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Evaluation of different methods for measuring 89Sr and 90Sr: Measurement uncertainty for the different methods as a function of the activity ratio
Applied Radiation and Isotopes, 140: 87-95
http://dx.doi.org/10.1016/j.apradiso.2018.06.016

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Evaluation of different methods for measuring $^{89}$Sr and $^{90}$Sr: Measurement uncertainty for the different methods as a function of the activity ratio

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HIGHLIGHTS

- Compares three measurement methods with regards to combined measurement uncertainty.
- Methods were tested on spiked water samples with $^{89}$Sr/$^{90}$Sr ratios between 0.3-170.
- Suggests independent measurement of $^{89}$Sr and $^{90}$Sr to get reliable results for ratios > 3.
- Suggests that a few representative samples should be measured with regards to $^{90}$Sr.

ARTICLE INFO

Keywords:
Measurement uncertainty
$^{90}$Sr
$^{89}$Sr
Deconvolution
Spectrum subtraction
Emergency preparedness

ABSTRACT

In case of a radiological emergency situation involving e.g. fission of uranium or plutonium, analysis of radioactive strontium will be of importance. The primary radionuclides of interest are $^{90}$Sr, its progeny $^{90}$Y and $^{89}$Sr. A few days following an event, $^{89}$Sr will be the predominant radioisotope of strontium. Most methods found in the literature are valid and applicable when measuring $^{90}$Sr, but when samples contain both $^{89}$Sr/$^{90}$Sr interference problematics arise. How these interferences are dealt with will have an effect on the uncertainty of the $^{90}$Sr determination.

This work aims at evaluating three measurement approaches, all mentioned in the literature, with respect to the measurement uncertainty when determining $^{90}$Sr in an emergency preparedness situation and to propose a suitable measurement strategy.

1. Introduction

Decision makers will, in case of a radiological emergency (e.g. a nuclear reactor accident or a nuclear weapons detonation) need reliable measurement results as a base for their choice of action in order to mitigate short- and long term consequences. One of the most important measurement tools to consider in a radiological emergency is the long-lived $^{90}$Sr. Its high priority is mainly due to three specific features; its chemical similarity to calcium, its relatively long half-life ($t_{1/2} = 28.8$ y) and the radiotoxicity through its daughter nuclide, $^{90}$Y. Works presenting rapid and robust determination methods have been thoroughly covered in the literature (Rondahl et al., 2017; Herranz et al., 2017; Maxwell et al., 2017; Jiang et al., 2017; Sáez-Muños et al., 2018; Habibi et al., 2016; Holmgren et al., 2016, 2014; Maxwell et al., 2013; Grahek et al., 2012, Groska et al., 2012; Herranz et al., 2011; Vajda and Kim, 2010; Maxwell et al., 2010; Maxwell and Culligan, 2009; Tovedal et al., 2009a, 2009b; Tovedal et al., 2008; Chobola et al., 2006; Ramebäck et al., 1994). However, methods using inductively coupled plasma mass spectrometry (ICP-MS) has not been considered in this work. The literature presents a possible approach to determine $^{90}$Sr (Takagai et al., 2014; Feuerstein et al., 2008; Taylor et al., 2007) but due to its short half-life ICP-MS is not a suitable alternative for determining $^{89}$Sr.

The most common approach, following the close to mandatory chemical separation, is to perform measurements using a liquid scintillation counter (LSC). An alternative to LSC is proportional counting (Habibi et al., 2016).

There are a number of ways to determine $^{90}$Sr and $^{89}$Sr using liquid scintillation counting. One method is spectrum deconvolution, i.e. to mathematically fit two or more component spectra to an experimentally obtained composite spectrum. This approach has been investigated in the literature as a feasible determination method for emergency response. By using deconvolution it has been shown that it is possible to determine $^{89}$Sr and $^{90}$Sr from a single activity measurement by LSC (Kabai et al., 2017; Kanisch, 2016; Kabai et al., 2011; Remetti and
S.H. Rondahl, H. Ramebäck

Applied Radiation and Isotopes 140 (2018) 87–95

A similar method is spectrum subtraction. Where one can use set measurement windows to discriminate the $^{89}\text{Sr}$ signal from the $^{90}\text{Sr}$ signal in a LSC spectrum. Or, makes use of the fact that $^{89}\text{Sr}$ has a high $E_{\text{max}}(\beta)$ and thus determining the $^{89}\text{Sr}$ activity via an initial Cherenkov measurement. The latter has been used in this work. Spectrum subtraction is a well-established method for determining $^{89}\text{Sr}$ and $^{90}\text{Sr}$ (Tayeb et al., 2016; IAEA/AQ/27, 2013; Salonen, 1978; Kim et al., 2009; Heiligset, 2000).

The third method relies on independent measurements of $^{89}\text{Sr}$ and $^{90}\text{Sr}$, using Cherenkov counting, which is achieved by a second chemical separation in order to isolate the in-grown $^{90}\text{Y}$. This can be done by strontium or yttrium chemistry (Horwitz et al., 1992; Tovedal et al., 2009a; Holmgren et al., 2014).

The literature published within this field has one primary objective: to ensure that decision making processes are not limited by sample throughput, regardless of the sample matrix. The range of analytical methods available for strontium analysis is vast. The method of choice is dependent on action limits, sample matrices, and how the method deal with both chemical as well as radioactive interferences, and of course on the experience of the laboratory. However, the aspect of combined measurement uncertainty and its impact on the reliability of the analysis has taken a back seat, not all authors take into consideration how the method of choice effects the combined measurement uncertainty of, in particular, $^{89}\text{Sr}$.

By theoretical calculations and empirical tests, we aim to show how the combined measurement uncertainty is affected by evaluating the most commonly published methods for determining $^{90}\text{Sr}$ in the presence of $^{89}\text{Sr}$. The evaluations were done with respect to the combined measurement uncertainty on water samples, spiked with $^{89}\text{Sr}$ and $^{90}\text{Sr}$ at different ratios, thereby bypassing any complications stemming from sample preparation (e.g. quench) as well as any other chemical or radiological interferences (Tovedal et al., 2009a; Holmgren et al., 2014). However, this does not mean that these factors can be disregarded when working on real samples. In order to perform correct $^{89}\text{Sr}$ and $^{90}\text{Sr}$ measurements it is paramount that the method of choice can handle interferences as well as complications stemming from sample preparation.

This work aims to contribute to an increased awareness regarding the combined measurement uncertainty, associated with the methods mentioned, in order to assure that an appropriate measurement strategy is used in an emergency situation.

2. Theory

2.1. Initial chemical separation

All methods in this work require an initial chemical separation of strontium from possible interferences as well as $^{90}\text{Y}$ (time of separation equals $t_0$ for $^{90}\text{Y}$). How the different methods differ from each other can be see in Fig. 1.

2.2. Method A: Second chemical separation

This method represents independent measurement of both $^{89}\text{Sr}$ and $^{90}\text{Sr}$. After the first separation $^{89}\text{Sr}$ can be quantified according to:

$$ A_{Y^{89}} = \frac{R_{\text{Sr89,\nu}} - R_{\text{Sr89,\nu B}}}{\Psi_{\text{Cheren,Sr89}}} $$  (1)

Where $R_{\text{Sr89,\nu}}$ is the net count rate (cps) of the $^{89}\text{Sr}$ measurement, $R_{\text{Sr89,\nu B}}$ is the net background count rate (cps) for the $^{89}\text{Sr}$ measurement, $\Psi_{\text{Cheren,Sr89}}$ is the chemical yield of the strontium separation, $\Psi_{\text{Cheren,Sr89}}$ is the measurement efficiency for $^{89}\text{Sr}$ using Cherenkov counting (cps/Bq). If there is no $^{90}\text{Sr}$ present in the sample the determination of $^{90}\text{Sr}$ can be performed, either during ingrowth of $^{90}\text{Y}$ using Cherenkov counting, directly using LSC counting or by other means, without need for further precautions.

However, if $^{89}\text{Sr}$ is present further steps are needed in order to determine $^{90}\text{Sr}$. Apart from spectrum deconvolution or spectrum subtraction (described in the sections below) the most common approach in the literature to date is another chemical separation (SRW01, 2003; Horwitz et al., 1992; Holmgren et al., 2014). The chemical separation can be performed by isolation of $^{90}\text{Y}$ by yttrium separation chemistry, e.g. DGA or Ln-resin (Maxwell et al., 2017; Tovedal et al., 2009a; McAlister and Horwitz, 2007), or by rinsing out the $^{90}\text{Y}$ that has grown into the $^{90}\text{Sr}$ solution by strontium separation chemistry, and collecting the rinse fraction. The latter method has been shown to give a 100% yield of yttrium, so there is no need for a second yield determination (EiChrom, 2003; Holmgren et al., 2014). In order to calculate the activity concentration of $^{90}\text{Sr}$ the following equations were used:

$$ A_{Y^{90}} = \frac{R_{\nu 90,\nu} - R_{\nu 90,\nu B}}{\Psi_{\nu 90}} $$  (2)

Where the parameters are the same as in Eq. (1) but for $^{90}\text{Y}$ instead of $^{89}\text{Sr}$. By calculating the activity of $^{90}\text{Y}$ at time $t_0$, i.e. the time allowed for ingrowth of $^{90}\text{Y}$ from $t_0$ (time of separation), one can determine the activity of $^{90}\text{Sr}$ according to:

$$ A_{S^{90}} = \frac{A_{Y^{90}}}{\left(1 - e^{-\lambda_{90}(t_{11})}\right)} \Psi_{S^{90}} $$  (3)

Where $\lambda_{90Y}$ is the decay constant of $^{90}\text{Y}$.

2.3. Method B: Spectrum subtraction

The calculation approach for spectrum subtraction is, in accordance with IAEA/AQ/27 (2013), expressed for the $^{89}\text{Sr}$ and $^{90}\text{Sr}$ activities at the reference time $t$ using the following equations:

$$ A_{S^{89}} = \frac{R_{\text{LSC,1,2,Che},\nu 89} - R_{\text{Cheren,1},\nu 90}}{\Psi_{\text{Che},\nu 89}} \cdot \Psi_{\text{LSC,1},\nu 89} \cdot e^{-\lambda_{89}(t_{11})} $$  (4)

$$ A_{S^{90}} = \frac{R_{\text{Cheren,1}(\nu Y_{\nu 90} + \Psi_{\text{Cheren,1,Yr},\nu 90} \cdot f_1 \cdot \Psi_{\text{LSC,1,Yr},\nu 89} \cdot f_2) - R_{\text{LSC,1,2,Che},\nu 90} \cdot \Psi_{\text{Che},\nu 90} \cdot \Psi_{\text{LSC,1,Yr},\nu 89} \cdot f_3}}{\Psi_{\text{Che},\nu 89} \cdot \Psi_{\text{LSC,1,Yr},\nu 90} \cdot \Psi_{\text{Che},\nu 90} \cdot \Psi_{\text{LSC,1,Yr},\nu 89} \cdot f_3} \cdot e^{-\lambda_{89}(t_{11})} $$  (5)

Where $R_{\text{Cheren,1,Yr}}$ is the count rate at $t_1$ for the Cherenkov measurement, and $R_{\text{LSC,1,2,Che}}$ the count rate at $t_2$ for the liquid scintillation counting measurement. As for the other two methods $\Psi$ represents measurement efficiencies. In this case the efficiencies are for $^{89}\text{Sr}$, $^{90}\text{Sr}$ and $^{90}\text{Y}$ when performing Cherenkov- or liquid scintillation counting, respectively (in cps/Bq). Concerning $f_1$, $f_2$, $f_3$ and $f_{subtr}$ they are defined as:

$$ f_1 = 1 - e^{-\lambda_{90}(t_{11})} $$  (7)

$$ f_2 = 1 - e^{-\lambda_{90}(t_{21})} $$  (8)

$$ f_3 = e^{-\lambda_{89}(t_{21})} $$  (9)

Where $\Psi_{\text{subtr}}$ is an auxiliary parameter used to simplify the presentation and calculation of $A_{S^{89}}$ and $A_{S^{90}}$.

$f_1$ and $f_2$ are correction factors for ingrowth of $^{90}\text{Y}$ between the time of separation ($t_0$) and the Cherenkov measurement ($t_1$) or the LSC measurement ($t_2$), and $f_3$ is the correction factor for $^{89}\text{Sr}$ decay between the Cherenkov measurement and the LSC measurement. The decay constants ($s^{-1}$) for $^{90}\text{Y}$ and $^{89}\text{Sr}$ are represented by $\lambda_{90Y}$ and $\lambda_{89}$. 

S.J. Heikel, H. Ramebäck

Applied Radiation and Isotopes 140 (2018) 87–95
2.4. Method C: Spectrum deconvolution

In this work deconvolution was done by least square fitting of pure background subtracted component LSC spectra of $^{90}$Sr and $^{89}$Sr to the sample composite spectra, i.e.:

$$ ESS = \sum A_i^2 = \sum (M_{ei} - M_i)^2 $$

(10)

Where $A_i$ is the residual, $M_i$ is the count rate (cps) in channel $i$ for the sample spectra, and $M_{ei}$ (the model) is described as:

$$ M_{ei} = \Psi_{LSC,Sr90,i} \cdot A_{90} + \Psi_{LSC,Sr89,i} \cdot A_{89} $$

(11)

Where $\Psi_{LSC,Sr90,i}$ and $\Psi_{LSC,Sr89,i}$ are the counting efficiencies (cps/Bq) of $^{90}$Sr and $^{89}$Sr, respectively, in channel $i$ (for LSC measurements the efficiencies over the entire energy window are equal to 1 in this case), $A_{90}$ and $A_{89}$ are the fitted activities (Bq) for $^{90}$Sr and $^{89}$Sr. The resulting activities for $^{89}$Sr and $^{90}$Sr were corrected with regards to chemical yield and decay.

The uncertainty of the fit was evaluated by performing a $\chi^2$-test according to Press et al. (2007), i.e. individually adjusting the component variables until the ESS had doubled its value compared to the minimum. For each component variable the value when the ESS is twice its minimum represents the variance, and the standard uncertainty is then simply the square root of the variance.

3. Methods and materials

3.1. Reagents and standards

The reagents used for the chemical separations were all of p.a. grade (Merck, Darmstadt, Germany).

Radioactive standards used for spiking and reference spectra were $^{90}$Sr, with $^{90}$Y in equilibrium, (SIZ44, Amersham International, UK) and $^{89}$Sr (SMYA72, Eckert & Ziegler Analytics, Atlanta, GA, USA). The radiochemical separation was performed using Sr and Ln-resin in 2 ml pre-packed columns, with a particle size of 50–100 µm (TrisKem International, Bruz, France). For LSC measurements Optiphase HiSafe 3 (PerkinElmer, Boston, MA, USA) was used. Stable Sr (1 000 µg/ml), for yield determination using ICP-OES, and Ho (10 000 µg/ml), as internal standard, were supplied by Teknolab Sorbent (Kungsbacka, Sweden).

3.2. Instrumentation

LSC and Cherenkov measurements were performed on a low background system, Wallac Quantalus 1220 (Perkin Elmer, Boston, MA, USA). The yield determination for the separations were performed using ICP-OES (iCap 7400, Thermo Scientific, Bremen, Germany).

3.3. Calibrations

Six (6) separate calibrations were made in order to determine the different measurement efficiencies of $^{90}$Sr, $^{90}$Y and $^{89}$Sr for Cherenkov counting and LSC, see Table 1.

The efficiencies for $^{90}$Sr and $^{90}$Y were determined after chemical separation.

3.4. Experimental

One round of experiments, for one method, consisted of seven spiked water samples ($^{90}$Sr/$^{89}$Sr activity ratio of 170, 100, 30, 10, 3, 1 and 0.3) and a blank sample. Each method was run three times with
each round having different added activities, but still in the ratios mentioned above. Experimental round 1 had variable 89Sr activities, and a set 90Y activity (approximately 9 Bq). Round 2 and 3 had set 89Sr activities (approx. 17 and 60 Bq respectively) and variable 90Sr activities. The added activities are listed with the measured ditto in the Result-section. In total 72 samples were prepared and measured. The total volume of the samples was 10 ml in an 8 M HNO3 matrix, stable strontium (100 μg) was added as stable yield tracer. An aliquot of 0.1 ml was taken out of the sample before chemical separation for yield determination.

All samples were chemically separated, initially, in order to remove 90Y. To facilitate the chemical separations vacuum boxes (VacMaster system, Biotage, Sweden) were used. The separation procedure consisted of loading the sample onto a pre-conditioned (5 ml 8 M HNO3) Sr-resin cartridge using a plastic column (25 ml) and then rinsing the sample beaker (2 × 2.5 ml 8 M HNO3). Following the sample loading the resin was rinsed using two 5 ml 8 M HNO3 aliquots. The strontium fraction was then eluted into plastic scintillation vials (18 ml) using 4 ml 0.05 M HNO3. This was done to assure equal treatment of all samples and still allowing an addition of 12 ml scintillation cocktail for LSC measurement. An aliquot of 0.04 ml was taken out of the sample after the chemical separation for yield determination.

A second chemical separation was performed in Method A in order to separate 90Y for the measurement of 89Sr. 4 ml of concentrated HNO3 was added to the eluate after the Cherenkov measurement of 90Sr in order to adjust the molarity of the sample prior the chemical separation using Sr-resin. After allowing for 16 h of ingrowth of 90Y the samples were taken to a second round of chemical separation. The samples were loaded onto a pre-conditioned (5 ml 8 M HNO3) Sr-resin cartridge using a plastic column. The sample container was rinsed with 2 × 2.5 ml 8 M HNO3. The rinse from the loading (total of 13 ml) was collected in a scintillation vial and subsequently measured for 90Y.

Unless stated otherwise the Cherenkov measurement times were 2 × 10 min for 89Sr, 4 h for 90Y, and 6 × 10 min for the LSC measurements.

Yield determination was performed by diluting the sample aliquots to 10 ml with added internal standard (Ho 1000 μg) and 2% HNO3.

3.5. Combined measurement uncertainty

The combined measurement uncertainties for all methods were calculated in accordance with the Guide to the Expression of Uncertainty in Measurement (GUM), ISO, 1995, using the software GUM Workbench (GUM Workbench, 2010). The combined measurement uncertainties presented in this work represent an estimation of all uncertainty components associated with the analysis method. The uncertainties throughout this paper are presented with a coverage factor $k = 2$, representing an approximate confidence level of about 95%, unless otherwise stated.

The combined measurement uncertainty for Method A was calculated using GUM Workbench and the equations associated with calculating the activity from the Cherenkov measurements. The same approach was applied for Method B, but using Eqs. (4)–(9) as the model equations. For Method C the activity and the associated uncertainty for each measurand was obtained by the χ²-method, which was subsequently corrected using the chemical yield. All results were corrected for decay to a set reference date.

In order to determine whether or not a method gives reliable results, with uncertainties that are fit-for-purpose, it will need to limit the combined uncertainty to 25% ($k = 2$). A minimum acceptable relative bias (MARB) of approximately 25% is what the IAEA usually allow for 90Sr determination in their proficiency tests (IAEA/AQ/3, 2009).

Based on the works by Currie (1968) and Lochamy (1976), Tovedal et al. (2008) show that samples at detection limit will have a relative combined uncertainty of about 30% ($k = 1$). Therefore, all results presented with a relative combined uncertainty of 60% ($k = 2$) or more will be judged as below detection limit.

Results with uncertainties between 25% and 60% may under certain circumstances be considered to be fit-for-purpose, and that its method can be applicable to some extent. However, the methods that result in relatively high uncertainties in this work will almost certainly give higher uncertainties for real samples, as they present other sources of uncertainty, such as measurements with high statistical uncertainty, matrix effects and interferences.

4. Results and discussion

As expected Method B and C both delivered results more rapidly than Method A, seeing as the latter requires 90Y ingrowth. However, contrary to what has been stated by many authors, one does not need to await radioactive equilibrium, which would take about two weeks, the second separation can be performed much earlier. Of course, the detection limit of 90Sr will be lower for longer ingrowth times for 90Y as it scales with the inverse of the fractional ingrowth of 90Y (the higher fractional ingrowth the lower the detection limit). After a radiological incident higher detection limits compared to environmental monitoring programs might still be fit-for-purpose, and therefore one can significantly reduce the ingrowth time of 90Y resulting in a more rapid method. In this work, the time used for ingrowth of 90Y was limited to 16 h, yielding a total analysis time of 23 h for the analysis of one sample and 44 h for six samples. For Method B and C the total analysis time came in at 5 h and 5.3 h respectively for one sample, 10 h and 12 h respectively for six samples. The increase in total analysis time is due to the time needed for the additional sample measurements, i.e. five more 90Y measurements for Method A and five 89Sr/90Sr measurements for Method B and C, respectively. Resulting in a relative increase of the total analysis time, when measuring one versus six samples, which is approximately the same for Method A–C.

These time frames are valid under the assumption that the separation of the six samples occur at the same time, that yield determination is performed during the ingrowth of 90Y and that the Cherenkov/LSC measurements are performed subsequently on one instrument. However, according to the work of Tovedal et al. (2009b) it will not be possible to measure either 89Sr or 90Sr with any certainty within the first few days of an incident involving fission of plutonium or uranium. This is due to the fact that short lived strontium and yttrium isotopes, e.g. 91Sr, 91Y and 92Y, will dominate the measurements. The recommended waiting time for, those radionuclides to decay to a manageable level, is 4–5 days in order to measure 89Sr.

The chemical yields ($Y_S$) of the three methods were around 70–90%, the differences were between the experimental rounds rather than between methods.

4.1. Determined 89Sr activity

All three methods performed well. The measured 89Sr activities were in agreement with added activities, see Table 2. This was no surprise as two of the methods (A and B) consist of separate 89Sr measurements and for the third one, Method C, 89Sr is not as influenced by the 90Sr content as vice-versa (as 90Sr has a higher β-energy than
4.2. Determined 90Sr activity using Method A: A second chemical separation

The results for the 90Sr determination using Method A are presented in Table 3. The results are in agreement with the added 90Sr activity for all samples. The performance of this method was proven earlier by Tovedal et al. (2009a) and by Holmgren et al. (2014).

The resulting relative uncertainties for 90Sr determination by the chemical separation method are between 11–20% depending on the activity level of the sample. The main contributor to the combined measurement uncertainty, excluding counting statistics for low activity samples, is the yield determination which contributes to 80–90% of the total variance. For measurements in need of lower uncertainties or lower detection limits it is recommended to extend the time for ingrowth of 90Y to approximately 64 h instead of the 16 h used in this work. During the first 24 h 90Y grows into the sample at a rate of approximately 1% per hour. By extending the allowed time for ingrowth to 64 h the detection limit, calculated according to Currie (1967), will be 30% lower than for 16 h.

Method A provides results that are fit-for-purpose and above detection limit, according to the previous definition, for 90Sr determination at the entire range of 89Sr/90Sr-ratios. This is due to the fact that 90Sr is measured independently, i.e. without the presence of 89Sr since a second chemical separation is done in order to isolate and measure 90Y.

4.3. Determined 90Sr activity using Method B: Spectrum subtraction

In this work, this method gave generally good results for activity ratios between 0.3–3.

The relative combined uncertainties for the method as a function of the activity ratio can be seen in Fig. 3. Method B is not fit-for purpose when determining 90Sr for 89Sr/90Sr-ratios above about 3, as they present relative combined uncertainties larger than 25% throughout all experimental rounds. Moreover, the method gives results below detection limit (rel. combined uncertainties > 60%, k = 2) for ratios 30–170. However, even though the precision in some cases is poor, the accuracy for round 1 is at least fair, see Table 4.

Similar results were presented for the IAEA rapid method, which was validated on spiked water and milk samples (IAEA/AQ/27 2013). For spiked water samples, the relative combined uncertainty was about 25% (k = 2) already at an activity ratio of about 2.5 and reached 100% (k = 2) for an activity ratio of about 40. Moreover, for spiked milk samples two standard deviations larger than 25% were obtained for replicate samples (n = 5) for 90Sr already at an activity ratio of about 2. For higher activity ratios (about 35) that method yielded relative biases of up to about 40%.

As seen in Fig. 3 the relative combined uncertainties are in general higher for round 1 than round 2 and 3. In order to explain it is necessary to look at the uncertainty budgets, see Fig. 4.

At activity ratios higher than about 3 the yield will no longer be the

Table 2

The added and measured activity for 89Sr, all samples, with their combined measurement uncertainty (k = 2). The number following the 89Sr/90Sr ratio in parenthesis gives which of the three experimental rounds the samples are from.

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<td>903 ± 19</td>
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<td>30 (1)</td>
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<td>10 (1)</td>
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<td>0.3 (1)</td>
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<td>170 (2)</td>
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<td>58.6 ± 1.2</td>
<td>46.8 ± 5.2</td>
<td>60.1 ± 1.2</td>
<td>53.6 ± 11</td>
</tr>
<tr>
<td>100 (3)</td>
<td>61.2 ± 1.2</td>
<td>57.2 ± 7.2</td>
<td>58.3 ± 1.2</td>
<td>51.7 ± 5.1</td>
<td>59.6 ± 1.2</td>
<td>57.9 ± 12</td>
</tr>
<tr>
<td>30 (3)</td>
<td>61.1 ± 1.2</td>
<td>53.5 ± 6.7</td>
<td>58.6 ± 1.2</td>
<td>49.7 ± 5.4</td>
<td>59.4 ± 1.2</td>
<td>57.2 ± 11</td>
</tr>
<tr>
<td>10 (3)</td>
<td>60.9 ± 1.2</td>
<td>57.8 ± 7.3</td>
<td>58.3 ± 1.2</td>
<td>48.4 ± 5.2</td>
<td>59.3 ± 1.2</td>
<td>57.8 ± 12</td>
</tr>
<tr>
<td>3 (3)</td>
<td>60.1 ± 1.2</td>
<td>66.5 ± 8.5</td>
<td>58.7 ± 1.2</td>
<td>54.3 ± 7.1</td>
<td>60.2 ± 1.2</td>
<td>55 ± 12</td>
</tr>
<tr>
<td>1 (3)</td>
<td>59.6 ± 1.2</td>
<td>58.0 ± 6.7</td>
<td>58.9 ± 1.2</td>
<td>55.9 ± 7.3</td>
<td>58.7 ± 1.2</td>
<td>55 ± 12</td>
</tr>
<tr>
<td>0.3 (3)</td>
<td>59.4 ± 1.2</td>
<td>67.0 ± 7.8</td>
<td>58.9 ± 1.2</td>
<td>67.3 ± 9.4</td>
<td>59.3 ± 1.2</td>
<td>59 ± 15</td>
</tr>
</tbody>
</table>
The relative combined uncertainties in measured $^{90}$Sr activities for the subtraction method as a function of activity ratio. The solid line represent samples with a fixed $^{89}$Sr activity (round 1), the dashed line is for samples from round 2 and the dotted line represents samples from round 3.

Table 3

<table>
<thead>
<tr>
<th>$^{89}$Sr/$^{90}$Sr ratio</th>
<th>Experimental round 1</th>
<th>Experimental round 2</th>
<th>Experimental round 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>170</td>
<td>9.08 ± 0.27</td>
<td>7.50 ± 0.83</td>
<td>0.120 ± 0.012</td>
</tr>
<tr>
<td>100</td>
<td>9.08 ± 0.27</td>
<td>8.31 ± 0.87</td>
<td>0.210 ± 0.013</td>
</tr>
<tr>
<td>10</td>
<td>8.93 ± 0.27</td>
<td>7.85 ± 0.91</td>
<td>0.650 ± 0.020</td>
</tr>
<tr>
<td>3</td>
<td>9.12 ± 0.27</td>
<td>7.59 ± 0.87</td>
<td>2.01 ± 0.05</td>
</tr>
<tr>
<td>1</td>
<td>9.09 ± 0.27</td>
<td>10.16 ± 1.2</td>
<td>6.68 ± 0.16</td>
</tr>
<tr>
<td>0.3</td>
<td>9.10 ± 0.27</td>
<td>10.36 ± 1.3</td>
<td>19.06 ± 0.19</td>
</tr>
</tbody>
</table>

Fig. 3. The relative combined uncertainties in measured $^{90}$Sr activities for the subtraction method as a function of activity ratio. The solid line represent samples with a fixed $^{89}$Sr activity (round 1), the dashed line is for samples from round 2 and the dotted line represents samples from round 3.

Method C could probably be deemed as fit-for-purpose when determining $^{90}$Sr for $^{89}$Sr/$^{90}$Sr-activity ratios 0.3–1. However, for experimental round 1 all ratios show a relative combined uncertainty larger than 25% and for round 2 the only sample which an uncertainty below 25% was for the 0.3 ratio. Furthermore, the method provides results below detection limit for activity ratios 10–170.

The relative combined uncertainties for round 1 are in general lower than for round 2 and 3 for activity ratios > 1. However, at the activity ratio 0.3 the relative combined uncertainty for round 1 is larger than for round 2 and 3, this is due to the relative low $^{90}$Sr activity in that sample (Fig. 5). For activity ratios 0.3 to 3 the chemical yield is the main contributor to the combined uncertainty.

The uncertainty in counting statistics is included in the model fit. This is apparent when comparing different counting times, see Fig. 6. The result is an uncertainty of 40–77% ($k = 1$) at an activity ratio of 3. When looking at lower activity ratios, e.g. 0.3, the uncertainty (7–9%) is not significantly reduced even for 200 min measurements, i.e. the major contributor to the uncertainty in those results is not from counting statistics. For higher activity ratios, i.e. $^{89}$Sr/$^{90}$Sr = 10–170, the uncertainty of the model fit is greater than 100%. This is because at those ratios a large value (the combined spectra) is subtracted by a similarly large value (the $^{89}$Sr contribution). Kabai et al. (2017), although not presenting any measurement results, stated that deconvolution of LSC spectra would be fit-for-purpose up to an activity ratio of 10, after which the method would become uncertain. This is similar to what was observed in this work.

4.5. Suggested measurement approach for a nuclear emergency situation

The results show that Method B and C are associated with large uncertainties for $^{90}$Sr at activity ratios greater than 3, which is hardly fit-for-purpose in an emergency situation. In case of a radiological emergency resulting in an activity ratio of 170 (instant fission) it will take approximately 320 days until the ratio has decreased to below 3, the respective time for an initial ratio of 10 (nuclear power plant accident) is 95 days. Given the fact that one cannot in advance know the $^{89}$Sr/$^{90}$Sr-activity ratio it is recommended to use the method which consistently delivers fit-for-purpose results.

The suggested approach is therefore that, in order to optimize the

Table 4

<table>
<thead>
<tr>
<th>$^{89}$Sr/$^{90}$Sr ratio</th>
<th>Experimental round 1</th>
<th>Experimental round 2</th>
<th>Experimental round 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>170</td>
<td>9.14 ± 0.25</td>
<td>9 ± 90</td>
<td>0.100 ± 0.008</td>
</tr>
<tr>
<td>100</td>
<td>9.18 ± 0.24</td>
<td>9 ± 47</td>
<td>0.170 ± 0.006</td>
</tr>
<tr>
<td>10</td>
<td>8.15 ± 0.24</td>
<td>4 ± 10</td>
<td>0.543 ± 0.022</td>
</tr>
<tr>
<td>3</td>
<td>9.14 ± 0.26</td>
<td>8.2 ± 4.3</td>
<td>1.678 ± 0.034</td>
</tr>
<tr>
<td>1</td>
<td>9.18 ± 0.24</td>
<td>5.3 ± 2.7</td>
<td>5.59 ± 0.11</td>
</tr>
<tr>
<td>0.3</td>
<td>9.15 ± 0.24</td>
<td>7.9 ± 1.1</td>
<td>19.43 ± 0.39</td>
</tr>
<tr>
<td></td>
<td>9.12 ± 0.24</td>
<td>8.51 ± 0.94</td>
<td>66.5 ± 1.3</td>
</tr>
</tbody>
</table>
use of resources and time, the bulk of samples in an emergency are measured only with regards to $^{89}$Sr using Cherenkov counting, about 4 days after an incident (Tovedal et al. 2009a). In order to determine the long time effect it is recommended that a few representative samples are analyzed with regards to $^{90}$Sr using the chemical separation method, in which $^{89}$Sr and $^{90}$Sr are measured independently and therefore will give reliable results.

5. Conclusions

This work shows the importance of performing independent measurement of $^{90}$Sr in order to obtain reliable results for both $^{89}$Sr and $^{90}$Sr, especially for activity ratios > 3, in case of a radiological incident involving fission of plutonium and uranium. By testing three different methods a conclusion was drawn as to the suitability of simultaneous determination, in this work represented by spectrum subtraction (Method B) and spectrum deconvolution (Method C). It was shown that simultaneous determination is associated with large uncertainties in particular for $^{90}$Sr activities, and especially for high activity ratios. Therefore, it is arguably more time and cost efficient to deliver reliable results.

Table 5
The added and the measured $^{90}$Sr activities, with their combined uncertainties, for all three rounds of experiments using Method C: Spectrum deconvolution.

<table>
<thead>
<tr>
<th>$^{89}$Sr/$^{90}$Sr ratio</th>
<th>Experimental round 1</th>
<th>Experimental round 2</th>
<th>Experimental round 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>170</td>
<td>9.11 ± 0.25</td>
<td>6 ± 18</td>
<td>0.079 ± 0.002</td>
</tr>
<tr>
<td>100</td>
<td>9.09 ± 0.24</td>
<td>7 ± 14</td>
<td>0.162 ± 0.003</td>
</tr>
<tr>
<td>10</td>
<td>9.12 ± 0.24</td>
<td>7 ± 8</td>
<td>0.494 ± 0.010</td>
</tr>
<tr>
<td>3</td>
<td>9.12 ± 0.26</td>
<td>11.6 ± 6.4</td>
<td>1.528 ± 0.030</td>
</tr>
<tr>
<td>1</td>
<td>9.10 ± 0.24</td>
<td>7.4 ± 3.5</td>
<td>5.015 ± 0.10</td>
</tr>
<tr>
<td>0.3</td>
<td>9.03 ± 0.24</td>
<td>8.8 ± 2.9</td>
<td>14.68 ± 0.29</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>50.1 ± 1.0</td>
</tr>
</tbody>
</table>

Fig. 4. Uncertainty budgets for the $^{90}$Sr determination using Method B (subtraction). The top figure is for round 1 (solid lines), the bottom left figure is for round 2 (dashed lines) and the bottom right is for round 3 (dotted lines).

Fig. 5. The relative combined uncertainties obtained by the deconvolution method for the measured $^{90}$Sr activities as a function of activity ratio. The solid lines represent samples with a fixed $^{90}$Sr activity (round 1), the dashed line is for samples from round 2 and the dotted line represents samples from round 3.
results, i.e. results with combined uncertainties no greater than 25% (k = 2), than saving a day or two on a method that delivers results that are less suitable for decision making. In conclusion, a comparison of the results shows that it is preferable to perform independent determination of $^{90}$Sr in a nuclear emergency situation, i.e. measure $^{90}$Sr after a first chemical separation and thereafter $^{90}$Sr via its daughter radionuclide $^{90}$Y after a second chemical separation. However, to optimize resources, the majority of the samples could be measured only with respect to $^{90}$Sr and only a few representative samples also with respect to $^{89}$Sr using the most reliable method which comprises of a second chemical separation (Method A), since this method facilitates independent measurements of $^{89}$Sr and $^{90}$Sr. Moreover, this method gives reliable results up to activity ratios representing instant fission, i.e. about 170.

Acknowledgements

The Swedish Ministry of Defence, Project no. A404618, is gratefully acknowledged for funding this work.

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