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Inter-laboratory exercise with an aim to compare methods for ^{90}Sr and ^{239,240}Pu determination in environmental soil samples

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Abstract In order to deliver reliable results for a multitude of different scenarios, e.g. emergency preparedness, environmental monitoring, nuclear decommissioning and waste management, there is a constant process of method development in the field of radioanalytical chemistry. This work presents the results of a method comparison exercise aimed at quantifying ^{90}Sr and ^{239,240}Pu in environmental soil samples, with the intention of evaluating the performance and applicability of different methods. From the methods examined in this work, recommendations are given in order to find a radioanalytical measurement procedure, for ^{90}Sr and ^{239,240}Pu analysis, which is fit-for-purpose for a particular scenario.

Keywords Method comparison · Radiochemical analysis · Pu · Sr · Soil

Introduction

For identification and quantification of radionuclides in demanding sample matrices, robust and reliable radiochemical analyses are imperative. These methods can be used in order to provide input for different purposes including environmental monitoring, nuclear emergency preparedness, nuclear decommissioning and waste disposal, radioecology and tracer studies as well as nuclear forensics. For the various situations mentioned above, the selected method will differ from situation to situation due to different analytical purposes and criteria of clearance limit. However, efficient analytical performance of the radiochemical method is desirable for all cases.

As to what constitutes an ideal radioanalytical method, it should have both characters of high analytical quality and low analytical cost. The analytical quality can be assessed by the detection limit, analytical accuracy/precision and robustness of the method, while the analytical cost should be related to labor intensity, analytical time, instrument cost and sample throughput. However, there is often a trade-off between the analytical quality, as defined above, and the cost. This is often denoted as the fitness-for-purpose, i.e. the measurement result should be able to support the decision making process.

In recent years, novel and effective sample treatment technologies and automated radioanalytical protocols are becoming attractive to many researchers to improve analytical efficiency [1–11]. As of today, many laboratories working with radiochemistry have initiated the development of rapid radiochemical methods using different novel and effective sample treatment techniques. The literature to date describes many rapid methods for nuclear emergency preparedness. However, these methods may need to be altered to suit the needs for nuclear decommissioning and

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environmental monitoring, encouraging further method development.

Sr-90 is a well-known radioisotope requiring extensive radiochemistry for most environmental samples and ^{239,240}Pu similarly requires a thorough purification regardless which detection approach is applied. In most situations with an unknown source, ^{90}Sr and ^{239,240}Pu would be of interest following gamma spectrometry. Therefore effective analytical methods for both ^{90}Sr and ^{239,240}Pu are desirable for most radiochemistry labs. Generally, it is representative for many labs to perform ^{90}Sr and ^{239,240}Pu analysis separately, but it could be relevant to employ combined methods with limited sample material and restricted time.

In this work, a method comparison was performed for determination of ^{90}Sr and ^{239,240}Pu in environmental soil samples to identify the advantages and pitfalls in these different methods. For the comparison, seven analytical methods were selected which were mostly developed by the laboratories participating this inter-comparison exercise. They include two ^{90}Sr methods, three ^{239,240}Pu methods and two methods which combined the analysis of ^{239,240}Pu and ^{90}Sr. Parameters for comparing the analytical performance of these methods are analytical precision and accuracy, detection limit, analytical turnover time, simplicity and robustness.

Experimental

Samples

Two reference materials were used in the method comparison. The first was a Danish soil (DS) which was obtained from a laboratory round-robin inter-comparison [12]. The DS comprised of the top 10 cm of soil (sieved using a mesh of 2 mm) collected from 12 different Danish locations during 2003 and pooled at Risø National Laboratory, Denmark. The soil was further sieved through a 0.6 mm and a 0.4 mm sieve, respectively, and coarsely mixed by hand following a single homogenization of all soil for 30 min in a large volume mixer.

The second reference material was a Syrian soil (SS) which was obtained from the IAEA-TEL-2015 ALMERA proficiency test (soil No. 5). The raw material of Syrian soil was collected and treated in Syria by the Syrian Atomic Energy Commission. After drying, it was milled, sieved under 90 µm, ashed at 650 °C, homogenised and packed into plastic bottles. The sample was sterilised by a gamma dose of 25 kGy.

The Danish soil was used in the method comparison for determination of ^{239,240}Pu, while the Syrian soil was used for both ^{90}Sr and ^{239,240}Pu determination.

Analytical methods for ^{90}Sr and ^{239,240}Pu determination

Seven analytical methods were used in the comparison including four methods for ^{90}Sr (Sr-A, Sr-B, Sr/Pu-A and Sr/Pu-B) and five analytical methods for ^{239,240}Pu (Pu-A, Pu-B, Pu-C, Sr/Pu-A and Sr/Pu-B). The schematic procedures of these methods are illustrated in Figs. 1, 2, 3, 4, 5, 6 and 7. The detailed operational protocols for these methods can be found in the on-line supporting information.

Calculation of accuracy and precision

Two tests, as described by IAEA, were used to evaluate the results obtained: the relative bias test and the precision test. The relative bias is calculated as

$$\text{Bias} = \frac{V_i - V_\mathrm{r}}{V_\mathrm{r}} \times 100\% \tag{1}$$

V_i is the value obtained by each method in the inter-comparison exercise, V_r is the reference value of the corresponding samples.

The precision was calculated as

$$P = \sqrt{\left(\frac{u_\mathrm{r}}{V_\mathrm{r}}\right)^2 + \left(\frac{u_i}{V_i}\right)^2} \times 100\% \tag{2}$$

V_i and u_i is the value and the uncertainty obtained by each method in the inter-comparison exercise, V_r and u_r is the reference value of the corresponding sample.

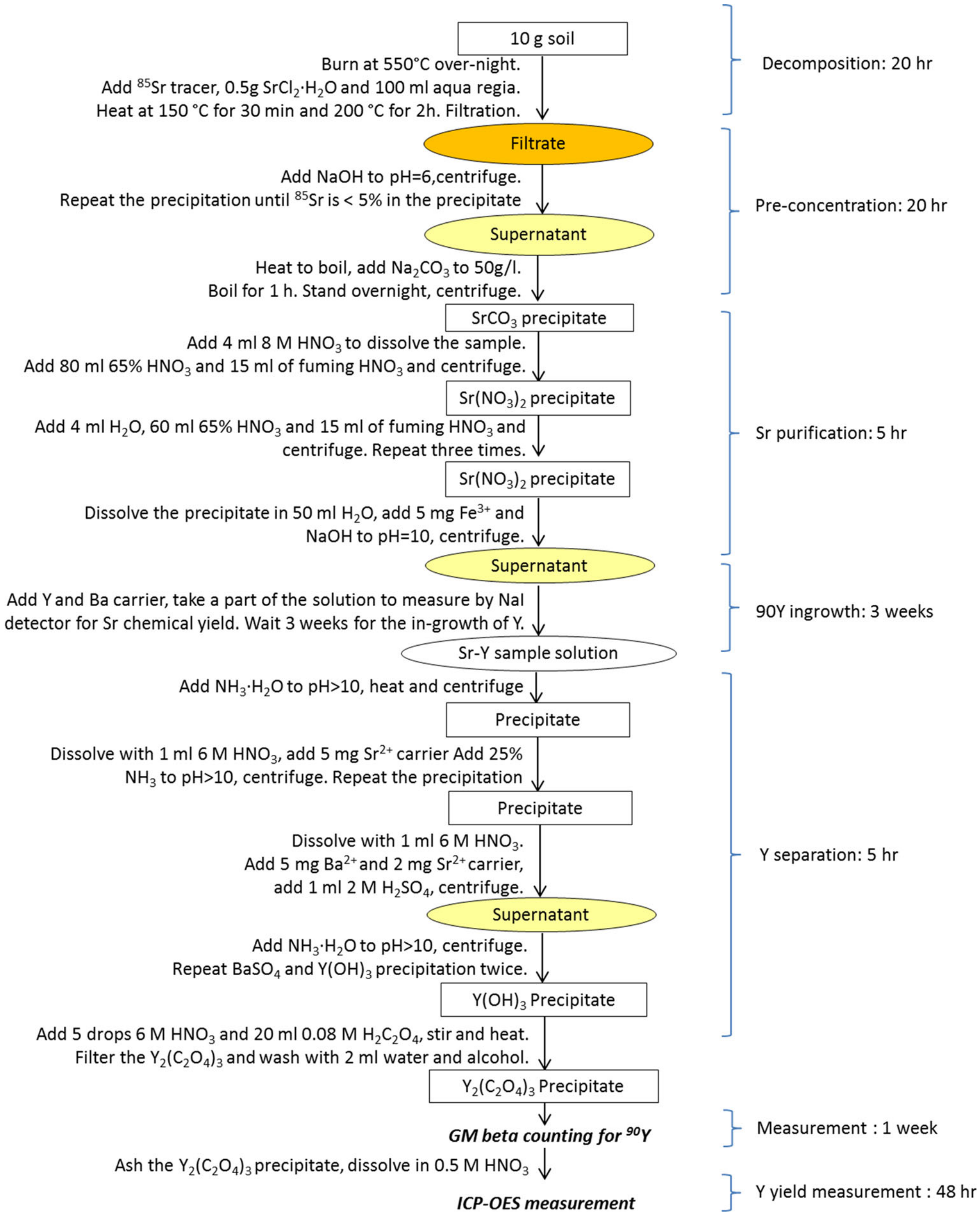
It is noted that the accuracy and precision required for emergency response versus routine monitoring may be different, as a larger bias and precision may be acceptable in an emergency as long as it can be assured that the activity found is below the dose concern limit. Whereas, in order to facilitate the evaluation of each method, an uniform criteria for accuracy and precision tests are employed according to IAEA recommendation [13]. If the Bias $<$ MARB (Maximum Acceptable Relative Bias) the result will be 'Acceptable' for accuracy. And if Bias $< k*P$ (where $k = 2.56$) and $P <$ MARB then the result will be 'Acceptable' for precision as well. The MARB value was set to 20% for both the ^{90}Sr and the ^{239,240}Pu analysis.

Calculation of limit of detection

The following equation, as described by Holmgren et al. [1] adapted from the works of Lochamy [14] and Currie [15], was used to calculate the limit of detection (LOD) for ^{90}Sr.

$$\text{LOD} = \frac{1}{U \cdot m \cdot \Psi} \frac{k^2 + 2k\sqrt{2}\sqrt{R_\mathrm{BG} t_m}}{\frac{(1-e^{-\lambda_Y t_m})}{\lambda_Y}(1 - e^{-\lambda_Y t_i})} \tag{3}$$

Fig. 1 Schematic analytical procedure of the Sr-A method



where U is the chemical yield, m is mass of sample in kg, ψ is the measurement efficiency for the measurement of ^{90}Y by LSC or beta counting, k is 1.64 for a 95% confidence interval, R_{BG} is the count rate in cps for the blank, t_m is the measurement time for the samples, t_i is the time of ingrowth for the samples ($t_i = \infty$ for the methods that awaited full ingrowth of ^{90}Y), and λ_Y is the decay constant for ^{90}Y.

Different equations were used to calculate the LODs for $^{239,\ 240}$Pu through ICP-MS and alpha spectrometry measurement, respectively. For ICP-MS, the equation from Miller and Miller [16] was used:

$$\mathrm{LOD_{MS}} = x_{\mathrm{blk}} + 3 \times s_{\mathrm{blk}} \tag{4}$$

where x_{blk} is the average concentration of the background signal, s_{blk} the standard deviation of the background. For alpha spectrometry, Currie's equation was used based on a 95% confidence interval [15]:

$$\mathrm{LOD_{AS}} = 2.71 + 4.65\sqrt{b} \tag{5}$$

where b is the number of counts in the background.

Results and discussion

Analytical performance of each method

Accuracy and precision

The overall results for ^{90}Sr and ^{239,240}Pu determination in this work are summarized in Tables 1 and 2, respectively.

Fig. 2 Schematic analytical procedure of the Sr-B method

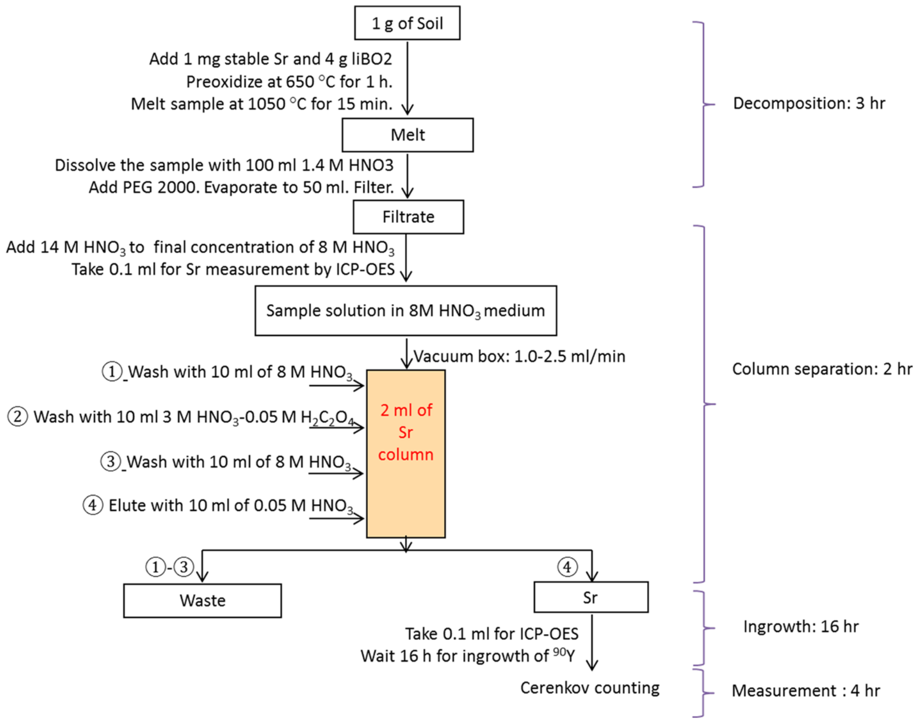


Fig. 3 Schematic analytical procedure of the Pu-A method

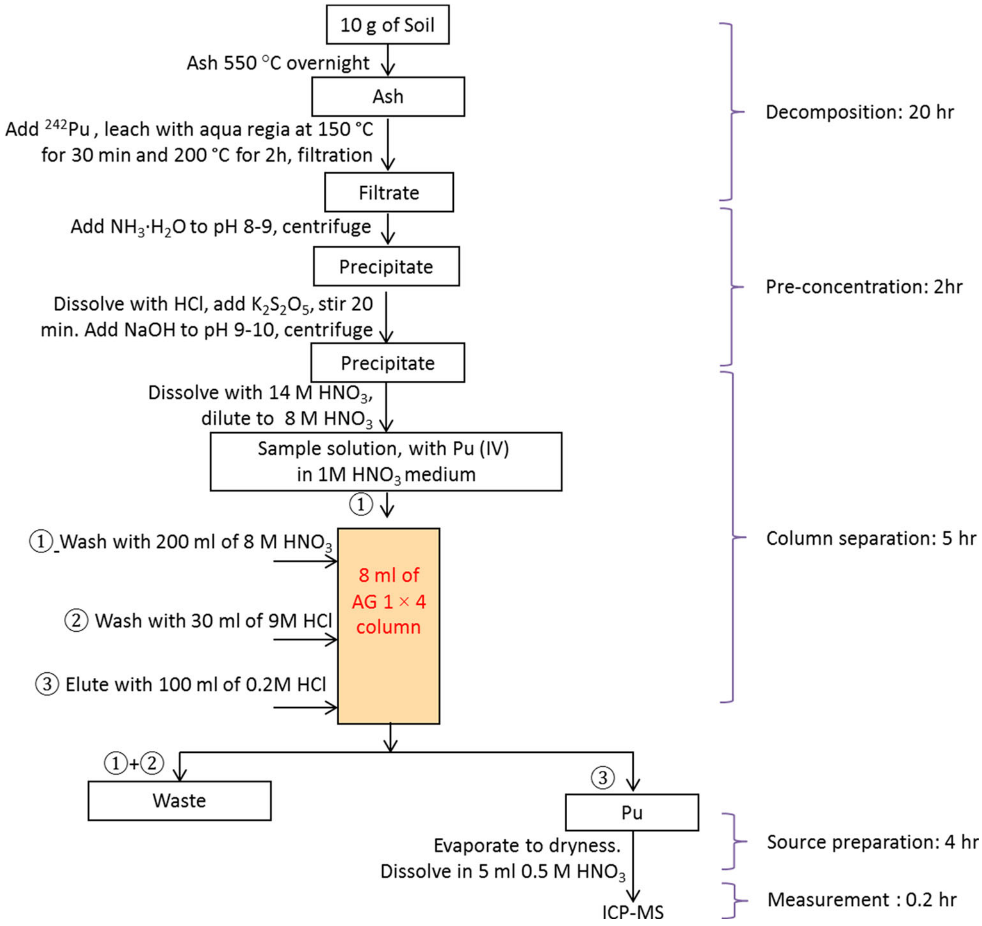
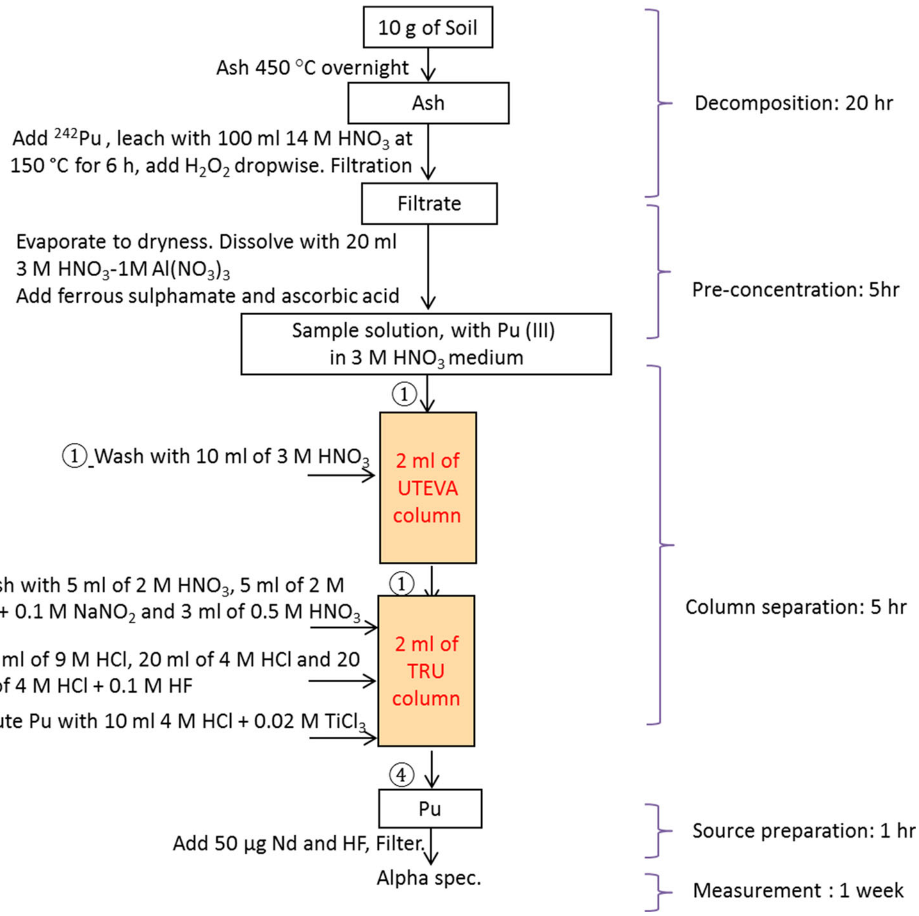


Fig. 4 Schematic analytical procedure of the Pu-B method



Uncertainties of the activity concentrations are given for 1σ.

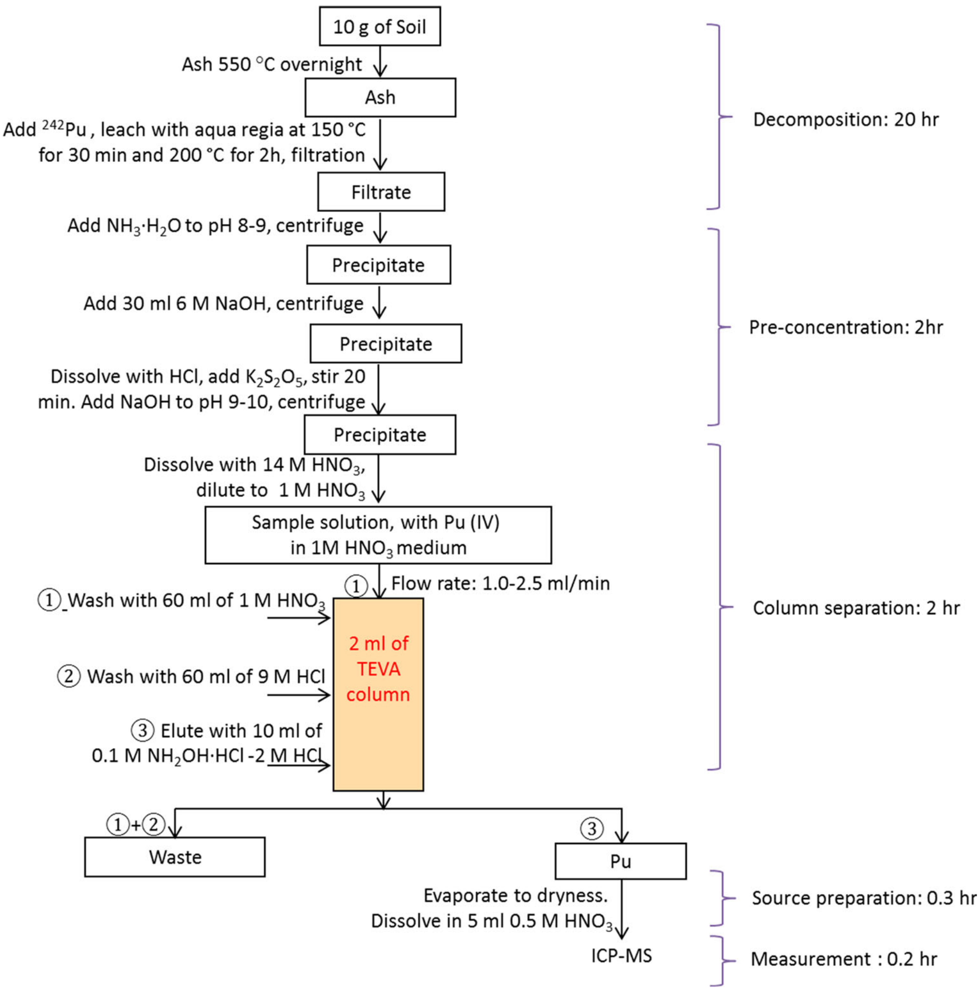
The reference value of ^{90}Sr in Syrian soil is (36.2 ± 2.7) Bq/kg. The ^{90}Sr concentrations obtained using Sr-A, Sr/Pu-B and Sr-B methods were (34.2 ± 4.7), (39.0 ± 3.0) and (42.3 ± 7.3) Bq/kg, respectively. These results show satisfactory accuracy, with relative bias of −5.5, 7.7 and 16.8%, respectively. *P* values obtained by these three methods for Syrian soil are within 20% and meet the criteria of Bias <2.56 *P*. However, the ^{90}Sr value for Syrian soil obtained by the Sr/Pu-A method significantly differs from the reference value (Fig. 8) with large relative bias (−60.6%) and large uncertainty ($P = 92.2\%$). The overall results indicate that, except for the Sr/Pu-A method, all the other methods (Sr-A, Sr/Pu-B and Sr-B) pass both the accuracy and the precision test.

The reference value of ^{239,240}Pu in the Syrian soil is (2.7 ± 0.4) Bq/kg. The results obtained using Pu-A and Sr/Pu-A methods are (2.82 ± 0.07) Bq/kg and (2.50 ± 0.10) Bq/kg, respectively, which agree well with the reference value with relative bias <8%. For the Danish soil, the recommended value of ^{239,240}Pu is (0.238 ± 0.014) Bq/kg [12]. Pu-C and Sr/Pu-B methods show relative bias within 5% for the Danish soil analysis, while Pu-B method indicates −16% relative bias (Fig. 9). Higher *P* value of 25% was obtained for Pu in Sr/Pu-B method, while the other methods achieved *P* values ranging within 10–15%. The overall results indicate that all methods pass both accuracy and precision test, except Sr/Pu-B method which only passes the accuracy test.

Limit of detection

It can be seen from Table 1 that, the LODs of ^{90}Sr vary from 0.2 to 24 Bq/kg among the four methods used in this work. Relatively high LOD was achieved for ^{90}Sr by Sr-B method (10.4 Bq/kg) compared to the other three methods (0.2–1.0 Bq/kg), this is due to the short time (16 h) allowed for ingrowth. It should be noted that after such a short ingrowth time, ^{90}Y has only reach about 16% of the equilibrium activity relative to ^{90}Sr. This will of course result in a higher LOD as well as a higher combined measurement uncertainty. It was calculated that the resulting LODs were 5.1 and 3.5 Bq/kg, when the time of ingrowth increased to 36 and 48 h, respectively. In the Pu determination (Table 2), when using ICP-MS (Pu-A and Pu-C methods), the LOD for ^{239,240}Pu is 0.00104 Bq/kg (with 0.00025 Bq/kg for ^{239}Pu and 0.00079 Bq/kg for

Fig. 5 Schematic analytical procedure of the Pu-C method



^{240}Pu, respectively). This is 1–2 order of magnitude lower than the values obtained by alpha spectrometry (0.018, 0.022 and 0.07 Bq/kg of ^{239,240}Pu in Sr/Pu-A, Pu-B and Sr/Pu-B method, respectively).

It should be mentioned that the criteria for evaluating the LOD of the analytical methods maybe different for emergency response and routine monitoring. Higher LOD may be acceptable in an emergency situation as long as it can be assured that the activity found is below the dose concern limit.

Chemical yield

Apart from the performance of the detecting instrument, chemical yield is also an important parameter affecting the LOD. High chemical yield is always desirable to ensure the lowest possible LOD for any analytical method.

The highest chemical yield (99%) for ^{90}Sr analysis was obtained in Sr-B method for 1 g of the Syrian soil (Table 1). Moderate chemical yield (70%) for ^{90}Sr was obtained in Sr-A method for 10 g of the Syrian soil. However, largely varying chemical yields (41–79%) were achieved in Sr/Pu-A method, whilst even lower (37%) chemical yield was obtained in Sr/Pu-B method.

The highest Pu chemical yield (95%) was obtained in Pu-C method for the Danish soil (Table 2). Satisfactory chemical yield (80%) for Pu was achieved in Pu-A method for the Syrian soil. However, the other three methods indicated relatively low chemical yields (<40%), whilst one method failed to measure ^{239,240}Pu in the Syrian soil due to the significant loss of Pu during sample preparation.

Analytical turnover time

The turnover time for ^{90}Sr determination in this work ranged from approximately 1–32 days, depending on the method employed (see Table 1). Apart from the Sr-B method, which can be completed within 24 h, all other methods presented in this work are very tedious. The major part of time used for ^{90}Sr analysis among these four methods was spent on ^{90}Y ingrowth. For example, a 3-week ^{90}Y ingrowth time was used in both Sr-A and Sr/

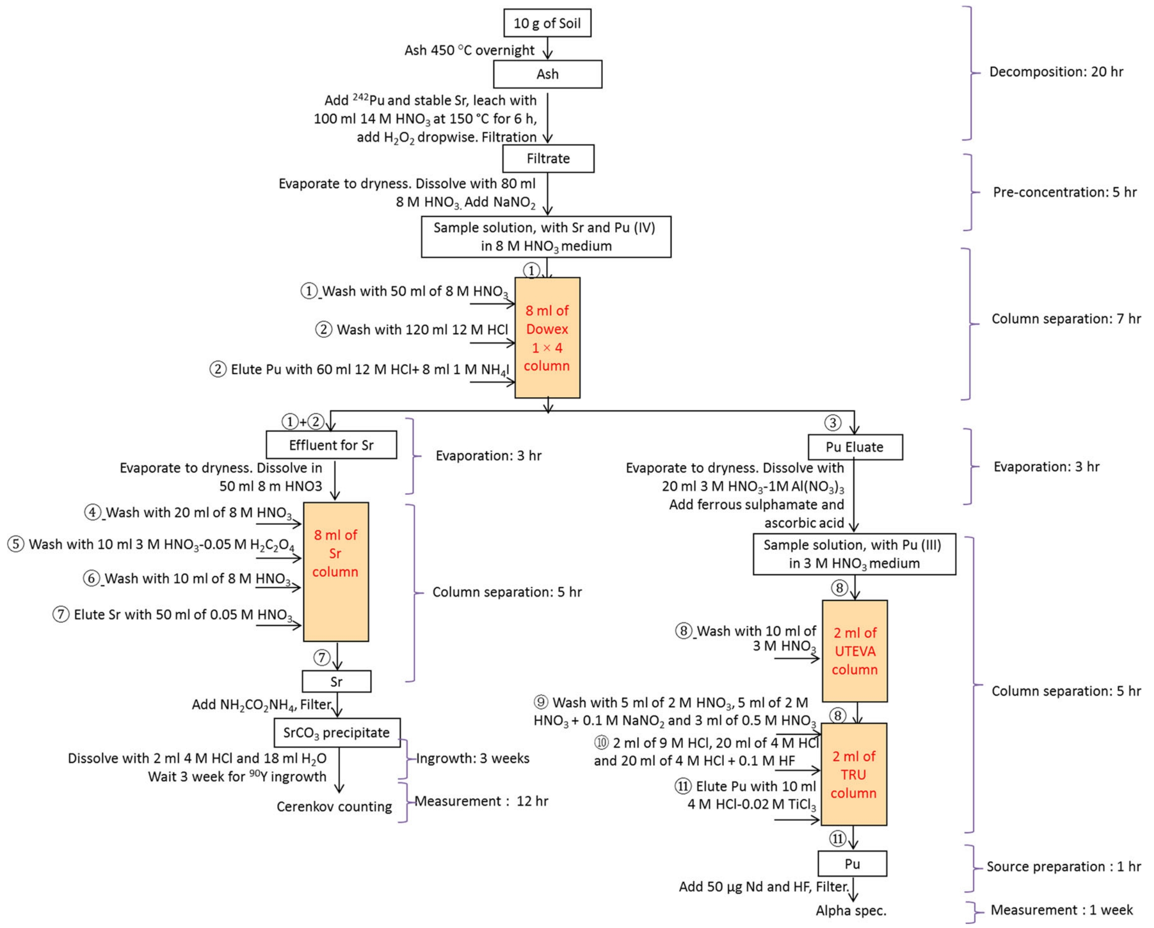


Fig. 6 Schematic analytical procedure of the Sr/Pu-A method

Pu-A method, while a 2-week ingrowth for Sr/Pu-B, and a 16 h ingrowth for the Sr-B method were employed. In addition to the time for ^{90}Y ingrowth (16 h to 3 weeks), beta counting (Sr-A and Sr/Pu-B method) is also a time-consuming step (1 week).

The entire analytical turnover time for ^{239,240}Pu determination ranged from 1 to 13 days among the methods used in this work. The most time consuming procedure was used in Sr/Pu-B method (13 days), whereas the most time-efficient analysis was reported by Pu-C method (1 day). Generally, the alpha spectrometric counting of Pu is the most time-consuming phase (7–9 days). In addition, the sample pre-treatment among the investigated methods also takes significant time (1–3 days).

Analytical turnover time is a crucial parameter especially in emergency situations. The analytical methods which take more than 1–2 days is not recommended for emergency purposes, but could be suited for routine analysis where analytical time is not a critical issue. Sr-B and Pu-C methods are applicable for both emergency and routine situations as long as their respective LOD meets the requirement for the analyzed samples.

Parameters affecting the analytical performance

Sample pre-treatment

In radiochemical analysis, pre-treatment for solid samples such as soil is aimed to quantitatively release the target radionuclides into a homogeneous solution. It is of importance to choose a suitable sample decomposition method that completely extracts the analytes contained in the sample into solution. In this work, three sample decomposition techniques were employed including acid leaching, total dissolution with HF and other mineral acids and alkaline fusion.

Acid leaching using either aqua regia (Pu-A and Pu-C methods) or HNO_3/H_2O_2 (Pu-B, Sr-A and Sr/Pu-A methods) was performed with heating (150–200 °C) and reflux of the leaching solution. Aqua regia is more aggressive and thus more effective compared to 14 mol/l HNO_3, even though the addition of H_2O_2 in the 14 mol/l HNO_3 would assist with further decomposition of organic matters contained in the sample. This might be a possible explanation for the somewhat lower ^{239,240}Pu values with relative bias

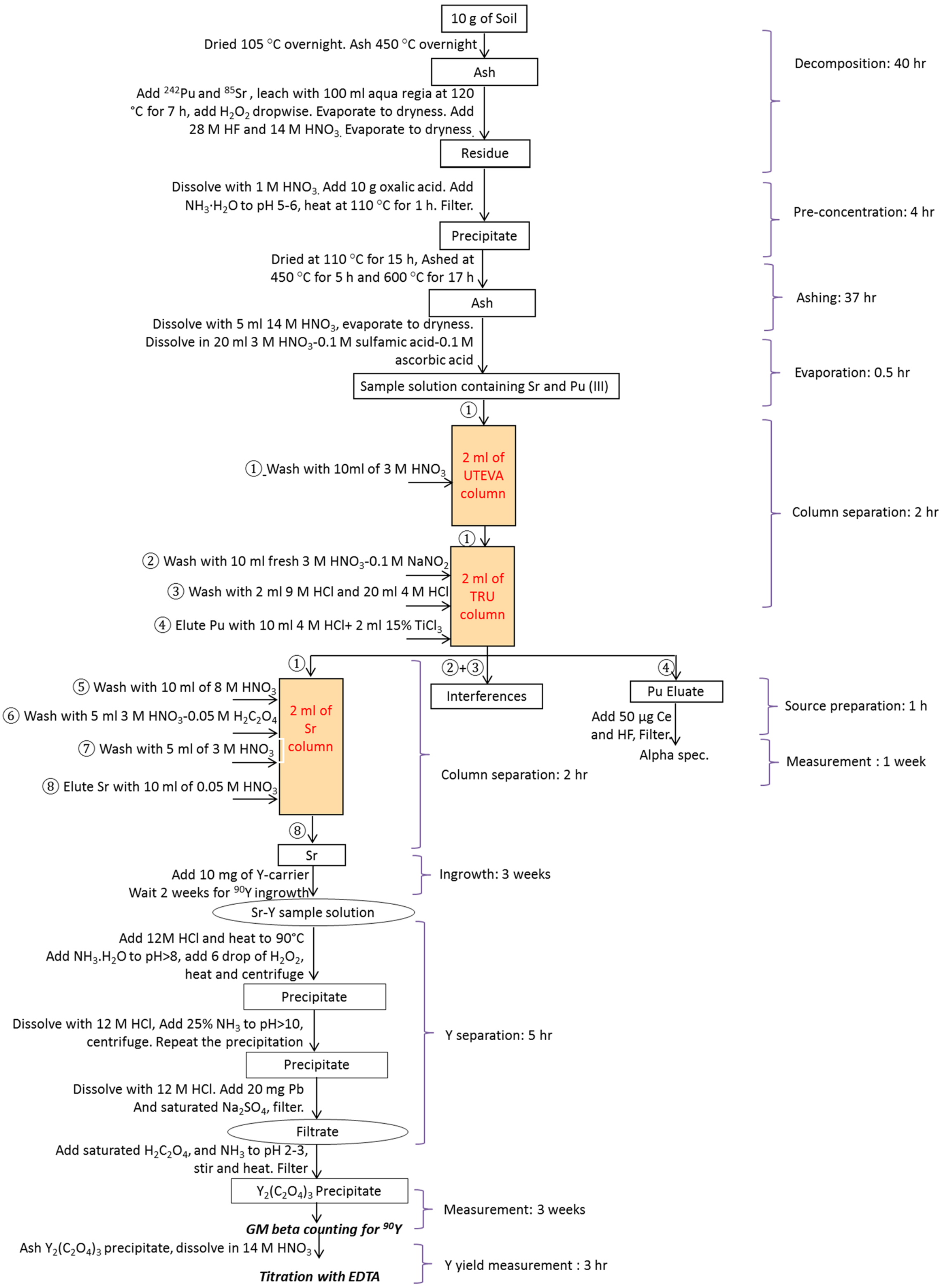


Fig. 7 Schematic analytical procedure of the Sr/Pu-B method

of −7.4% and −16%, obtained by Pu-B and Sr/Pu-A methods, respectively. The extraction of Pu might not be completed with the use of 14 mol/l HNO_3/H_2O_2 in both methods.

Acid leaching is a very simple and flexible approach, which is favourable for processing low-level environmental samples, where a large sample amount is needed. However, the literature indicates a potential risk of underestimating

Table 1 Overall analytical results of ^{90}Sr in the Syrian soil, uncertainties are given for 1σ

Method	Sample size, g	Description	Overall chemical yield[c] (%)	^{90}Sr activity (Bq/kg)[a]	LOD (Bq/kg)	Bias (%)	*P* (%)	Turnover time, day
Sr-A	10	Dry ashing—aqua regia digestion—$Fe(OH)_3$ precipitation—repeated $Ca(OH)_2$, $SrCO_3$ and $Sr(NO_3)_2$ precipitation—3-week ^{90}Y ingrowth-repeated $Fe(OH)_3/Y(OH)_3$ and $BaSO_4/SrSO_4$ precipitation—$Y_2(C_2O_4)_3$ precipitation—beta counting (^{90}Y)	70.1 ± 7.0	34.2 ± 4.7	0.4	−5.5	15.6	32.1
Sr/Pu-A	10	Dry ashing—conc.HNO_3/H_2O_2 digestion-evaporation—Dowex 1 × 4 + Sr column—$SrCO_3$ precipitation—3-week ^{90}Y ingrowth—LSC (^{90}Y Cerenkov counting)	60.0 ± 19.0	14.3 ± 13.1	1.0	60.6 (NP)[b]	92.2 (NP)	23.2
Sr/Pu-B	10	Dry ashing—aqua regia/H_2O_2//HF digestion—CaC_2O_4 co-precipitation-UTEVA/TRU/Sr column—2-week ^{90}Y ingrowth- repeated $Fe(OH)_3/Y(OH)_3$ precipitation—$PbSO_4/SrSO_4$ precipitation—$Y_2(C_2O_4)_3$ precipitation—beta counting (^{90}Y)	37.0 ± 3.7	39.0 ± 3.0	0.2	7.7	10.7	24.9
Sr-B	1	Dry ashing—$LiBiO_2$ fusion—Sr resin—16 h ^{90}Y ingrowth—LSC (^{90}Y Cerenkov counting)	99.5 ± 8.6	42.3 ± 7.3	24	16.8	18.8	1.0
Reference value				36.2 ± 2.7				

[a] Decay corrected to reference date 15th Oct 2015. Bias and *P* values are calculated using the mean value ± SD, for reference purpose only

[b] NP: not pass the corresponding accuracy or precision test

[c] Overall chemical yield into Sr or Sr·Y

the Pu concentration for samples containing refractory oxides or hot particles, due to the incomplete dissolution of the sample matrix and therefore potential losses of target radionuclides in the pre-treatment step using acid leaching [17]. The two soils analysed in this work are environmental samples with Pu originating mainly from global fallout, the content of Pu refractory oxides in these two samples may be negligible. This is also confirmed by the good analytical accuracy obtained by the Pu-A and Pu-C methods.

A rapid alkaline fusion with $LiBO_2$ was performed in the Sr-B method, wherein the entire operation could be completed within 20 min. Many works have proved that alkaline fusion is more effective than acid leaching to completely dissolve refractory oxides contained in soil [17]. For small-sized samples (e.g., <1 g), the fusion can be directly performed without ashing the sample, which significantly shortens the operational time. However, handling large-sized samples is still a challenge in alkaline fusion process and the maximum fusion capacity, as found in the literature to date, has been reported to be 20 g of soil [18].

Total dissolution with aqua regia/HF/H_2O_2 was used in Sr/Pu-B method and it was noticed that the sample matrix composition affected the effectiveness of the total dissolution. It was observed in the experiment that Syrian soil is very fine-grained and contains an iron-rich matrix component, which was very difficult to dissolve. The complex matrix composition of the Syrian soil made it impossible to achieve total dissolution even using HF. In the literature, total dissolution using HF in combination of other mineral acids have been widely used for decomposition of solid samples [19–22], especially for the determination of natural radionuclides (e.g., uranium and thorium) in geological studies. Having said that, it must be noted that in some cases HF could not totally dissolve the refractory particles of radionuclides especially when the sample size is larger than about 5 g [23]. Under such circumstances, alkaline fusion method should be recommended instead of HF dissolution.

After sample decomposition, pre-concentration is needed to reduce the sample volume or transform the sample to a suitable form prior to further chemical purification. In this work, precipitation/co-precipitation was used as a pre-concentration step, except for the Pu-B, Sr-B and Sr/Pu-A methods which employed direct evaporation. A simple $Fe(OH)_3$ co-precipitation was used in Pu-A and Pu-C methods for Pu pre-concentration. $CaCO_3$-$SrCO_3$ precipitation was used in Sr-A method to pre-concentrate Sr, and CaC_2O_4 co-precipitation was applied in Sr/Pu-B method for pre-concentration of both Pu and Sr.

Table 2 Overall analytical results for Pu isotopes in the Danish soil and the Syrian soil, uncertainties are given for 1σ

Sample ID	Method	Description	Pu chemical yield (%)	$^{239+240}$Pu activity (Bq/kg)	LOD (Bq/kg)	Bias (%)	*P* (%)	Turnover time, day
SS (10 g of each)	Pu-A	Dry ashing—aqua regia digestion- $Fe(OH)_3$ co-precipitation-AG 1x 4 chromatography-ICP-MS	80.1 ± 8.0	2.82 ± 0.07[a]	0.00025 (^{239}Pu) 0.00079 (^{240}Pu)	4.4	15.0	1.3
	Sr/Pu-A	Conc. HNO_3 + H_2O_2 digestion—evaporation-Dowex + UTEVA/TRU chromatography-alpha spectrometry	40.0 ± 5.0	2.50 ± 0.10	0.012 (^{238}Pu) 0.018 ($^{239+240}$Pu)	−7.4	15.3	8.7
	Sr/Pu-B	Dry ashing—aqua regia/H_2O_2//HF digestion-CaC_2O_4 co-precipitation—UTEVA/TRU column—alpha spectrometry	NA[b]	NA				12.5
	Reference value			2.7 ± 0.4				
DS (10 g of each)	Pu-B	Dry ashing—conc. HNO_3 + H_2O_2 digestion—evaporation—UTEVA/TRU column—alpha spectrometry	40.0 ± 5.0	0.20 ± 0.02	0.014 (^{238}Pu) 0.022 ($^{239+240}$Pu)	−16.0	11.6	8.3
	Pu-C	Dry ashing—aqua regia digestion- $Fe(OH)_3$ co-precipitation-automated TEVA chromatography-ICP-MS	95.3 ± 4.7	0.23 ± 0.03 ^{239}Pu: 0.14 ± 0.01 ^{240}Pu: 0.09 ± 0.02	0.00025 (^{239}Pu) 0.00079 (^{240}Pu)	3.4	14.3	1.0
	Sr/Pu-B	Dry ashing—aqua regia/H_2O_2/HF digestion-evaporation—UTEVA/TRU column—alpha spectrometry	25.6 ± 2.6	0.25 ± 0.06	0.07 (^{238}Pu) 0.07 ($^{239+240}$Pu)	5.0	24.7 (NP)[c]	12.5
	Reference value [12]			0.238 ± 0.014(^{239}Pu: 0.140 ± 0.008, ^{240}Pu: 0.098 ± 0.006)				

[a] ^{240}Pu:^{239}Pu atomic ratio was measured to be 0.186

[b] NA: not available

[c] NP: not pass the corresponding accuracy or precision test

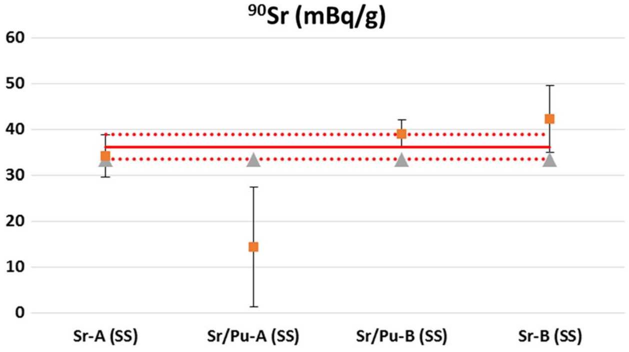


Fig. 8 Activity concentration of ^{90}Sr in Syrian soil (SS) obtained by different methods utilized in this work. The *solid* and *dotted lines* represent the reference value and confidence limits of the reference value for ^{90}Sr. The *error bars* of the results represent the expanded uncertainty with a coverage factor, $k = 1$

Even though the operation of evaporation is simpler than precipitation/co-precipitation, the latter could provide an additional function of partially eliminating matrix elements, which could facilitate the following purification step. It can be seen from the results (Table 2) that much lower chemical yields (<45%) for Pu were achieved when using direct evaporation (Sr/Pu-A and Pu-B methods). This could be explained by the high competitive adsorption of matrix elements in the following chromatographic separation. Therefore, a preliminary removal of matrices might be recommended, especially when handling large-size environmental samples with high matrix elements content.

It can be seen that the sample ashing and evaporation are the most time-consuming steps in the sample pre-treatment. Shortening the ashing time with increased temperature and performing co-precipitation instead of evaporation can be recommended to reduce the time for sample pre-treatment.

Chemical purification for ^{90}Sr

The protocol used for the chemical purification of radiostrontium depends on the measurement techniques

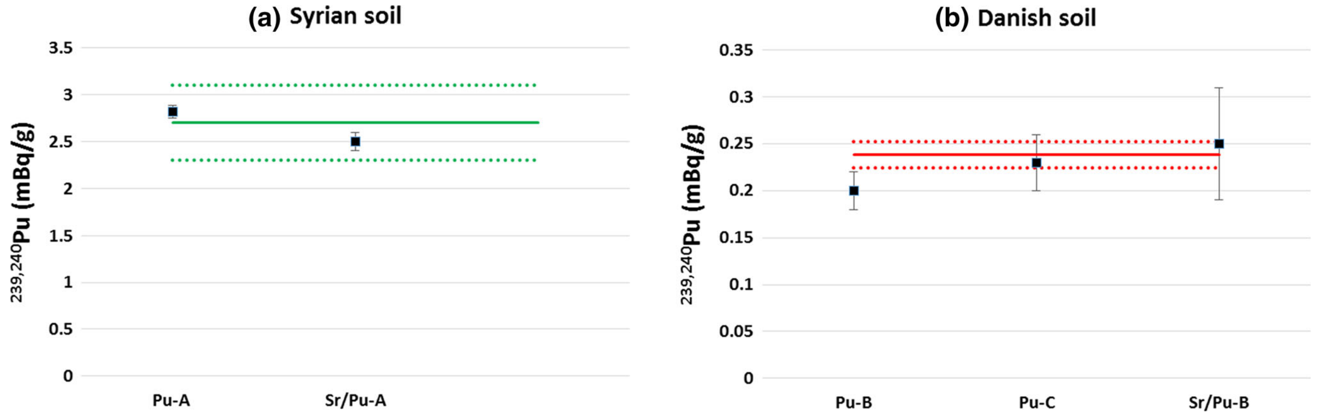


Fig. 9 The activity concentrations of ^{239,240}Pu in Syrian soil (SS) and Danish soil (DS) obtained by different methods used in this work. The *solid* and *dotted lines* represent the reference values and confidence limits of the reference values for ^{239,240}Pu. The *error bars* of the results represent the expanded uncertainty with a coverage factor, $k = 1$. (Color figure online)

selected. ^{90}Sr is a pure beta emitter, which can be measured either directly by beta counting/liquid scintillation counting (LSC), or indirectly through its daughter ^{90}Y. The yttrium chemistry is very much different from strontium, so the isolation of first strontium and then the ingrown ^{90}Y provides an excellent way of assuring results that are free from interferences. Additionally, ^{90}Y has much higher beta energy, providing higher measurement efficiencies on beta counters and LSC. Therefore, in this work, all methods used for ^{90}Sr were based on the indirect measurement of ^{90}Y.

For methods involving LSC (e.g., Sr-B and Sr/Pu-A methods), no second ^{90}Sr-^{90}Y separation was needed since Cerenkov counting was performed for ^{90}Y, discriminating the contribution of the relatively low-energy beta particles from ^{90}Sr, and there were no ^{89}Sr present [1]. Whereas for the beta counting(e.g. Sr-A and Sr/Pu-B methods), the chemical purification procedure generally includes two stages: first purification of ^{90}Sr from matrix element including Y and interfering radionuclides, secondly purification of ^{90}Y from Sr and other interferences. For the latter stage, two chemical yields need to be determined in order to obtain the actual activity concentration of ^{90}Sr: one is the chemical yield of Sr during the chemical purification of Sr, and the other is the chemical yield of Y during the separation between Sr and Y before beta counting.

One way of determining the yield of Sr is to add stable strontium as a chemical yield tracer (Sr/Pu-A and Sr-B methods) and determine it gravimetrically (Sr/Pu-A method) or by ICP-OES (Sr-B method). Another way is to use ^{85}Sr as a radioactive yield tracer, measured by gamma spectrometry to determine the chemical yield of Sr (Sr-A and Sr/Pu-B methods). The chemical yield of Y could be determined through measuring stable Y concentration before and after the ^{90}Sr-^{90}Y separation either by EDTA titration (Sr/Pu-B method), ICP-OES (Sr-A method) or by gravimetric methods.

It was noted that handling the gravimetric determination was not as straightforward as the ICP-OES technique which was directly performed in 0.05 M HNO_3. As can be seen in Table 2, that large variation was obtained for Sr chemical yield in the Sr/Pu-A method, which might be a consequence of low repeatability when using the gravimetric method. To reduce the uncertainty in the Sr or Y chemical yield monitoring, ICP-OES, AAS or ion chromatography, as well as use of ^{85}Sr tracer, are possible alternatives [24, 25].

For chemical purification of ^{90}Sr, a variety of approaches have been reported [24, 26–30]. In this work, a series of precipitation/co-precipitation was employed in the Sr-A method to purify Sr. This method is very robust and reliable, which has been applied to many different sample matrices [31–33]. However, due to the relatively low selectivity, repeated precipitation/co-precipitation is needed which makes the protocol very tedious. Sr-A method also involves the use of aggressive chemical-fuming nitric acid, which imposes potential safety concerns.

Since the early 1990s, the application of Sr resin has become more and more popular in radiochemistry analysis for ^{90}Sr due to its high selectivity and its rapid separation process [28, 34]. In this work, Sr resin was used in all methods, except for the Sr-A method. However, it has been reported that the performance of Sr resin is sensitive to the matrix content of the samples [35, 36], for example, for a 3 g Sr resin loaded with a sample of high Ca content, approximately 0.3 g, the chemical yield of Sr dropped to 40% [36]. The relatively low Sr chemical yield (40–60%) obtained in the two combined methods (Sr/Pu-A and Sr/Pu-B) might be related to the competitive adsorption of matrix elements on Sr resin, since no preliminary removal of matrix elements have been carried out in the sample pretreatment.

As the secular equilibrium between ^{90}Sr and ^{90}Y is reached after about 14 days, the samples need to stand for some time prior to the separation to allow for the ingrowth of ^{90}Y. In the different methods used in this work, the samples were allowed to stand 16 h to 3 weeks before the ^{90}Sr-^{90}Y separation can be performed to get a purified fraction of ^{90}Y.

For ^{90}Sr-^{90}Y separation, a conventional method via series of precipitations/co-precipitations was employed in Sr-A and Sr/Pu-B methods. Sr-resin has been reported as a method of choice to isolate ^{90}Y, as was done in the Sr-B method, in order to decrease the total combined uncertainty of the method [37]. Ln-resin has also been tested, however, it was found to give a lower chemical yield of Y (approx. 50–60%) [38]. The recent work by Amano and Maxwell using DGA Resin indicated higher affinity for Y^{3+} [39, 40].

Source preparation and measurement of ^{90}Y

In this work, the detection of ^{90}Y was performed by either low background beta counting (Sr-A and Sr/Pu-B methods) or LSC (Sr-B, Sr/Pu-A methods). For the beta counting, ^{90}Y source was prepared as $Y_2(C_2O_4)_3$ precipitate. No source preparation is needed for Cerenkov counting for ^{90}Y by LSC. However, the Cerenkov counting approach for determining ^{90}Y requires that there is no ^{89}Sr (or any other high energy beta emitter) present in the sample.

The benefits from low background beta counting are the low detection limits. However, the sample throughput using beta counting in this work is limited due to the long-term measurement for achieving sufficiently low detection limit. On the other hand, LSC is more straightforward and does not require much sample preparation. Modern LSC instruments (e.g., Quantulus) could also provide very low detection limits. As Cherenkov counting discriminates against low energy radiation, LOD could be decreased even further. LSC in combination with Cherenkov counting could be recommended especially for emergency situations to prompt the analytical speed, and moreover, previous work show that the ^{90}Y ingrowth time could be shorten to less than one day [37, 38]. However, it should be noted that there are published methods successfully measured ^{90}Y by gas flow proportional counting for emergency situations. LCS with cocktail instead of Cerenkov could also be used with higher efficiency than Cerenkov counting. [41] Furthermore, it is worth noting that by switching to LSC counting or gas flow proportional counting instead of Cherenkov counting results in a method more sensitive to other beta emitting radionuclides, seeing as it does not discriminate against low energy beta.

Chemical purification for ^{239,240}Pu

For the chemical purification of Pu, a single chromatographic purification step was used in both Pu-A and Pu-C methods, with the use of AG 1 × 4 and TEVA resin, respectively. UTEVA/TRU tandem column was employed for Pu-B and Sr/Pu-B methods. A combination of ion exchange chromatography (Dowex) and tandem extraction chromatography (UTEVA/TRU) was performed in Sr/Pu-A method.

In the chromatographic purification process, TEVA indicates higher absorption capacity for Pu(IV) and superior decontamination of U compared to traditional anion exchange resin. However, experiences have shown that TEVA is sometimes more sensitive to matrix content in the sample solution compared to anion exchange resin [42, 43]. In cases of handling complex matrices or high matrix content samples, a guard column (normally anion exchange column) could be used to avoid deteriorated performance of the TEVA column. The iron-rich matrix in Syrian soil created more $Fe(OH)_3$ precipitates which in turn makes it difficult for a single TEVA column to handle. Therefore, a larger anion exchange column was used in Pu-A method for the chemical purification of Pu.

The UTEVA resin has high absorption of tetra- and hexavalent radionuclides e.g., U(VI) and Th(IV), while TRU has high absorption for trivalent radionuclides, e.g., Am(III) and Pu(III). The application of a tandem UTEVA/TRU column could thus separate Pu from the major interfering radionuclides (U, Th).

Potential reason for the relatively low Pu chemical yields in Sr/Pu-A, Pu-B and Sr/Pu-B methods could be the high competitive adsorption of matrix elements on the column separation, or the oxidization of Pu(III) to Pu(IV) in 3 mol/l HNO_3 solution, which became retained on UTEVA. The failure of Sr/Pu-B method in the Pu analysis for the Syrian soil might be related to the challenges imposed by the complex matrix composition of the sample as mentioned before.

It was observed in the experiment that due to the high content of matrix elements in the sample loading solutions (especially for the Syrian soil), the column separation was very slow. Therefore, an automated sequential injection (SI) system (Pu-A method) and a vacuum box system (Sr/Pu-B method) were used with a controllable flow rate for the column separation. It is advantageous to improve the sample throughput when vacuum box and automated chromatographic separation are employed, since in many cases, the column separation for Pu can be extremely prolonged due to the blockage of column by inseparable particulate matter contained in the sample solution. An additional advantage of applying a fully automated SI chromatographic separation is to reduce the labour intensity and human errors in the operation.

Source preparation and detection of ^{239,240}Pu

Among the five analytical methods used for Pu detection, ICP-MS measurement was used in Pu-A and Pu-C methods, while traditional alpha spectrometry was used in the other methods. In the methods that employed alpha spectrometry, fluoride co-precipitation was used for source preparation [23]. For ICP-MS, the Pu eluate was reconstituted to dilute HNO_3 (typically 0.5 mol/l) prior to measurement. In Table 2 it can be seen that the turnover times are remarkably reduced by replacing alpha spectrometry with ICP-MS measurement. Besides the relatively fast measurement by ICP-MS, another advantage of using ICP-MS is to be able to distinguish between ^{239}Pu and ^{240}Pu, and thereby the isotopic ratio ^{240}Pu/^{239}Pu can be obtained for investigating e.g. source terms. However, ICP-MS is very sensitive to the impurity of Pu eluate, especially the content of U, as tailing from ^{238}U as well as ^{238}U^{1}H interfere with the detection of ^{239}Pu. In Pu-A method, the results indicated that decontamination of uranium was not sufficient by using a single anion exchange column separation. To correct for the interferences caused by uranium in the Pu sample, an additional calibration was performed to subtract the contribution of ^{238}U^{1}H^{+} and tailing of ^{238}U to ^{239}Pu signal in the data evaluation.

Conclusions

Most methods used in this work successfully determined the activity of ^{239,240}Pu and ^{90}Sr in the relevant samples. The analytical turnover time varied from 1 to 13 days for ^{239,240}Pu and from 1 to 32 days for ^{90}Sr. The most rapid methods (Pu-C and Sr-B) are suitable for time sensitive emergency situations, given that the detection limit of the methods are acceptable. Preliminary removal of matrix elements in the sample pre-treatment is useful to facilitate following chemical purification and to improve the chemical yields. Therefore precipitation/co-precipitation instead of direct evaporation for sample pre-concentration is recommended, especially when processing a large sized environmental sample with complex matrix composition.

For ^{239,240}Pu determination, it is apparent that ICP-MS technique provides advantages of shortening the measurement time and reducing the LOD. Determination of ^{90}Sr through its daughter ^{90}Y requires sufficient ingrowth time for ^{90}Y. Gas flow proportional counting has a lower LOD except for Quantalus ultra low level LSC and can measure a batch of samples simultaneously. However, in this work, LSC measurement for ^{90}Sr works more effectively compared to beta counting. Rapid techniques including sequential injection and vacuum-box-assisted chromatographic separation were applied in this work, which are advantageous when aiming to improve the analytical efficiency.

This work highlights the importance of knowing the limitations of a method, as scenario dependent parameters will put different kinds of demands on e.g. sample throughput, turnover time, measurement uncertainty, and detection limit. These parameters are crosslinked and also affected by each other, for example, longer measurement time would improve the uncertainty and detection limit, but prolong the turnover time and thus reduce the sample throughput. It is always important to bear this in mind when set the criteria for selecting the fit-for-purpose analytical method in different situations. For emergency preparedness, the analytical turnover time would be the most important parameter as long as the method LOD is below the dose concern limit. While for routine environmental monitoring, low detection limit and uncertainty might be needed.

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