Estimation of Strontium-90 Concentrations in Pakistan Using Combination of TBP Solvent Extraction, Precipitation and Cherenkov Counting Methods

I. Ahmad[1], M. I. Anjum[2], S.U. Rehman[3], J. Ali[4*]

ORCID: 0009-0009-5839-5264, 0009-0007-8845-7345, 0000-0002-3668-8404, 0000-0001-7392-3912

[1] Larkana Institute of Nuclear Medicine & Radiotherapy (LINAR) Cancer Hospital, Larkana, Sindh, Pakistan
[2] Pakistan Institute of Nuclear Science and Technology (PINSTECH), Islamabad, Pakistan
[3] Pakistan Institute of Engineering and Applied Sciences (PIEAS), Islamabad, Pakistan
[4] Larkana Institute of Nuclear Medicine & Radiotherapy (LINAR) Hospital, Larkana, Sindh, Pakistan

ABSTRACT

^{90}Sr does not exist in nature. Its main sources in the environment are global fallout of past nuclear accidents or nuclear detonations. ^{90}Sr is radiologically significant because of its relatively long physical and biological half-lives and its chemical resemblance to calcium. In order to estimate the radioactivity level of ^{90}Sr around Pakistan Institute of Nuclear Science and Technology (PINSTECH) Islamabad, environmental samples (soil, water, vegetation, and water) and food samples (wheat, milk, poultry) were collected from the different selected sites around PINSTECH within the area of about 12.5 km in radius. All samples were pretreated using the guidelines of International Atomic Energy Agency (IAEA) Technical Reports Series No. 295. ^{90}Sr was indirectly determined through its progeny ^{90}Y in secular radioactive equilibrium. ^{90}Y was radiochemically separated using combination of Tri-n-butyl Phosphate (TBP) solvent extraction and precipitation. Finally, the activity was measured on Tri-Carb Liquid Scintillation Counter (LSC) through Cherenkov radiation. The activity concentrations of ^{90}Sr in all samples were too low to be detected by the LSC system, except for a vegetation sample from Rawal Dam where a minimum activity of 0.16 ± 0.04 Bq/kg of fresh weight was found. No considerable activity concentration of ^{90}Sr was found around PINSTECH research facilities.

1. Introduction

Radio-strontium is not found in nature. The most important radioactive form of strontium is ^{90}Sr [1]. The main source of ^{90}Sr in environment (soils, vegetations, water etc.) is nuclear fission [1], global fallout after nuclear accidents & nuclear explosions [2-6]. The hazardous effects of ^{90}Sr on human health are due to its high radioactivity and relatively long physical and biological half-lives [7]. The chemical properties of ^{90}Sr are similar to calcium so it follows the same path in food chain as calcium. Like calcium, ^{90}Sr is accumulated in bones for years posing a high risk to human health [4, 6, 8, 9]. ^{90}Sr follows various paths to penetrate the human

body e.g. direct exposure, inhalation (fine particles in air), and ingestion (food and water). Therefore, in the events of nuclear accidents, nuclear explosions, and routine monitoring of nuclear facilities, the determination of ^{90}Sr in environmental and various food samples is one of the important tasks regarding radiation protection [4, 6, 8].

^{90}Sr and ^{90}Y are pure beta emitters with maximum beta energies of 546 keV and 2280 keV respectively. ^{90}Sr has a very long half-life as compared to its progeny ^{90}Y, therefore both radionuclides are often found in secular

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equilibrium [10]. In secular equilibrium, ^{90}Sr can be determined by estimation of either ^{90}Sr or ^{90}Y. However, the environmental and food samples containing ^{90}Sr and ^{90}Y also contain ^{89}Sr which is also a pure beta emitter with max beta energy of 1463 keV. Therefore, ^{90}Sr can not be measured directly using beta counters because of the overlap of spectra of ^{89}Sr, ^{90}Sr, and ^{90}Y. Therefore, the measurement of ^{89}Sr or ^{90}Sr needs to analyze of the beta spectral distribution obtained by a special beta counting system such as LSC. In this case, ^{90}Sr is measured by estimating the activity of its progeny ^{90}Y in environmental and food samples in which, ^{90}Y is radiochemically separated from ^{90}Sr in secular equilibrium [11] and then indirectly determined through Cherenkov radiation because of its high counting efficiency in aqueous medium. Cherenkov radiation is produced when a charged particle like an electron moves with a speed greater than the speed of light in a transparent medium. This radiation ranges from the ultraviolet region to the visible part (blue), with a peak at 420 nm. [12, 13]. Every transparent medium has a threshold value of beta energy for production of Cherenkov radiation, which is 263 keV for water [10]. The procedure of estimation of high energy beta emitting radionuclides through Cherenkov counting is advantageous than conventional liquid scintillation counting because of low cost, easy sample preparation, and automatic counting mechanism of Liquid Scintillation Counter (LSC) [14]. However, less counting efficiency and more color quenching are the drawbacks of Cherenkov counting.

Several radiochemical separation techniques have been proposed for determination of ^{90}Sr in environmental and food samples. Some of these radiochemical separation techniques are extraction chromatography [15, 16], solvent extraction [17, 18], colloid formation [19], and ion exchange methods [20]. In the present study, a combined approach of Solvent Extraction through Tri-n-Butyl Phosphate (TBP), precipitation and measurement through Cherenkov radiation on Tricarb Liquid Scintillation Counter (3170TR/SL) has been used. The LSC used is capable of detecting extremely low levels of beta and alpha radioactivity. The purpose of the study was to estimate the activity concentration of ^{90}Sr around PINSTECH Research Reactor in Islamabad within 12.5 km radius.

2. Materials and Methods

2.1 Sample Collection and Sample Preparation

Environmental samples (soil, water and vegetation) were collected from different selected sites around PINSTECH within the area of 12.5 km radius. Food samples (wheat, milk, and poultry) were also collected from neighboring areas of PINSTECH. A rain water sample was also collected from the interior of PINSTECH area. The details of the samples are tabulated in Table 1.

The collection of the samples and their pre-treatment were carried out according to guidelines of International Atomic Energy Agency (IAEA, 1989) Technical Reports Series No. 295. Before analysis, soil, vegetation, wheat, milk, and poultry samples were dried at 105-110ºC, ashed at 450-500ºC and homogenized in order to get constant reference weight which is used for calculating activity concentrations in the units of Bq/kg of dry weight. The water samples were reduced in volume on hotplate from 10 L to 150 mL after the addition of 10 mL nitric acid (69-70.5%) in each sample as shown in Table 1 [21].

2.2 ^{90}Sr Analysis in the Samples

^{90}Sr analysis was done using a radiochemical separation procedure. The chemicals and reagents that were used in the study are of analytical grade. The radiochemical procedure used in this research article was divided into three main parts: (1) steps before solvent extraction (2) solvent extraction through Tri-n-Butyl Phosphate (TBP) (3) precipitation, filtration, and counting a vial through LSC.

1. For ashed samples, 100 mL of de-ionized water, 1 mL of Sr-carrier (10mg/mL) and 5 g of Na_2CO_3 were added to 10 g of ash the sample in 250 mL beaker and heated for 30 minutes on a hotplate along with magnetic stirring. For water samples, 75 mL of nitric acid and 1 mL of Sr (10mg/mL) and Y carriers (10mg/mL) were added to 50 mL of water sample.

2. The ashed samples were then centrifuged and washed with 0.1 M solution of Na_2CO_3. The residue of each sample was leached out through 75 mL 14.4M HNO_3 in the presence of different carrier solutions like Y carrier (10mg/mL), La-Carrier (10mg/mL) and Ba-carrier (10mg/mL) in nitrate form for 2 hours heating on hotplate. The solution was then cooled and filtered. While for water samples, volume was reduced to 50 mL through evaporation using hotplate.

3. The solution obtained for ashed samples or water samples was then poured into a separating funnel. Solvent extraction of ^{90}Y was carried out using 30 mL of equilibrated Tri-n-Butyl Phosphate (TBP) shacked for 10 minutes with the sample. The solution was then allowed to settle the two layers. The aqueous layer (lower) was separated and the first separation time was noted. The process was repeated three times in order to get maximum extraction. The organic phase containing ^{90}Y was then stripped in two steps each with 30 mL of water.

^{90}Y was then precipitated as Yttrium-oxalate by addition of 80 mL of 2% solution of oxalic acid and adjusting the pH to between 4 and 5. The precipitate was then filtered using vacuum pump filtration assembly.

The filter paper (Whatman-41,125 mm diameter) containing Y-oxalate was then washed two times with 10 mL of ethanol (99.7-100) %. The precipitate stayed on the filter paper. The filter paper was dried in oven to constant weight. The weight of Y-oxalate was found by diminishing the weight of blank filter paper from weight of filter paper containing Y-oxalate.

The filter paper was then dissolved in 15 mL of 2M HCl contained in a 20 mL polythene vial.

The vial was then counted on the LSC.

The LSC system has the ability to read 408 standard 20 mL vials. These vials are placed in the cassettes each with a capacity for 12 vials. Each cassette has its own number and flag. The order of the cassette number and associated flag plays a vital role in counting process. A cassette along with four standard vials containing tritium, ^{14}C, background and an empty vial having a flag tagged as SNC is used for self normalized calibration.

The whole radiochemical separation process for ashed and water samples are depicted in Fig.1 and Fig.2 respectively.

The gravimetric factor (GF) was calculated with Eq.1 [22].

$$GF = \frac{Y_2}{Y_2(C_2O_4)_3.9H_2O} = \frac{177.81}{603.01} = 0.294 \qquad (1)$$

Chemical recovery (η) was calculated using the Eq.2 [22].

$$\eta = \frac{GF \times (\text{Weight of Yttrium Oxalate precipetate})}{(\text{Weight of Yttrium Carrier added})} \qquad (2)$$

The minimum detectable activity (MDA) of the Liquid Scintillation Counter Tri-Carb 3170 model for ^{90}Sr was calculated using the Eq.3 [22].

$$MDA \left(\frac{Bq}{Kg \text{ or } L}\right) = \frac{2.71 + 4.66\sqrt{BG}}{t \times \varepsilon \times \eta \times \text{Mass or Volume}} \qquad (3)$$

where BG is the total background counts, t is the counting time in seconds, ε is the efficiency of the counting system and η is the chemical recovery.

Activity concentration (AC) of each sample was calculated using the Eq.4 [22].

$$AC \left(\frac{Bq}{kg \text{ or } L}\right) = \frac{(C_S - C_{BG}) \times e^{\lambda \times \Delta t}}{60 \times \varepsilon \times \eta \times \text{Mass or Volume}} \qquad (4)$$

where C_S is the sample's counts per minute and C_{BG} is the background counts per minute is the decay constant of ^{90}Y, Δt is the time difference between counting time and the time of first separation of yttrium and λ is the decay constant of ^{90}Y.

The uncertainty in activity concentration (σ) was calculated with Eq. 5 [22].

$$\sigma = \frac{\left(\sqrt{\frac{C_{BG}^2}{T} + \frac{C_S^2}{T}}\right) \times e^{\lambda \times \Delta t}}{60 \times \varepsilon \times \eta \times \text{Mass or Volume}} \qquad (5)$$

In above equation, T is the counting time in minute.

3. Results and Discussion

The average percentage chemical recovery (%η) of ^{90}Sr for ashed samples was 83.44% while for water samples, average percentage chemical recovery of ^{90}Sr was 84.43%. The results of ^{90}Sr activity concentrations in soil, vegetation, wheat, water, milk and poultry samples are shown in Table 2.

It is clear from Table 3 that the activities found in all samples are too low to be detected by our measuring system (LSC) except for vegetation sample of Rawal dam where minute activity of 0.16 ± 0.04 Bq/kg of fresh weight was found. No activity was detected in the soil sample of the same site. The absence of ^{90}Sr activity concentration in the soil sample of Rawal dam may be due to uptake of ^{90}Sr by the plant roots or its high mobility downward in the soil as all soil samples were collected from the upper part (less deep) of the ground. Therefore, the presence of ^{90}Sr in deeper soil layers is possible, and deep soil sampling may be required. The activity concentrations of ^{90}Sr in soil samples from various regions around the world have been estimated [23-26] and are compared with the present study, as shown in Table 3.

It is clear from Table 3 that the activity concentrations of ^{90}Sr in the present study are below the Minimum Detectable Activity (MDA) value, which is much smaller than the ^{90}Sr concentrations reported in different regions of the world, as shown in Table 3. Therefore, the population in the interested study areas are not exposed to ^{90}Sr activity concentrations higher than those found in other regions, as mentioned in Table 3 [23-26]. The uptake of ^{90}Sr from soil to plants and other vegetation depends on different chemical and physical parameters like soil type, plant species, climate etc. The only possible reason for the presence of minute amounts of ^{90}Sr in the environment of the study area is the global fallout from past nuclear accidents and nuclear detonations. The current study indicates that there is no significant activity concentration of ^{90}Sr around PINSTECH research facilities.

Table 1. Details of environmental and food samples collected

| Location	Location Coordinates	Aerial Distance from PINSTECH	Sample Type	Fresh Wt.	Dry Wt./ Reduced Wt.	Sub Sample Dry Wt.	Ash wt.
Simli Dam	33º43′08.0″ N & 73º20′24.9″ E	9.8 km	Soil	4.2 kg	3.7 kg	250 g	237 g
			Vegetation	900 g	400 g	N/A	42 g
			Water	10 L	100 mL	N/A	N/A
Swan River	33º38′43.8″ N & 73º17′58.2″ E	4.3 km	Soil	4.2 kg	3.9 kg	372 g	365.5 g
			Vegetation	1.35 kg	300 g	N/A	41 g
			Water	10 L	100 mL	N/A	N/A
Kirpa	33º37′10.6″ N & 73º13′55.9″ E	4.5 km	Soil	1.4 kg	1.25 kg	323 g	310 g
			Vegetation	1.1 kg	250 g	N/A	30.5
			Water	10 L	100 mL	N/A	N/A
Rawal Dam	33º42′06.0″ N & 73º08′31.9″ E	12.4 km	Soil	1.1 kg	1.07 kg	376 g	365 g
			Vegetation	850 g	500 g	N/A	29.5 g
			Water	10 L	100 mL	N/A	N/A
PINSTECH	33º39′11.1″ N & 73º15′32.8″ E	0 km	Rain Water	10 L	100 mL	N/A	N/A
Near PINSTECH	33º39′11.1″ N & 73º15′32.8″ E	3 km	Wheat	2 kg	1.9 kg	N/A	42.5 g
			Milk	10 L	700 g	N/A	54.4 g
			Egg	5.3 kg (Without Shells)	1.3 kg	N/A	37 g
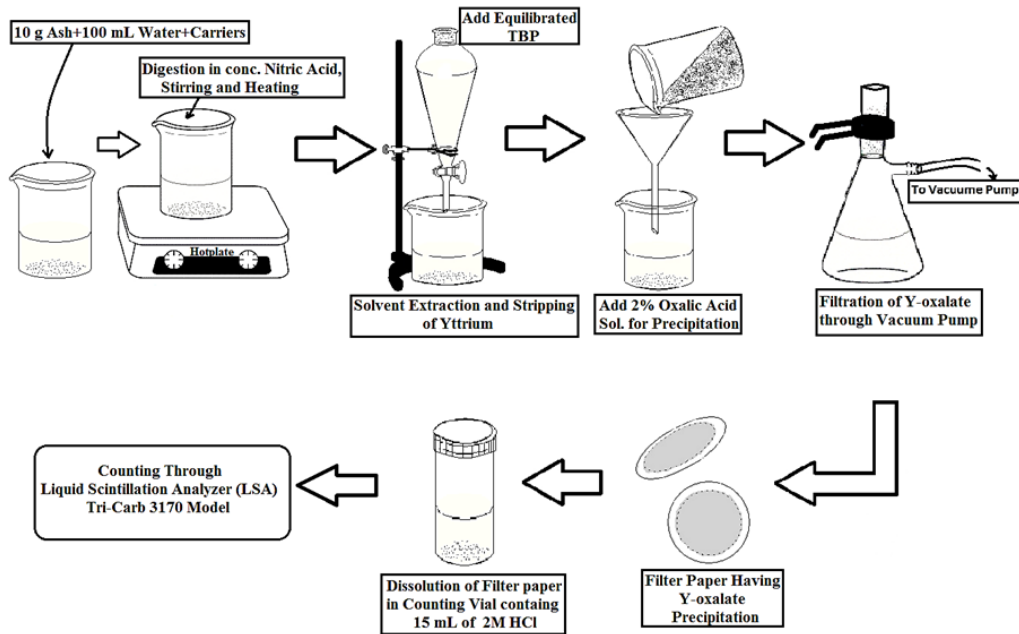
Fig. 1 *Radiochemical separation technique for ^{90}Sr analysis in ashed samples*
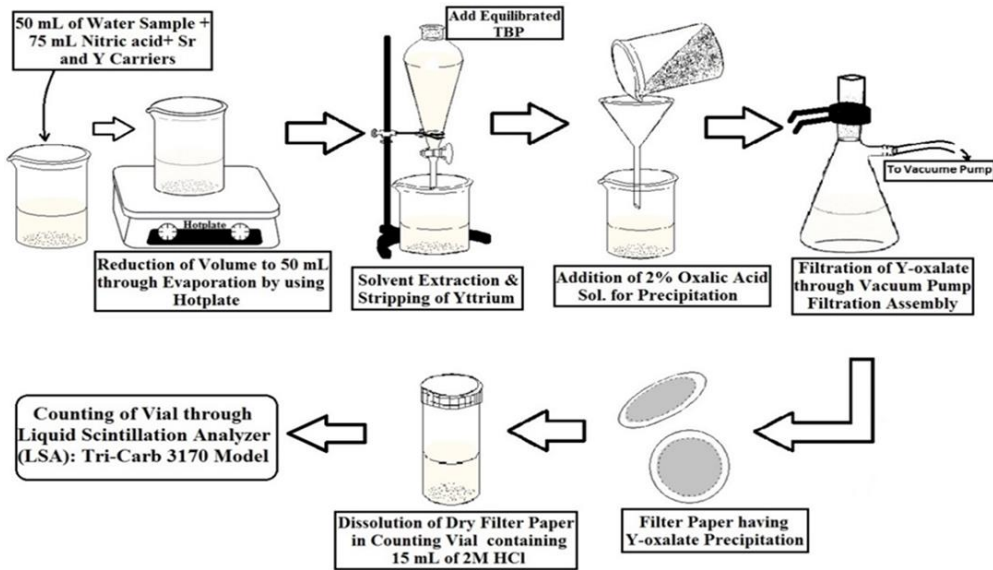
Fig. 2 *Radiochemical separation technique for ^{90}Sr analysis in water samples*

Table 2. ^{90}Sr activity concentration in all samples

Sr#	Location	Sample Type	Activity (Bq/kg of fresh weight)	Minimum Detectable Activity (MDA)
1	Simli Dam	Soil	< MDA	3.04 Bq/kg of fresh weight
2	Swan River		< MDA	
3	Kirpa		< MDA	
4	Rawal Dam		< MDA	
5	Simli Dam	Vegetation	< MDA	0.12 Bq/kg of fresh weight
6	Swan River		< MDA	
7	Kirpa		< MDA	
8	Rawal Dam		0.164 ± 0.038	
9	Near PINSTECH	Wheat	< MDA	
10	Simli Dam	Water	< MDA	0.01 Bq/L of fresh volume
11	Swan River		< MDA	
12	Kirpa		< MDA	
13	Rawal Dam		< MDA	
14	PINSTECH	Rain Water	< MDA	
15	Near PINSTECH	Milk	< MDA	0.02 Bq/L of fresh volume
16	Near PINSTECH	Poultry	< MDA	0.01 Bq/kg of fresh weight

Table 3. Comparison of ^{90}Sr activity concentrations in soil samples [23-26]

Sr#	Country/site	^{90}Sr (Bq/kg) in ashed sample
1	Northern Switzerland	30
2	Western Switzerland	10
3	Savannah River	15.91
4	Majorca	4.45
5	Spain	2.85
6	Pakistan (present study)	< MDA*

*MDA: Minimum Detectable Activity = 3.43 Bq/kg of ash

Conclusions

^{90}Sr activity concentrations in all samples were too low to be detected by the LSC, however minute activity concentration was found in the vegetation sample of Rawal dam and not in the soil sample. The reason of absence of ^{90}Sr activity in the soil sample may be due to its uptake by the plant roots or its downward movement into deeper soil layers. Therefore, deep soil sampling is required for a more detailed study. To expand this study to a larger radius from the PINSTECH research facilities, additional sampling sites should be selected.

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Authors' contributions

Muhammad Iftikhar Anjum and Shakeel Ur Rehman prepared concept and designed the study. Israr Ahmad and Muhammad Iftikhar Anjum collected data. Javaid Ali analyzed the data. Israr Ahmad and Javaid Ali wrote the paper. All authors participated in discussion of results, and reviewing and editing of the manuscript.

Conflict of interest

The authors have no conflict of interest. The authors have no conflict of interest. The authors have no competing or financial interests relevant to this article.

Availability of data and materials

The data sets used and analyzed in this study are available from the corresponding author upon reasonable request.

Ethical Approval

All authors have read, understood, and have complied as applicable with the statement on "Ethical responsibilities of Authors" as found in the Instructions for Authors.

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