chose the default MCA (multi-channel analysers) setting for low energy beta emitters (3H protocol), as ^{241}Pu is a beta emitter of maximum energy 20.8 keV (Table 1) and enables us to subtract the interfering random coincidence signal, as chemiluminescence (Thomson, 2014), from the full sample signal (beta + alpha signals). By using this protocol, peaks from alpha emissions of ^{238}Pu , $^{239+240}Pu$ and ^{242}Pu , isotopes that could be present in the same vial as ^{241}Pu , are also registered in the spectrum; so in just one spectrum, beta and alpha emissions are shown.

Alpha and beta spectral windows definition was performed after carrying out the measurements described below:

Six different samples were prepared, five of them containing different Pu radionuclides and different activity values: 3 Bq of ^{241}Pu , 0.07 Bq of ^{238}Pu , 0.44 Bq of ^{240}Pu , 0.29 Bq of ^{242}Pu , 0.08 Bq of $^{238+239+240+242}Pu$ and a blank sample. All samples were measured for the same counting time by using 3H protocol.

In Fig. 2, spectrum of three alpha emitters (^{238}Pu , $^{239+240}Pu$ and ^{242}Pu) is displayed together with that of a blank sample. As can be seen, beneath channel 500 there is no contribution of these radionuclides to the background.

We can also see that, as expected, alpha emissions of different Pu alpha emitters cannot be separated in the spectrum; only the use of numerical simulations can help us deconvolute these figures, but the uncertainties obtained from these methods are typically a problem. Thus, in this measurement it is not viable to use ^{242}Pu as a tracer for the ^{241}Pu , as can be done for Pu alpha emitters in the alpha spectrometry measurements. Therefore, in this work, the total alpha signal has been considered, as shown in Fig. 2, originating from all Pu alpha emitters for the evaluation of the lixiviation yield in ^{241}Pu assessment.

In Fig. 3, spectrum of ^{241}Pu is shown together with spectra obtained from two samples, with ^{240}Pu and ^{242}Pu respectively, and a blank sample.

In Fig. 3, we can see that the beta signal coming from ^{241}Pu is limited up to channel 350 and the Pu alpha signal begins at around channel 500. Thus, we can conclude that no interference is expected in spectra between alpha and beta emitting plutonium isotopes, if the window for

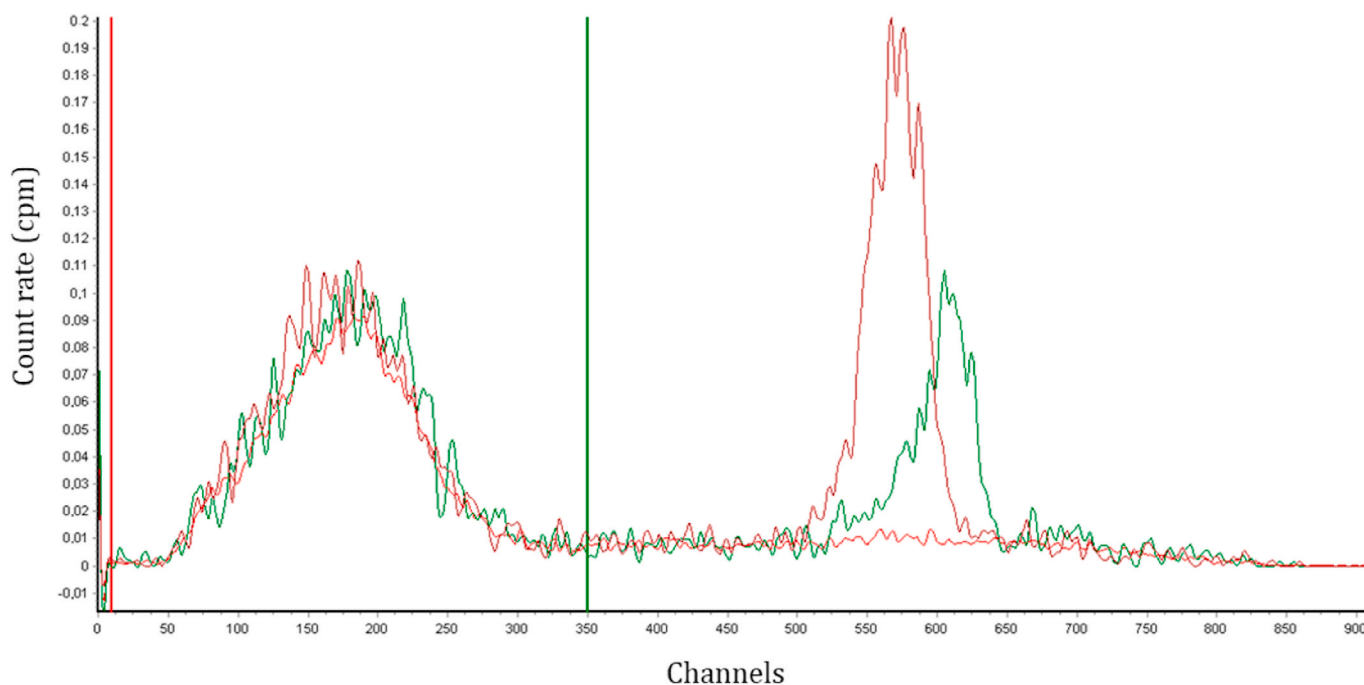


Fig. 2. Spectra of ^{238}Pu (in green), $^{238+239+240+242}Pu$ (in brown) and a blank sample (in red). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

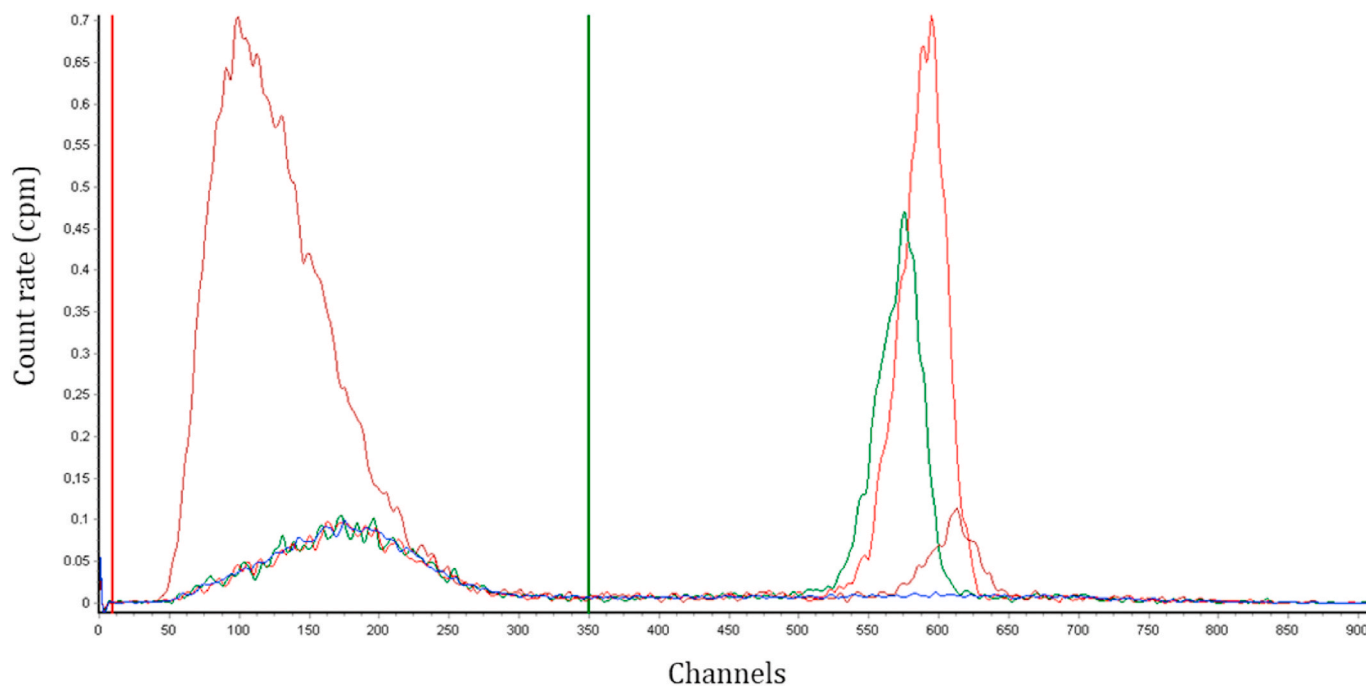


Fig. 3. Spectra of ^{241}Pu and ^{241}Am (in brown), ^{240}Pu (in red), ^{242}Pu (in green) and a blank sample (in blue). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

^{241}Pu is defined between channels 10 and 350, while the window for Pu alpha emitters is defined between channels 500 and 650, being the windows clearly separated.

Certainly, in Fig. 3, a peak of ^{241}Am in the brown spectrum is observed, as there is some ^{241}Am grown from ^{241}Pu in the ^{241}Pu tracer solution and the tracer solution was directly added to the vials to obtain these spectra. However, in real samples ^{241}Am is not expected to be found in their spectra, as a chemical isolation of Pu from sample matrix is carried out in this method.

2.2.4. Uncertainty and total yield assessment of ^{241}Pu activity concentration

In the LSC measurements, the same counting time (t_L) for blanks and samples have been assumed. Only counting times for the measurement of calibration sources and the standards for the quench curve are different from those devoted to blanks and samples.

Activity concentration of ^{241}Pu (a_1) and its relative uncertainty in the sample, according to GUM (GUM, 2008), is obtained by Eqs. (5)–(7):

$$a_1 = \frac{r_1 - r_{01}}{R \varepsilon_\beta m} = \omega (r_1 - r_{01}) \quad (5)$$

$$u_{rel}^2(a_1) = \frac{(r_1 + r_{01})}{t_L (r_1 - r_{01})^2} + u_{rel}^2(\omega) \quad (6)$$

With:

$$u_{rel}^2(\omega) = u_{rel}^2(\varepsilon_\beta) + u_{rel}^2(m) + u_{rel}^2(R) \quad (7)$$

Where:

a_1 is the activity concentration of ^{241}Pu , in Bq kg^{-1} ; r_1 is the gross count rate of ^{241}Pu , in s^{-1} ; r_{01} is the background count rate of ^{241}Pu , in s^{-1} ; R is the total yield of the process (chemical isolation plus planchet lixiviation); ε_β is the beta-counting efficiency, which depends on quenching; m is the mass of the sample, in kg; ω is a parameter that summarises $(R \varepsilon_\beta m)^{-1}$.

Beta-counting efficiency (ε_β) of any sample is obtained through a quench standard curve by measuring its SQP, as the quench curve relates beta-counting efficiency with SQP. The quench standard curve is made of a series of vials with a constant volume of scintillation cocktail (15 mL of Ultima Gold LLT), a constant activity of ^{241}Pu tracer and an increasing volume of quenching agent (nitromethane). All these vials were measured under the same conditions and their counting efficiency was calculated as expressed in Eq. (2), s being ^{241}Pu tracer in this case. The quench curve was obtained (SQP – efficiency) from measurements using the QUENCH software (Cassette, 2016; LNHB, 2016), that provides the quench curve function and its associated uncertainty $u^2(\varepsilon_\beta)$, also considering the uncertainty of the SQP parameter (Fig. 4).

As can be seen in Fig. 4, the maximum value of the measured detection efficiencies for ^{241}Pu is 38% when no quench agent is added, at the maximum value of SQP.

This beta counting efficiency can be obtained by using ^3H instead of ^{241}Pu as a standard. This is due not only to the similar maximum beta energies, 18.591 keV for tritium and 20.8 keV for ^{241}Pu , but also because of the similar shape of their beta spectra, that are shown in Fig. 5:

To probe the viability of this approximation, the same quench standard curve has been obtained under the same conditions but by using ^3H instead of ^{241}Pu . Both curves were compared obtaining differences in the range of 3–4% at each experimental point. As a conclusion, this ^{241}Pu method can be applied by using ^3H as a standard, considering that the percentage differences between both curves are smaller than the typical uncertainties of the method.

Corcho Alvarado et al. carried out an additional Pu isolation step to eliminate traces of Fe, Ni, Cu and Pt from the lixiviate, as they could cause quenching and decrease the efficiency of LSC measurement and luminescence (Corcho Alvarado et al., 2011). However, in our experience this process is not needed if SQP of each test sample is measured and the quench curve is used to get specific sample detection efficiency value from measured SQP. To avoid luminescence, vials are stored in the dark inside the scintillation chamber at a constant temperature, around 15 °C, a minimum of 6 h before LSC measurement.

The estimation of the yield of the complete process, total yield (R), from sample digestion to measurement of ^{241}Pu by LSC, requires the

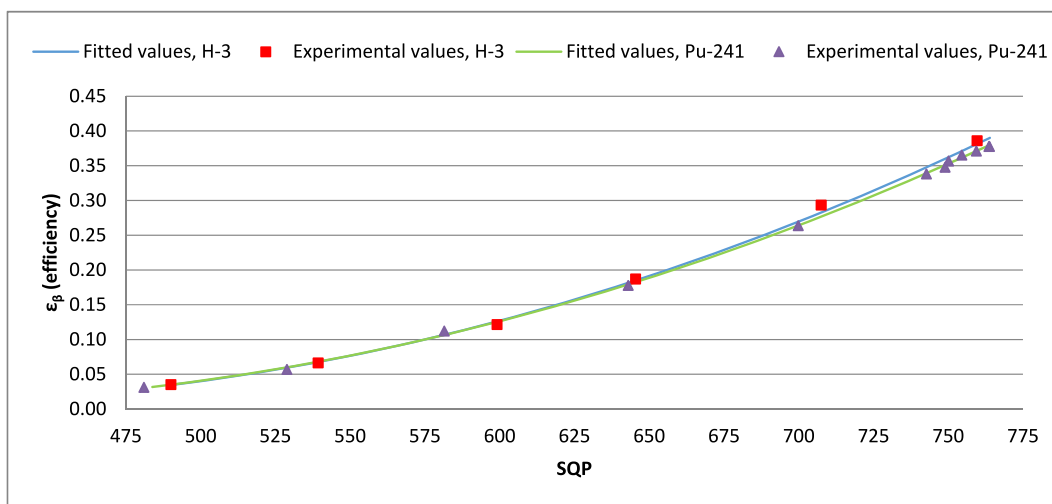


Fig. 4. Quench standard curves for ²⁴¹Pu, using ³H and ²⁴¹Pu standards. Experimental values are in red and purple and fitted ones in blue and green, respectively. R² coefficient of determination for fitted curve with ³H standard is 0.9979 and with ²⁴¹Pu standard is 0.9995. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

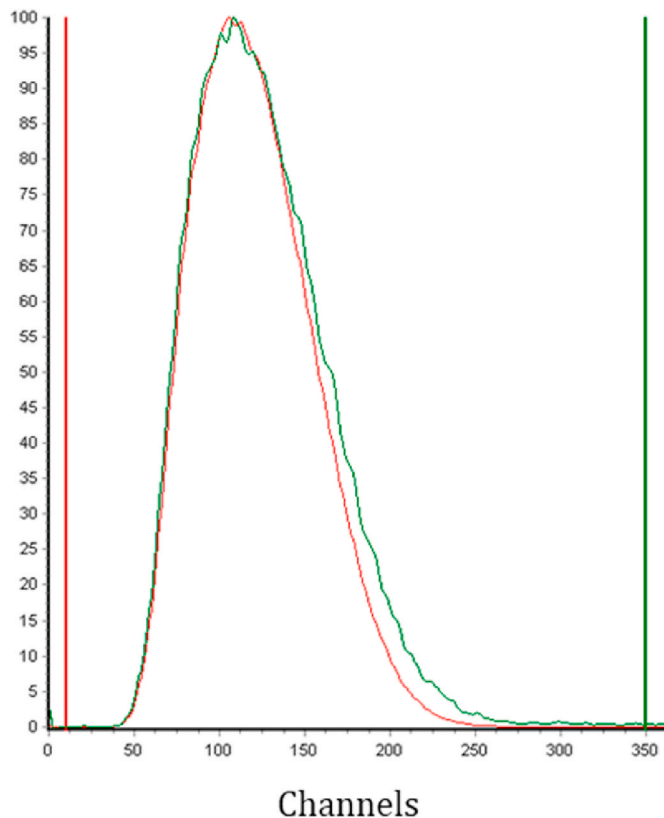


Fig. 5. Spectra of ³H (in red) and ²⁴¹Pu (in green), in auto scale. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

calculation of the planchet lixiviation yield, and can be obtained by using Eq. (8):

$$R = R_{\alpha} R_{\beta} \tag{8}$$

Where:

R_{α} is the chemical yield of Pu, obtained from Eq. (4); R_{β} is the yield of the planchet lixiviation.

Regarding R_{β} , some authors consider that by optimising planchet lixiviation, its value can be taken as equal to 100% (L'Annunziata, 2012; Hou, 2018). However, in our experience, in standard conditions, this value cannot be guaranteed, but can be easily conferred from the total alpha signal in the spectrum obtained in the LSC measurement.

In order to test the variability of planchet lixiviation process, samples containing Pu activities, ranging from 0.081 Bq to 1 Bq, were prepared and the whole process – radiochemical isolation, electrodeposition, alpha measurement, lixiviation and LSC – was performed for each of them. Obtained lixiviation yields range from 37 to 100%.

R_{β} and its relative uncertainty can be calculated by Eqs. (9) and (10), through the measurement of the Pu alpha-signal in the obtained LSC spectrum. These Pu alpha-signals come from the ²⁴²Pu added as a tracer in the first step of the chemical isolation of Pu and the other Pu alpha emitter isotopes present in the sample. The amount of each of them in the planchet can be calculated by using Eq. (1), but only a percentage of them, R_{β} , will potentially be removed from the planchet in the lixiviation process.

$$R_{\beta} = \frac{r_{\alpha} - r_{0\alpha}}{A_{\alpha} \varepsilon_{\alpha}} \tag{9}$$

$$u_{rel}^2(R_{\beta}) = \frac{(r_{\alpha} + r_{0\alpha})}{t_L (r_{\alpha} - r_{0\alpha})^2} + u_{rel}^2(A_{\alpha}) + u_{rel}^2(\varepsilon_{\alpha}) \tag{10}$$

Where:

r_{α} is the gross count rate of Pu alpha emitters in LSC, in s⁻¹; $r_{0\alpha}$ is the background count rate of Pu alpha emitters in LSC, in s⁻¹; A_{α} is the total activity of Pu alpha emitters in the planchet, in Bq; ε_{α} is the detection efficiency of Pu alpha emitters in LSC.

The total activity of Pu alpha emitters in the planchet (A_{α}) and its uncertainty are calculated through Eqs. (11) and (12), from the sum of each Pu isotope activity obtained in Eq. (1):

$$A_{\alpha} = \sum_i A_i \tag{11}$$

$$u_{rel}^2(A_{\alpha}) = \frac{1}{t} \frac{\sum_i (r_i + r_{0i})}{(\sum_i (r_i - r_{0i}))^2} + u_{rel}^2(\varepsilon) \tag{12}$$

Then, considering the expressions for R_{α} and R_{β} , R is calculated as:

$$R = \frac{r_t}{A_t \varepsilon} \frac{(r_\alpha - r_{0\alpha})}{A_\alpha \varepsilon_\alpha} \quad (13)$$

As the total activity of Pu alpha emitters in the planchet (A_α) is calculated in Eq. (11), it contains r_t as one of its components. The existence of this covariance should be considered for R uncertainty calculations, and then R can be expressed as:

$$R = \frac{r_t(r_\alpha - r_{0\alpha})}{A_t \varepsilon_\alpha (r_8 - r_{08} + r_9 - r_{09} + r_t)} \quad (14)$$

and its relative uncertainty, as:

$$u_{rel}^2(R) = \frac{1}{t(r_8 - r_{08} + r_9 - r_{09} + r_t)^2} \left\{ (r_8 + r_{08} + r_9 + r_{09}) + \frac{(r_8 - r_{08} + r_9 - r_{09})^2}{r_t} \right\} + \frac{r_\alpha + r_{0\alpha}}{t_L(r_\alpha - r_{0\alpha})^2} + u_{rel}^2(A_t) + u_{rel}^2(\varepsilon_\alpha) \quad (15)$$

r_8 and r_9 are the gross count rates of ^{238}Pu and $^{239+240}\text{Pu}$, respectively, in alpha spectrometry; r_{08} and r_{09} are the corresponding background count rates of ^{238}Pu and $^{239+240}\text{Pu}$ ROI, in s^{-1} .

The relative uncertainty of A_t takes into account the uncertainty coming from the certificate of the ^{242}Pu standard and all the other sources of uncertainty originating from the preparation of the ^{242}Pu dissolution used as a tracer and its introduction in the sample, typically on balances and micropipettes.

Detection efficiency of Pu alpha emitters in LSC (ε_α), and its relative uncertainty are calculated by Eqs. (16) and (17):

$$\varepsilon_\alpha = \frac{r_{pa} - r_{0pa}}{A_{pa}} \quad (16)$$

$$u_{rel}^2(\varepsilon_\alpha) = \frac{(r_{pa} + r_{0pa})}{t_p (r_{pa} - r_{0pa})^2} + u_{rel}^2(A_{pa}) \quad (17)$$

Where:

r_{pa} is the gross count rate of p calibration source, prepared by using an alpha emitter, in s^{-1} ; r_{0pa} is the background count rate, in s^{-1} ; A_{pa} is the activity of p , in Bq; and t_p is counting time used for this detection efficiency measurement in LSC, in seconds. Usually, r_s is much greater than r_{0s} , and then r_{0s} can be ignored.

As in the case of the relative uncertainty of A_t , $u_{rel}(A_{pa})$ takes also into account the uncertainty coming from the certificate of the standard used and all the other sources of uncertainty originating from A_{pa} preparation to its addition into the vial.

To obtain the alpha efficiency value in LSC we have used the ^{241}Am certified content present in the ^{241}Pu CS, updated by considering its ingrowth from the ^{241}Pu . This way, through only one calibration process (one calibration source preparation and one source measurement) both calibrations, alpha and beta, are simultaneously recorded. The value obtained was 100% for the alpha efficiency with a relative uncertainty of 1.70%. As expected (Perkin Elmer, 1992; Fons-Castells et al., 2017), no quenching effects were noticed.

2.2.5. Calculation of decision threshold and detection limit

From Eqs. (5)–(7), and following the ISO standard 11929 (ISO 11929, 2019), expressions for decision threshold (L_C) and detection limit (L_D) are obtained:

$$L_C = k \omega \sqrt{2 \frac{r_{01}}{t_L}} \quad (18)$$

$$L_D = \frac{2L_C + (k^2 \omega)}{1 - k^2 u_{rel}^2(\omega)} \quad (19)$$

Where k is the quantile of the standard normal probability distribution with a value of 1.65 for a confidence level of 95%. In this case, the probabilities $1-\alpha$ and $1-\beta$ from definition of decision threshold (L_C) and detection limit (ISO 11929, 2019) are taken as equal.

As seen in Eqs. (18) and (19), the decision threshold and detection limit depend on different parameters, background being one of the most important.

3. Results and discussion

3.1. Assessment of tracer quantity to be used

Alpha emitters considered in this work present an LSC efficiency (around 100%) higher than that of alpha spectrometry (around 25%). However, background count rates for those radiometric techniques differ greatly: around 1 cpm in LSC and lower than 10^{-5} cpm in alpha spectrometry. Thus, the usual amount of ^{242}Pu used for tracer in alpha spectrometry measurements may not be sufficient for LSC.

As a quality control of the method, a minimum value of R is required to be 50%. In addition, to limit the impact of the uncertainty of the leaching yield $u_{rel}(R_\beta)$ on the uncertainty of ^{241}Pu activity, we establish a maximum $u_{rel}(R_\beta)$ of 5%. So, we have to assess the amount of ^{242}Pu used as a tracer, A_t , to guarantee these values.

This is a key point for ^{241}Pu activity concentration calculation (Eq. (5)) and its uncertainty, both obtained through Eqs. (5)–7 and 13–15.

To carry out this evaluation, we assume the following:

1. $u_{rel}(\varepsilon_\alpha)$ can be decreased by increasing the amount of standard in the sample prepared to obtain ε_α , and also its counting time, but it has the lower limit of the standard uncertainty; in our case this value is 0.45%.
2. $u_{rel}^2(A_\alpha)$ also depends on the amount of ^{242}Pu added as a tracer, the value we are aiming to optimise, but $u_{rel}^2(A_\alpha)$ has also a lower limit that is the uncertainty of the calibration planchet used to get the alpha-spectrometry efficiency ($u_{rel}(A_s)$). In our case this value is 1.97%.
3. In the worst-case scenario, from a radiometric point of view, the sample does not contain any ^{238}Pu or $^{239+40}\text{Pu}$. Thus, alpha emissions in the test sample only come from ^{242}Pu .
4. In the LSC used, $r_{0\alpha}$ is around 1 cpm and r_{01} is around 8 cpm.

Thus, only two parameters can be balanced for getting the minimum $u_{rel}(R_\beta)$ value: sample-counting time in LSC (t_L) and the amount of ^{242}Pu tracer added (A_t).

Taking these assumptions into account and applying Eq. (10), if 24 h is chosen as a long but reasonable sample counting time in LSC (t_L), an activity of 0.05 Bq of ^{242}Pu tracer is needed.

To reduce the amount of ^{242}Pu tracer to use, we studied the possible effects of plastic and glass vials. After preparing and measuring, in equal conditions, blanks in plastic vials and in glass vials the results obtained show that while $r_{0\alpha}$ is around 1 cpm using glass vials, it decreases to around 0.5 cpm when plastic vials are used. The implementation of this change provides us with an amount of ^{242}Pu needed of 0.035 Bq. However, it should be taken into account that as the sample is directly

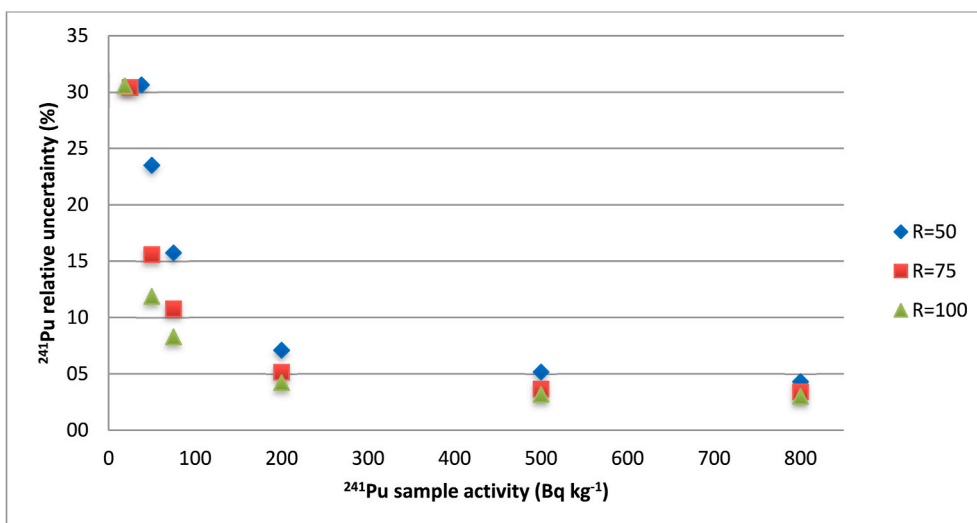


Fig. 6. Variation of relative uncertainty of ^{241}Pu activity concentration (%) with activity concentration (Bq kg^{-1}) and total yield, R (%).

dried in the vial, it is always easier to carry out this step in glass rather than plastic vials. Hence, a ^{242}Pu tracer value of 0.05 Bq has been considered in this work.

3.2. ^{241}Pu uncertainty and detection limit

The values of relative uncertainty of ^{241}Pu , obtained when using the sample and background measurement times, by LSC, previously established at 24 h, and a tracer quantity of 0.05 Bq, are shown in Fig. 6, for three different R values (50, 75 and 100%). The other parameters ($r_{0\alpha}$ and r_{01}) take the values shown in the previous section, which are the usual ones for the glass vial, cocktail and ratio used.

In Fig. 6, uncertainties can be observed that reach a value of around 30% for samples with activities of ^{241}Pu equal to the detection limit. Uncertainties decrease quickly to reach values lower than 5%, for activities of ^{241}Pu around 5 times higher than the detection limit of the method, once stabilised.

In addition, at low concentrations of ^{241}Pu , close to the detection limit of the method, higher values of R can produce much lower values of ^{241}Pu relative uncertainty, which can double if R moves from 100 to 50% (Fig. 6). At the detection limit, a common 30% relative uncertainty

is achieved. When ^{241}Pu activity increases, that is, for values of around 10 times the detection limit, the differences between the uncertainties, always present, become negligible.

These values can be compared with those obtained by using the conventional method, which does not control R_{β} and assumes it as 100% under the same conditions (Fig. 7). For the lowest ^{241}Pu activity concentration values, the values from the conventional method are very similar, marginally lower than those obtained by applying the method used in this paper. However, for extremely high ^{241}Pu activities, and when non-negligible ^{238}Pu and $^{239+240}\text{Pu}$ activities are present in the sample, this tendency changes and the ^{241}Pu uncertainties become smaller when using the method proposed in this paper.

The application of this methodology in the calculation of the detection limit of ^{241}Pu results in values of the detection limit in the range of 14–40 Bq kg^{-1} , for 1 g samples, depending on R values, from 50 to 100%, when using the sample and background measurement times, by LSC, previously established at 24 h, and a tracer quantity of 0.05 Bq. The other parameters ($r_{0\alpha}$ and r_{01}) take the values shown in the previous section, which are typical for glass vial and cocktail used.

These values for the detection limit are exceptionally low for the measurements carried out in the fields of D&D programmes or waste

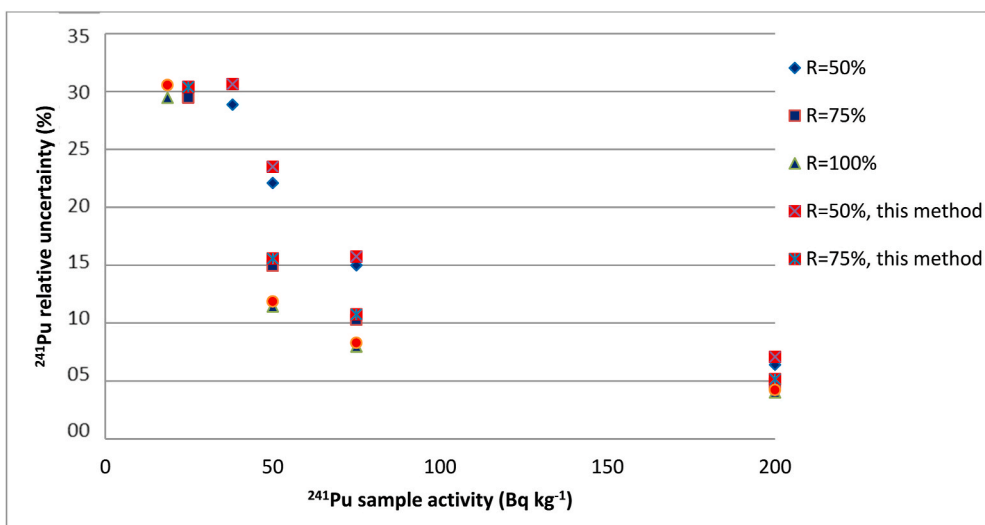


Fig. 7. Variation of relative uncertainty of ^{241}Pu activity concentration (%) with activity concentration (Bq kg^{-1}) and total yield, R (%), for both the conventional and the method proposed in this paper.

characterization but necessary for determinations in the environmental monitoring field. However, if higher detection limits are needed, mass or detection time can be decreased, i.e. employing 10800 s for LSC counting time, detection limits of around 100 Bq kg^{-1} are obtained. However, the uncertainty for R_p increases to 10%.

Comparing the detection limits of the proposed method and the conventional one, which considers R_p equal to 100%, the former are slightly higher (4%) than the latter, a difference which is almost negligible.

3.3. ^{241}Pu uncertainty sensitivity analysis

An estimation can be made of the percentage contribution in the combined uncertainty of each of the parameters, thereby indicating on which parameter efforts should be focused to reduce the combined uncertainty.

Only 5 uncertainty components of the ^{241}Pu evaluation provide significant contributions. These are the count rates of ^{241}Pu (r_1), its background (r_{01}), the total alpha count rate on the LSC (r_α), the alpha count rate of alpha calibration source in LSC (r_{pa}) and the ^{242}Pu activity added as a tracer (A_t).

Fig. 8 shows the relative contribution (%) of these 5 parameters on the ^{241}Pu activity concentration uncertainty for different values of ^{241}Pu activities.

The first two count rates mentioned clearly constitute a large part of the uncertainty until higher activities, where r_{pa} is the largest contributor (Fig. 8). At ^{241}Pu high activities, if combined uncertainty is to be reduced, then more effort should be made to reduce the uncertainty of r_{pa} by adding more standard to the calibration source or by measuring for a longer time period. At ^{241}Pu activities close to detection limits, its contribution to the uncertainty can only be slightly reduced by increasing LSC counting times.

4. Conclusions

^{241}Pu as well as the other α -emitting Pu nuclides of longer half-lives are important nuclides in monitoring actinides concentration. Particularly, ^{241}Pu is the largest contributor to the total plutonium radioactivity released in the environment. Its determination has rather difficulty, as it is a low energy beta emitter. For its assessment, radiochemical isolation of Pu is needed and two measurement methods can be considered: alpha

spectrometry + LSC and ICP-MS. ICP-MS allows getting low detection limits with short counting times but it has demerits in cost of the equipment and its relatively high measurement uncertainty in the ^{241}Pu assessment. The more conventional and worldwide used radiometric methods of liquid scintillation spectrometry together with alpha spectrometry are possible for ^{241}Pu assessment. This measurement procedure is usually the preferred technique because it requires less maintenance, it is cheaper than ICP-MS and it allows achieving precise activity quantifications with low detection limits using one day of counting time. For these reasons, in this paper the radiometric procedure has been selected to carry out activity determinations of ^{241}Pu .

Thus, the chosen method consists of the radiochemical isolation of Pu contained in the sample, previously traced by ^{242}Pu , its measurement by alpha spectrometry to obtain the isolation yield, the lixiviation of the planchet to recover the Pu, and its measurement by using LSC.

Usually, it is assumed that the lixiviation yield is always 100% and so its uncertainty is not considered in the ^{241}Pu uncertainty evaluation neither in its detection limit.

In this paper, a method to evaluate this lixiviation yield through a simultaneous alpha + beta measurement of the sample by LSC is presented. This lixiviation yield is obtained through the measurement by LSC of the alpha signal originating from the Pu alpha emitters present in the sample plus the ^{242}Pu added as a tracer. This measurement is carried out simultaneously on the beta signal coming from the ^{241}Pu , since Pu alpha emitters do not interfere in ^{241}Pu signal. Observations show that lixiviation yields range from 37 to 100%, so the usual assumption is not always correct when routine sample preparations are performed.

Firstly, detection parameters for the LSC equipment employed, a Quantulus, have been chosen. Subsequently, formulas to be used for yields, activity concentrations and detection limits are defined, considering the appearance of these two yields: radiochemical isolation and lixiviation. Alpha and beta LSC calibration are also simultaneously performed by using a liquid standard of ^{241}Pu that also contains known amounts of ^{241}Am .

Quench standard curves made with ^3H and ^{241}Pu show differences in the range of 3–4% at each experimental point. Hence, either ^3H or ^{241}Pu can be used as a standard, considering that relative differences between both curves are smaller than the typical uncertainties of the method. However, when ^3H is used, ^{240}Pu or ^{242}Pu tracers are needed for alpha calibration in LSC.

The amount of ^{242}Pu tracer and the LSC measurement time needed to

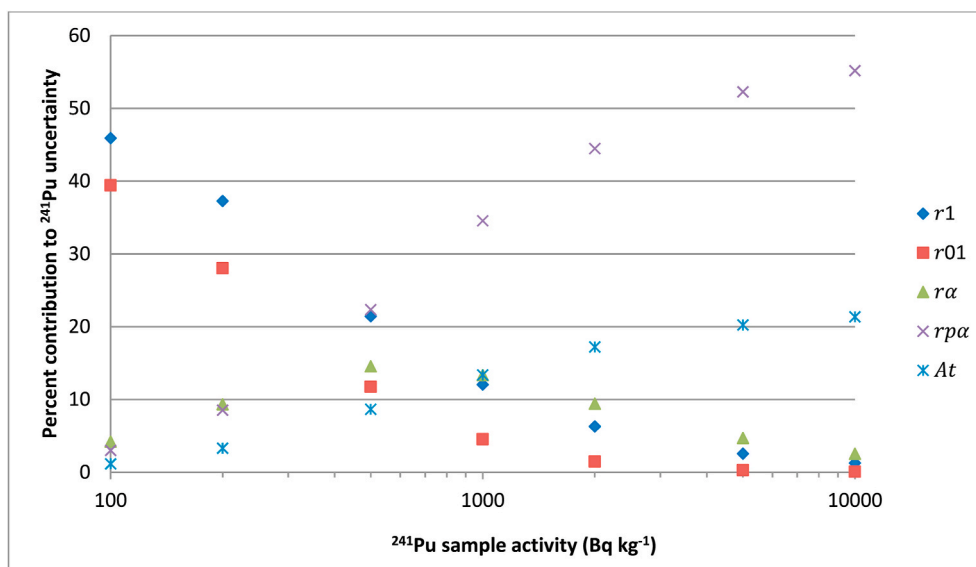


Fig. 8. Variation of the relative contribution of different parameters to the uncertainty of ^{241}Pu activity concentration (%) with ^{241}Pu activity concentration (Bq kg^{-1}).

limit the uncertainty of the lixiviation yield to 5% have been obtained. Values of 0.05 Bq and 86400 s are proposed for both parameters.

With these selections, detection limits obtained range from around 14 to 30 Bq kg⁻¹ for 1 g samples, depending on the total yield value (from 100 to 50%). These values are marginally higher than those obtained when only the radiochemical yield is considered and the lixiviation yield and its uncertainty are neglected. This means that this proposed method does not significantly increase detection limits in any case.

Relative uncertainties obtained range from 30%, for ²⁴¹Pu activity values close to the detection limit of the method, to 5% for activities higher than around 10 times the detection limit of the method. These uncertainties are slightly higher than those obtained when only the radiochemical yield is considered but again it does not suppose a significant increase.

Naturally, the values provided in this paper are dependent on the equipment and standards used so users should consider these factors. In any case, a clear conclusion of this work is that the lixiviation yield and its uncertainty can be easily evaluated using the formulas provided, with no loss in the quality of results and in the level of uncertainties and detection limits of ²⁴¹Pu activity.

CRedit authorship contribution statement

S. Rozas: Methodology, Investigation, Writing – review & editing. **M. Herranz:** Methodology, Investigation, Writing – review & editing. **R. Idoeta:** Methodology, Investigation, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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