DOI: 10.1007/s10967-008-0512-2 *Journal of Radioanalytical and Nuclear Chemistry, Vol. 276, No.2 (2008) 357–362*

Determination of ^{90}Sr in preparedness: Optimization of total analysis time for multiple samples

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(Received March 2, 2007)

In radiological emergency, rapid determination of radiostrontium will be necessary. The required quantification levels will be relatively high which offers smaller sample sizes and shorter ingrowth and counting times. In this paper a rapid method for the determination of ^{90}Sr in fresh milk in emergency preparedness is presented. The method is based on microwave digestion, chemical separation of Sr, ingrowth of ^{90}Y and Cherenkov measurements. In order to minimize the total analysis time, a mathematical model was developed. For a given number of samples the model minimizes the analysis time by optimizing the ingrowth and counting time in order to reach a detection limit fit-for-purpose.

Introduction

Radioactive strontium is produced with a high yield in the neutron induced fission of, e.g., ^{235}U and ^{239}Pu, and has been released to the environment, mainly from atmospheric nuclear explosions, nuclear waste discharges and from the Chernobyl accident.[1] The most long-lived radioactive strontium isotope is ^{90}Sr, which has a half-life of 28.8 years. Due to its similarity to calcium it will accumulate in bone.

In the case of a radiological emergency, e.g., nuclear power plant accidents, fallout from nuclear detonations or radiological attacks,[2] rapid determinations of ^{90}Sr in different sample matrices must be done. Since ^{90}Sr is a pure β^--emitter, and its daughter nuclide ^{90}Y only has one weak γ-ray at 1760.7 keV ($I_\gamma = 0.0115\%$), γ-spectrometry is not an analytical option.

^{90}Sr can be analyzed either by atom counting, i.e., detecting the isotope itself, using mass spectrometric techniques, or via the detection of the emitted β^--particle produced in the radioactive decay of ^{90}Sr or its daughter ^{90}Y. Mass spectrometric techniques that have been considered are inductively coupled plasma mass spectrometry (ICP-MS),[3–5] accelerator mass spectrometry (AMS)[3,6] and resonance ionization mass spectrometry (RIMS).[7] Of these, ICP-MS is by far the most wide-spread technique and is less complex compared to AMS and RIMS regarding both instrumentation and sample preparation. However, ICP-MS methods for the determination of ^{90}Sr will, to some extent, suffer from interferences, e.g., the isobaric interference of ^{90}Zr and abundance sensitivity, i.e., the tail from stable strontium ($m/z = 88$) present in the sample on $m/z = 90$.[5]

A common radiometric method for the determination of ^{90}Sr involves the detection of its high energy β^--emitting daughter nuclide ^{90}Y by means of Cherenkov counting after chemical separation followed by an ingrowth time.[8] If radioactive equilibrium is to be reached, the ingrowth time will be about two weeks. However, the measurement of ^{90}Y can be done before radioactive equilibrium is reached, but at the expense of the detection limit. Moreover, in the immediate response of a radiological emergency, the lowest detection limits may not be needed. In a later phase after an event, more sensitive methods can be applied. For example, the generic action level for ^{90}Sr in foodstuff after a nuclear or radiological emergency is 100 Bq/kg.[9] This offers both a considerably shorter counting and ingrowth time, as well as smaller sample amounts. It has been shown that a limited total analysis time for ^{90}Sr optimally could be shared between ingrowth of ^{90}Y and counting.[10] However, in that study the optimization was done only for a single sample.

In the present work a mathematical model that optimizes a limited analysis time in the analysis of ^{90}Sr for multiple samples is presented. The model takes into account the detection limit needed, the number of samples to be analyzed (in sequence) and the total time for a result to be delivered. Results from the model are the time to be spent on ingrowth of ^{90}Y and the measurement time for the Cherenkov counting of ^{90}Y. As an example, output from the model has in this study been applied on the determination of ^{90}Sr in 10 milk samples.

Theory

The radiometric method studied comprises the following parts: sample pre-treatment → isolation of strontium (^{90}Sr) → ingrowth of ^{90}Y → Cherenkov counting of ^{90}Y. The ingrowth of ^{90}Y follows the equation of secular equilibrium:

$$A_{\mathrm{Y}} = A_{\mathrm{Sr}}^{0}(1 - e^{-\lambda_{\mathrm{Y}} t}) \tag{1}$$

or

$$A_{\mathrm{Sr}}^{0} = A_{\mathrm{Y}} \cdot \frac{1}{(1 - e^{-\lambda_{\mathrm{Y}} t})} \tag{2}$$

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0236–5731/USD 20.00

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Springer, Dordrecht

where A^0_{Sr} is the ^{90}Sr activity at the time of separation $t=0$, A_Y the ^{90}Y activity at the time t ($A_Y=0$ at $t=0$) and λ_Y is the decay constant of ^{90}Y. The time t is defined as:

$$t = t_i + 0.5t_m \tag{3}$$

where t_i, the ingrowth time, is the time between the separation and the start time of measurement of the first sample and t_m is the measurement time for each sample. The term $0.5t_{\mathrm{m}}$ is an approximation to consider the ingrowth during the measurement of the first sample. It can be shown that for measurement times set below 20% of the half-life, the underestimation of the activity will be less than 1%. For ^{90}Y with a half-life of 64.0 hours that means measurement times of less than 12.8 hours. The highest underestimation (1%) occurs if the measurement start immediately after the separation ($t_i=0$) when the rate of ingrowth is as highest.

The relation between the ^{90}Y and ^{90}Sr activities in Eq. (2) is also valid for the relation between the detection limits (L_D). Using Eq. (2) for the detection limits and substituting t with Eq. (3) gives:

$$L_D^{\mathrm{Sr}} = L_D^{\mathrm{Y}} \cdot \frac{1}{1-e^{-\lambda_{\mathrm{Y}}(t_i+0.5t_m)}} \tag{4}$$

where the detection limit of ^{90}Y (L_D^{Y}), as defined by CURRIE[11] and further developed by LOCHAMY,[12] is:

$$L_D^{\mathrm{Y}} = \frac{k^2}{t_m} + 2k\left[\frac{R_b}{t_b}\left(1+\frac{t_b}{t_m}\right)\right]^{\frac{1}{2}} \tag{5}$$

where L_D^{Y} is expressed in cps, k is the constant 1.65 at the one-sided confidence level of 95% in the normal distribution, R_b is the background count rate in cps, t_b is the background measurement time and t_m is the sample measurement time, both expressed in seconds.

Substituting Eq. (5) into Eq. (4), at a fixed background, yields the detection limit of ^{90}Sr, L_D^{Sr}, expressed as a function of t_m and t_i. In the model the detection limit of ^{90}Sr as a function of the total analysis time, t_{tot}, and sample measurement time, t_m, for a number of samples, n is studied.

$$t_{tot} = t_i + nt_m \tag{6}$$

or

$$t_i = t_{tot} - nt_m \tag{7}$$

Combining Eqs (4), (5) and (7) gives:

$$L_D^{\mathrm{Sr}} = \left[\frac{k^2}{t_m} + 2k\left[\frac{R_b}{t_b}\left(1+\frac{t_b}{t_m}\right)\right]^{\frac{1}{2}}\right] \cdot \frac{1}{1-e^{-\lambda_{\mathrm{Y}}(t_{tot}-(n-0.5)t_m)}} \tag{8}$$

where L_D^{Sr}, expressed in cps, is the detection limit for the first measured sample.

For a known counting efficiency, Ψ, and chemical yield, U, the L_D^{Sr} can be expressed in Bq per sample:

$$L_D^{\mathrm{Sr}} = \frac{1}{\psi \cdot U}\left[\frac{k^2}{t_m} + 2k\left[\frac{R_b}{t_b}\left(1+\frac{t_b}{t_m}\right)\right]^{\frac{1}{2}}\right] \cdot \frac{1}{1-e^{-\lambda_{\mathrm{Y}}(t_{tot}-(n-0.5)t_m)}} \tag{9}$$

In this way the L_D^{Sr} will be calculated for the first measured sample which is the limiting sample because of its shortest ingrowth time.

The generic action level for ^{90}Sr in milk

After a radiological or nuclear event, the generic action level of ^{90}Sr in milk is 100 Bq/l.[9] In a situation where it is important to classify the activity in milk as less than the action level, the definition of the Less-Than-Level[12] (L_t) is useful. The mathematical expression for L_t is given by:

$$L_t = R_s + k\sigma_s \tag{10}$$

where L_t is expressed in cps, R_s is the measured net count-rate in cps, k is the constant 1.65 at the one-sided confidence level of 95% in the normal distribution and σ_s is one standard uncertainty from the counting statistics.

It can be shown that the relative standard uncertainty at the detection limit, as defined in Eq. (5), is 30%–40% (1σ). Thus Eq. (10) can be written:

$$L_t = L_D + 1.65 \cdot 0.4 L_D \tag{11}$$

$$L_t = 1.67 L_D$$

or

$$L_t \approx 2 L_D \tag{12}$$

This means that for a detection limit which is in the order of about half the action level, sample activities below the detection limit (50 Bq/l for milk in this case), will with 95% confidence be classified as less-than the action level.

Experimental

Reagents and standards

The reagents used for sample preparation were oxalic acid dehydrate, hydrogen peroxide (Perhydrol 30%) and nitric acid 65% (all p.a. grade, Merck, Darmstadt, Germany), ^{90}Sr/^{90}Y standardized solution (SIZ44, combined uncertainty 1.36%, $k=3$, Nycomed Amersham plc, Buckinghamshire, UK), strontium nitrate (99+%) and yttrium(III) oxide (99.99%, both

Aldrich Chemical Company Inc., WI, USA). Sr-resin (Eichrom, Darien IL, USA) was used for separation of strontium. The separations were performed in disposable plastic 10-ml columns (Poly-prep, Bio-Rad, Hercules, CA, USA).

Instrumentation

A microwave accelerated reaction system (MARS 5, CEM Corporation, USA) with high-pressure teflon vessels (HP 500, 100 ml, maximum 350 psi and 210 °C), were used for sample digestion. The Cherenkov counting of ^{90}Y was performed using a liquid scintillation counter, LSC (1220 Quantulus, Wallac, Finland). The strontium chemical yield was carried out using standard analytical methods on an atomic absorption spectrometer (Aanalyst 300, Perkin Elmer, USA).

Sample preparation

Ten samples of 5 ml fresh milk (fat rate 4.4%) were transferred to microwave vessels and spiked with ^{90}Sr/^{90}Y standard solution to the concentrations of about 0, 50, 100 (three samples each) and 400 Bq/l (one sample). 1 ml of stable strontium solution (5 mg/ml) and 8 ml of concentrated HNO_3 (65%) were added to each sample. Before sealing the vessels the samples were left for 10 minutes for predigestion. The vessels were placed in the microwave oven in a symmetrical pattern to ensure a uniform irradiation. The digestion process was controlled by ramping to the pressure 350 psi for 20 minutes followed by holding pressure for 30 minutes at a power of 1200 W. During the process the temperature typically rose to about 170 °C. The microwave program was evaluated for 8–10 vessels. The samples were cooled to about 50 °C and 0.5 ml of H_2O_2 were added to each vessel.

Strontium separation

Sr-resin (2 ml) were added to plastic columns and the resins were conditioned with 5 ml 8M HNO_3. The ten samples were loaded on the resins and the vessels were rinsed once with 5 ml 8M HNO_3, also added to the resins. The resins were rinsed with 5 ml 8M HNO_3, 5 ml 3M HNO_3 – 0.05M $H_2C_2O_4$ and another 5 ml 8M HNO_3.[13] The time for the completed drain of the last rinse was recorded as the start time of ^{90}Y ingrowth. Strontium and yttrium were eluted into LSC plastic vials using 15 ml 0.05M HNO_3. Stable yttrium (0.2 ml, 10 mg/ml) was added and 0.1 ml of each sample solution was collected for the determination of the strontium chemical yield.

Sample counting and calculation

The samples were left for ingrowth during 13 hours before Cherenkov counting of ^{90}Y. The counting time was 30 minutes for each sample and the sequential measurements of the 10 samples were finished within 5.5 hours. The ^{90}Sr activity (A_{Sr}^{0}) at separation time was calculated as:

$$A_{\mathrm{Sr}}^{0} = \frac{R_{\mathrm{Y}} - R_b}{\psi U (1 - e^{-\lambda_{\mathrm{Y}} t})} \qquad (13)$$

where R_{Y} is the count rate of ^{90}Y in cps, R_b is the background level in cps, Ψ is the counting efficiency, U is the chemical yield, λ_{Y} is the decay constant of ^{90}Y and t is the time between separation and the middle of measurement as explained above.

Results and discussion

Mathematical model for optimization of ^{90}Sr analysis

For a given number of samples, n, the L_D^{Sr} in Eq. (9), can be plotted as a function of measurement time, t_{m}, and total analysis time, t_{tot}. In Figs 1a and 1b the model is shown, for $n = 10$, in contour and surface view, respectively. The parameters in Table 1 were used for the calculations. The graphs show that there is an optimum balance between the time for measurement, t_m, and the time for ingrowth, t_i, in order to minimize the detection limit for different total analysis times. On the contrary, for a specified detection limit, the model shows how rapidly the analysis results can be obtained, and how the time should be divided between measurement and ingrowth time.

When measuring during the ingrowth of ^{90}Y, and not waiting for full equilibrium between ^{90}Sr and ^{90}Y, it is important to define the time between separation and measurement as precise as possible. As mentioned above, a good approximation is obtained by setting the measurement time point to the middle of the measurement time [Eq. (3)]. However, the start time of the interval, i.e., the process of separation, is not instantaneous. An estimation of the uncertainty in the separation time to ±5 minutes, implements that the ingrowth time should be greater than two hours so to not contribute to the relative uncertainty in the result of ^{90}Sr activity greater than 5%.

Table 1. Parameters used in the model

Background count-rate, R_b	0.0136 cps
Background measurement time, t_b	43200 s
Chemical yield, U	0.50
Counting efficency, Ψ	0.65

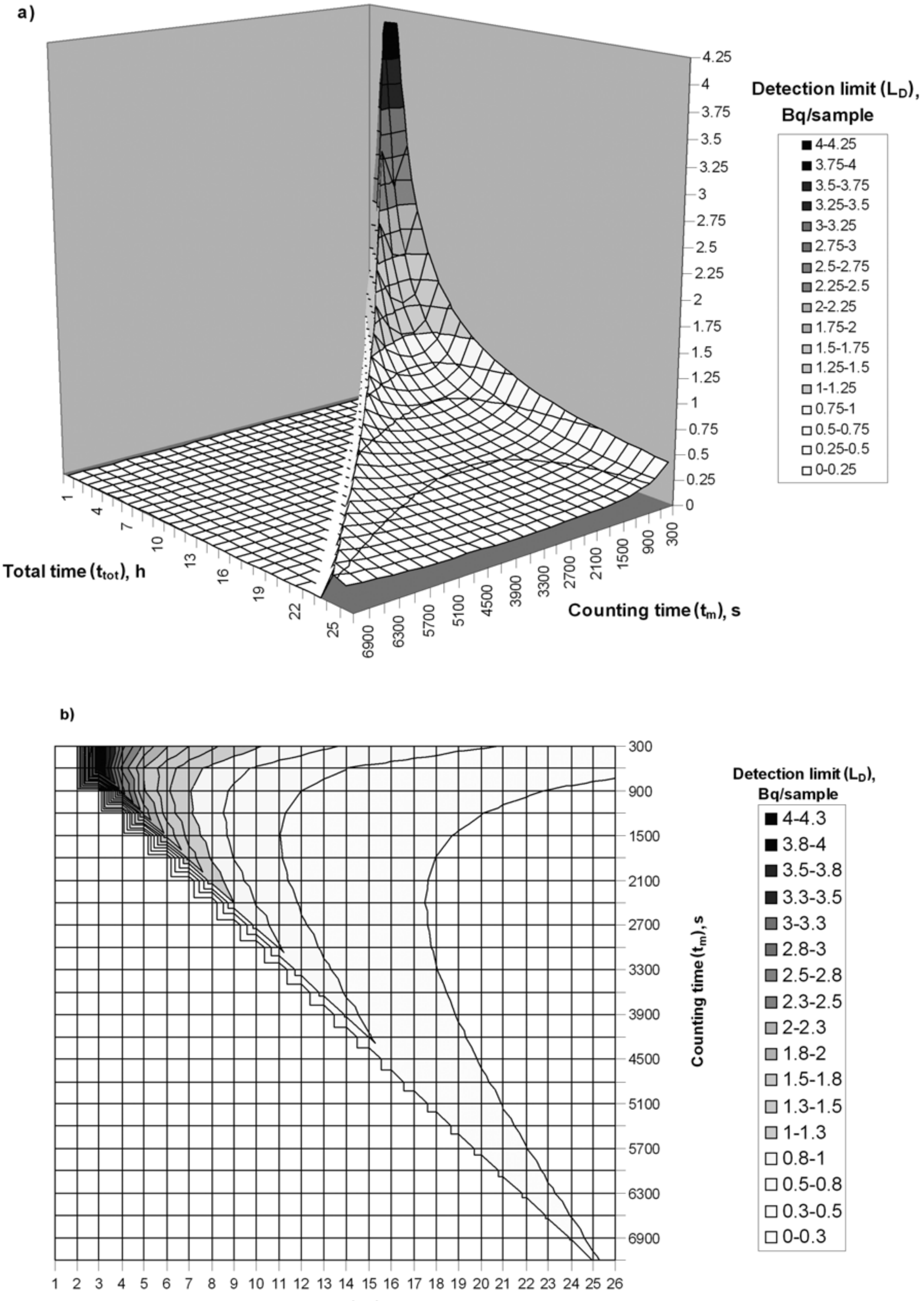

Fig. 1. The detection limit as a function of total analysis time and measurement time for 10 samples measured in sequence. The graph in Fig. 1b shows the same data as in Fig. 1a, but plotted in a surface view

Experimental application of the model

The developed model was used to optimize an analytical procedure for the determination of ^{90}Sr in milk for emergency preparedness. Microwave digestion was chosen for treatment of the milk samples prior to separation due to the relative short time required for digestion using this technique. For our microwave system, 5 ml milk proved to be a safe volume for digestion. As described above, a suitable detection limit is 50 Bq/l milk which corresponds to 0.25 Bq ^{90}Sr in each sample. According to the model, a detection limit of 0.25 Bq for a batch of 10 samples requires an ingrowth time of 13 hours and a measurement time of 30 minutes per sample. A schematic picture of the process is shown in Fig. 2. In the figure, the time spent on each individual process of the experimental procedure is shown. As can be seen from the figure, the 10 samples were processed and analyzed in less than 24 hours.

The results of the determinations are displayed in Table 2. As can be seen from the table, the measured ^{90}Sr activities are in agreement with the activity added (within the expanded uncertainties). It can also be seen, that the "less than values" for the samples containing 50 Bq/l are all below the generic action level of 100 Bq/l. The risk of misclassification of samples with activities close to the action level decreases with decreasing uncertainty of the determined activity. However, since a decreased uncertainty in the analytical results involves longer total analysis times, an adjustment between these parameters has to be made. A higher precision can be achieved by choosing a lower detection limit [Eq. (12)].

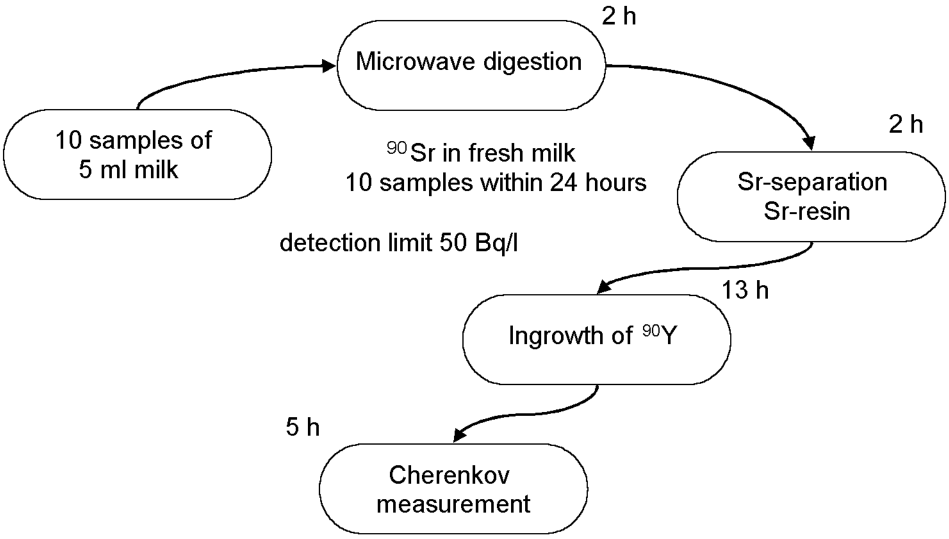

Fig. 2. Outline of the experimental analytical procedure

Table 2. Determined ^{90}Sr activities, 18 hours after separation

Added ^{90}Sr activity, Bq/l	Combined uncertainty, $k = 2$, Bq/l	Determined ^{90}Sr activity, Bq/l	Combined uncertainty, $k = 2$, Bq/l	Less than value 95% confidence, Bq/l
0		3	11	<12
0		10	13	<20
0		9	12	<19
49.7	0.5	60	23	<79
50.2	0.5	40	20	<57
50.2	0.5	56	22	<75
100	1	126	31	
100	1	125	30	
101	1	113	29	
402	4	380	56	

The chemical yield of the Sr separation used in the model was 0.50 (Table 1) which appeared to be an underestimation of the method. The average of the chemical yields obtained was 0.82±0.13 ($k=2$). This underestimation resulted in lower relative uncertainties of the determined ^{90}Sr activities than expected. The relative uncertainties were 19, 25 and 20% at the predicted detection limit level of 50 Bq/l, compared to the expected level of 30–40%. Recalculation of the model using the obtained chemical yield shows that an ingrowth time of 8 hours would have been sufficient, which provides the possibility for the first 10 results to be delivered in about 17 hours. This is an example of how the precision of the model is dependent on the input parameters R_b, ψ and U, and that a more precise prediction can be made if the analytical method is well known.

The method described here is based on separation of ^{90}Sr and ingrowth and determination of ^{90}Y. In emergency preparedness different scenarios must be considered, such as intentional contamination of, e.g., foodstuff or drinking water with ^{90}Sr as well as fallout from a reactor accident or a nuclear weapons detonation where a more complex composition of radionuclides will be present. This model is primarily intended when ^{90}Sr is the dominating radioactive Sr isotope. For the latter cases, ^{89}Sr as well as ^{91}Sr and ^{92}Sr can initially be of higher activity than ^{90}Sr. Hence, future work is to expand the model, as well as the analytical method, to be valid for these scenarios as well.

Conclusions

In this paper a mathematical model which optimizes the analysis of ^{90}Sr for multiple samples with respect to the detection limit is presented. The model gives the optimum time that has to be spent on ingrowth of ^{90}Y and measurement time for the subsequent Cherenkov counting of ^{90}Y, for multiple samples, in order to reach a required detection limit. The model was successfully tested on milk samples spiked with ^{90}Sr. For ten samples, using a single LSC and a required detection limit of 50 Bq/l milk, the result could be reported in less than 24 hours including sample preparation.

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This work was partly financed by the Swedish Radiation Protection Authority, SSI.

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