DOI: 10.1007/s10967-007-7277-5 *Journal of Radioanalytical and Nuclear Chemistry, Vol. 279, No.2 (2009) 377–384*

Determination of ^{90}Sr in environment of district Swat, Pakistan

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(Received March 13, 2008)

Assessment of ^{90}Sr is of great interest owing to the fact that this artificially produced radionuclide has high radiological importance because of its high fission yield, chemical similarity to calcium and its relatively long biological and physical half-life. To assess the likely hazard to population, low level ^{90}Sr in environmental samples is determined using pre-equilibrated tri-butyl phosphate (TBP) solvent and extraction-liquid scintillation procedure. ^{90}Y is selectively extracted from nitric acid solution into TBP solvent and stripped into aqueous phase as oxalate. The activity is finally measured by low level liquid scintillation counter using Cerenkov radiation. The specific activity is found only in three vegetation samples with average value of 2.86±1.7 $Bq \cdot kg^{-1}$ of dry weight. In all other samples analyzed, the activity is below the detectable limit, i.e., 0.03 Bq. Results obtained are comparable with other areas of Pakistan. The chemical recovery of ^{90}Y varies from 75 to 90% for soil, vegetation and water. The present study provides a general background of the detectable radionuclide for the surveyed area that will be helpful in any radiological emergency.

Introduction

The presence of ^{90}Sr in environmental and biological samples is due to atmospheric weapon testing, nuclear waste discharges and nuclear accidents. ^{90}Sr decays by β^- emission into radioactive ^{90}Y which further decays by β^--emission into the stable element ^{90}Zr. This artificially produced radionuclide has high ecological importance because it accumulates in bone tissues and has a long physical and biological half-life of 28.6 and 49.3 years, respectively. For this reason, ^{90}Sr has been a principal subject for environmental monitoring and radioecological research.[1]

The potential harmfulness of the fission product ^{90}Sr is based on the chemical similarity to calcium that is an essential element incorporated into vertebrates from both food and water.[2] Studies have shown that ^{90}Sr is not leached from soil very easily, even under high rainfall. In particular, the determination of ^{90}Sr in soil, vegetation and water is of great importance since plants are a way of incorporation into the food chain.

^{90}Sr can be determined by measuring the radioactivity of either ^{90}Sr, ^{90}Y or of both: if the degree of secular equilibrium is known. Separation and measurement of ^{90}Y give information only about ^{90}Sr while separated strontium can give data about both ^{90}Sr and ^{89}Sr.[3]

A variety of methods have been described for Sr-separation such as precipitations, liquid-liquid extraction, ion-exchange and chromatography.[4] Many well known extractants such as bis(2-ethylhexyl) phosphoric acid (HDEHP), tri-n-butylphosphate (TBP), tri-n-octylphosphine oxide (TOPO), octylphenyl-N,N-di-isobutyl carbamoylphosphine oxide (CMPO), thenoyltrifluoroacetone (TTA), tri-n-octylamine (TNOA), tri-n-octylmethylammonium chloride have been used in extraction and chromatographic separation.[5]

As ^{90}Sr and ^{90}Y are pure beta-emitters, their analysis is difficult due to beta-particle energy continuum. In the present work, a Perkin Elmer Tricarb 3170TR/SL ultra low level scintillation counter has been utilized for determining ^{90}Sr from the measurement of ^{90}Y. Furthermore, a combined TBP solvent extraction Cerenkov radiation measurement has been carried out to examine the activity. However, in emergency situations Sr-Resin separation is recommended due to both its simplicity and since this procedure contrary to TBP-extraction, also allows the determination of ^{89}Sr. Sr-Resin extracts Sr at the same nitric acid concentration as TRU-Resin extracts Pu and Am. Hence, these resins can also be coupled to achieve a sequential determination of Sr, Pu and Am.[5]

The present research is an effort to prepare area wise profile of artificial radionuclide concentration level. In a country like Pakistan, where development of protection standards as well as regulatory measures on radiation protection for the general public are under process, this study will provide a useful base line data for adopting safety measures and to deal effectively with a radiation emergency. However, study area has no source of ^{90}Sr except nuclear tests or accidents. A radiological environmental monitoring survey has already been accomplished for some other areas of Pakistan.[6,7]

Experimental

Reagents

Analytical grade reagents were used. Pre-equilibrated tri-butyl phosphate (TBP) was made by shaking equal volume of nitric acid (65%) and TBP for

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ten minutes. ^{90}Sr (no-carrier-added) in 2M HCl was used as tracer (Amersham, UK). Strontium carrier (1 mg $Sr \cdot mL^{-1}$) was made from 12.08 g of $Sr(NO_3)_2$ in 500 mL of deionized water. Yttrium carrier (10 mg $Y \cdot mL^{-1}$) was made from 20.52 g of high purity $Y(NO_3)_3 \cdot 5H_2O$ in 500 mL of deionized water.

Apparatus

Perkin Elmer Tricarb Model No. 3170 TR/SL an ultra low level scintillation counter along with polyethylene vials (Packard Co.). Heraeus Christ centrifuge machine Model No. 2204 (6 rpm). Orion pH meter Model No. 420 A.

Location of study area

The Swat district, situated in the North of NWFP (Pakistan), as shown in Fig. 1a, has a total area of 5337 km^2. It has a total population of approximately 1,250,000 with a density of 236 inhabitants·km^{-2}. It is located in the northern mountain ranges of the Indo-Pak sub-continent, i.e., in the temperate zone at a latitude of 35° and a longitude of 72°. The elevation of Swat varies from 760 to 2280 m. The temperature remains between 22 °C to –2 °C, with an average rainfall of 864 mm.

Fig. 1. Location of Swat district (highlighted in yellow) within NWFP province of Pakistan

Sampling

Soil samples were collected from various locations of the Swat district of NWFP. The sampling sites are marked in Fig. 2. The sampling was carried out on an equidistant basis at longitude and latitude, each line of the grid covered the distance of 25×27 km^2, respectively. From the same sampling points, vegetation and drinking water were also collected. The sampling and pretreatment were performed by adopting procedures as given in IAEA Technical Report 295.[8] Ashing is believed to be required because organic matter may affect solvent extraction chemistry.[3] The percentage of organic carbon in soil and vegetation samples was calculated and is given in Table 1.

Procedure

The general procedure involving various steps is summarized in the chemical separation scheme of ^{90}Y as shown in Fig. 3.

Soil/grass ash (10 grams), 100 mL of water and 5 g of Na_2CO_3 were heated in the presence of 1 mL of strontium carrier to remove silicates by centrifugation. The residue was then leached with 75 mL of nitric acid (14.4M), Y^{3+}, Ba^{2+}, Cs^+ and La^{3+} carriers for almost two hours by slow evaporation. A small amount of peroxide may be added if high carbon content is present. The solution was cooled, filtered (75 mL) and processed for extraction of yttrium from strontium and other actinides.

The solution was then transferred to a separatory funnel and the aqueous phase was shaken with 30 mL of pre-equilibrated TBP for 10 minutes. The first separation time was recorded after collecting the organic layer. For maximum extraction, the same process was repeated with the aqueous layer for three times. The yttrium in the organic phase was finally stripped into 60 mL of deionized water.

To separate yttrium from other elements, NaOH was added to adjust pH to 4–5. The precipitates of $Y(OH)_3$ were separated and dissolved in 80 mL of 2% oxalic acid solution. White cloudy precipitates of $Y_2(C_2O_4)_3 \cdot 9H_2O$ were then allowed to settle for an hour, filtered, dried and weighed to obtain the percentage yield using a gravimetric factor as follows:

$$\frac{Y_2}{Y_2(C_2O_4)_3 \cdot 9H_2O} = \frac{177.81}{603.01} = 0.2943 \qquad (1)$$

The percentage recovery of Y was calculated from:

$$\left[\frac{0.2943 \times \text{Wt. of air dried Y} - \text{Oxalate}}{\text{Wt. of Y} - \text{Carrier added}}\right] \times 100 \qquad (2)$$

The activity was determined as given by the formula:[10]

$$\text{Activity (Bq/sample)} = \left[\frac{(i_{sample} - i_{bg})e^{\lambda t}}{\varepsilon \times \eta \times 60}\right] \qquad (3)$$

where i_{sample} is the activity of sample (cpm), i_{bg} is the background (cpm), t is the decay time, λ is the decay constant, ε is the efficiency, and η is the chemical yield.

The percentage recovery and decay time used in the calculations are shown in Table 2.

Radioactivity was then measured with the low level liquid scintillation counting system. A system with the efficiency of 59.51% by a standard solution S6/11/142 provided by IAEA Amarsham, England was used. Background count rates were determined by counting a vial with all other reagents except the element of interest for 200 minutes.

Results and discussion

The ^{90}Sr activity (with 2 sigma deviation) in environmental samples is shown in Table 3. Measured activity was below the lower limit of detection (LLD) (0.03 Bq for all samples) except in vegetation samples collected from Bahrain, Mingora and Saidu Sharif in which activity was determined with an average value of 2.86±1.7 Bq·kg^{-1} of dry weight. Even for this small amount, it can be assumed that it may originate from past nuclear weapon tests in the atmosphere and also the accident at the Chernobyl nuclear power plant in 1986. Absence of ^{90}Sr in surface layer of soil may also be attributed to its high mobility in the soil column.[11] FRIEDLI et al.[12] reported that ^{90}Sr migrated quite rapidly from the surface to the lower layer of soil.

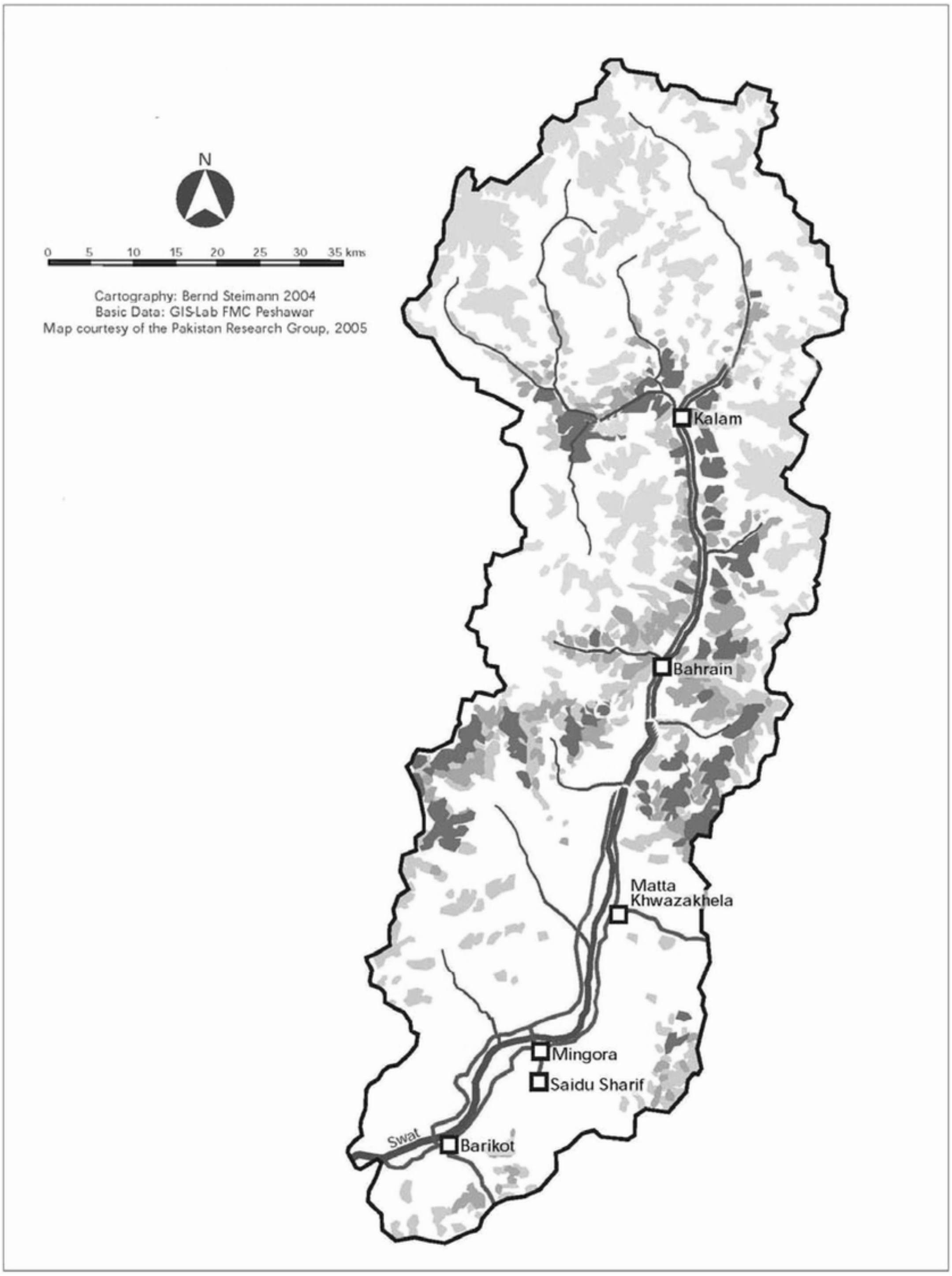

Fig. 2. Detailed map of sampling points

Table 1. Percentage of organic carbon in soil and vegetation samples

Sampling points	Dry weights, g		Ash weights, g		Organic carbon, %	
	Soil	Vegetation	Soil	Vegetation	Soil	Vegetation
Barikot	2700	500	2683	78	1	84
Kalam	2400	1100	2251	54	6	95
Bahrain	2700	500	2538	47	6	91
Mutta Khawaza Khela	2005	250	1938	39	3	84
Mingora	1900	750	1843	64	3	92
Saidu Sharif	1600	250	1552	54	3	79

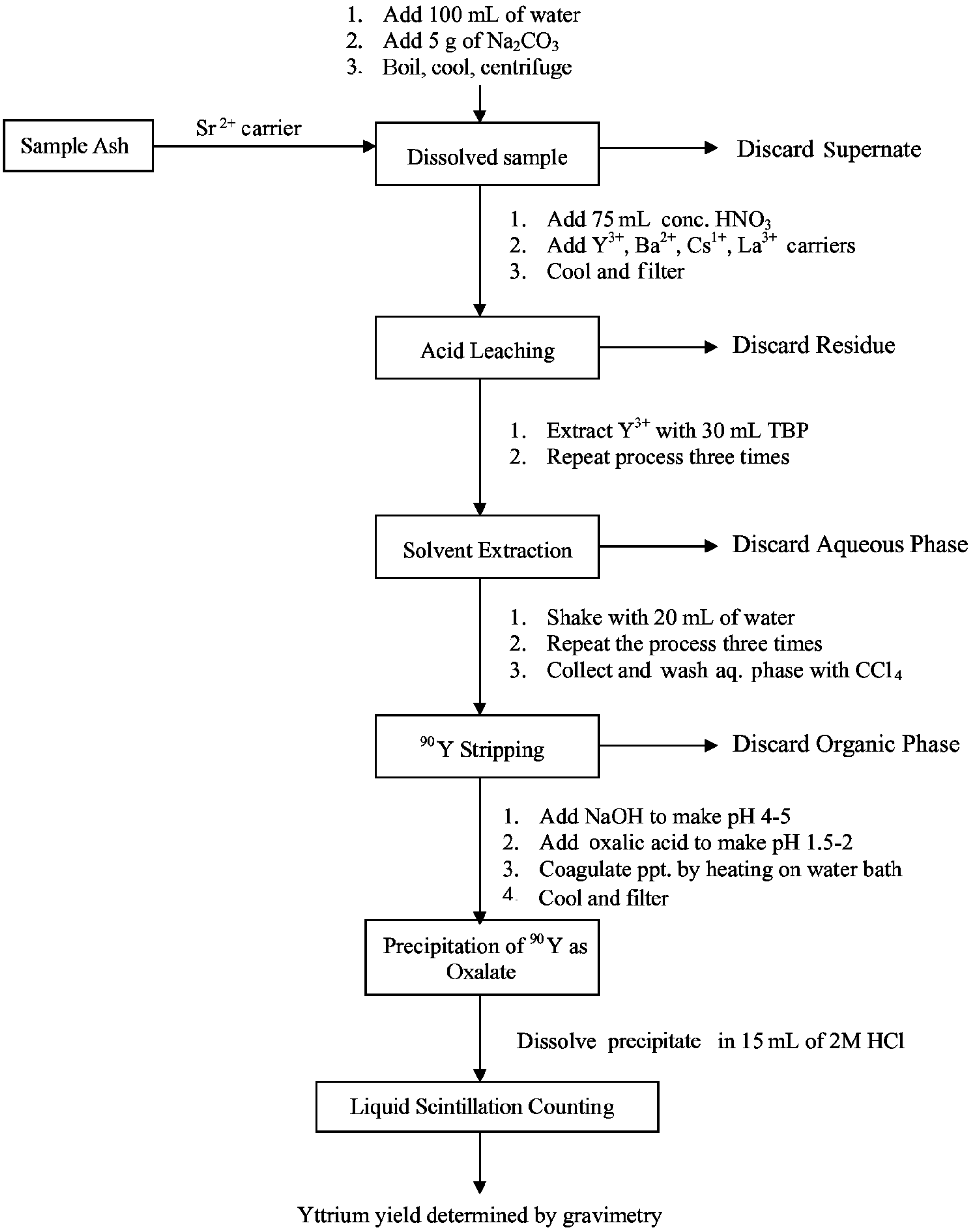

Fig. 3. Chemical separation scheme of ^{90}Y

Table 2. Yttrium recovery yields and experimental half-life of ^{90}Y determined in environmental samples

Sampling points	Yield, %			^{90}Y half-life, h		
	Soil	Vegetation	Water	Soil	Vegetation	Water
Barikot	75	90	77	32	7	28
Kalam	87	87	81	28	10	31
Bahrain	85	87	84	30	14	32
Mutta Khawaza Khela	86	84	84	34	11	35
Mingora	79	86	78	35	7	49
Saidu Sharif	88	86	76	13	10	53

Table 3. ^{90}Sr activities measured in environmental samples

Sampling point	^{90}Sr activity ± σ, Bq·kg^{-1} of dry weight		
	Soil	Vegetation	Water
Barikot	<LLD	<LLD	<LLD
Kalam	<LLD	<LLD	<LLD
Bahrain	<LLD	1.032 ± 0.09*	<LLD
Mutta Khawaza Khela	<LLD	<LLD	<LLD
Mingora	<LLD	3.05 ± 0.08*	<LLD
Saidu Sharif	<LLD	4.5 ± 0.214*	<LLD

LLD: Lower limit of detection = 0.03 Bq.
* Results are shown in Bq·kg^{-1} of dry weight.

Table 4. Comparison of ^{90}Sr concentration in soil of different areas

Country/area	^{90}Sr activity, Bq·kg^{-1} of ash
Western part of Switzerland	10
Northern part of Switzerland	30
Majorca	4.45
Handford Site	6.29
Spain	2.85
Savannah river	15.91
Present study	<LLD

LLD: Lower limit of detection = 0.03 Bq.

IAEA certified sample has also been measured as quality assessment of the method. The experimental result (13.14 Bq) for the sample is quite close to the actual value (14.423 Bq).[17]

On comparing the ^{90}Sr activity of the study area, the present value found is much smaller than values reported for the western part of Switzerland in 1976 and the southern part of Switzerland shortly after Chernobyl,[12] Majorca in 1997,[13] Hanford site in 1997,[14] Spain in 2001,[15] Savannah river site in 2004[16] as shown in Table 4. Therefore, it is expected that the population residing in Pakistan is not exposed to ^{90}Sr level larger than in other parts in the world.

While comparing ^{90}Sr activity measured in the present study, with the values obtained for other areas of Pakistan, like Bannu, Tank, Paniala[7] and Islamabad,[6] almost the same results are produced as shown in Fig. 4. Based on FRIEDLI et al.[12] observations, it is expected this disappearance of ^{90}Sr from soil surface in all areas might take place by rapid underground migration and uptake from soil to plants. However, low activity in vegetation samples of Islamabad (average 1.05±0.91 Bq·kg^{-1} of dry weight) and Swat (average 2.86±1.7 Bq·kg^{-1} of dry weight) can be explained on the basis of fact that plant roots are present in lower soil layer. Also, plant uptake of radioactive Sr varies considerably between species and is closely correlated with different physical and chemical factors of the soil like organic matter, inorganic colloids (clay) and competing elements (Ca).[17,18] In fact, the study area has no other source of fission fragments except nuclear accidents in past, so the distribution and mobility of ^{90}Sr in study area requires further investigation.

The ^{90}Sr determination method is assumed to be based on complexation of TBP with Y(III) which is believed to behave chemically in the same way as Ln(III) cations. The extraction from concentrated HNO_3 separates Y from alkali and alkaline earth cations. The advantage of Na_2CO_3 extraction is the elimination of U and Th as water-soluble complexes.[19] Separation of Y from the environmental samples using liquid-liquid extraction was chosen due to following reasons.

(1) Measurement of Cerenkov radiation because of the simplicity and advantage of inherent energy threshold, suitable for higher energy beta particles emitted from ^{90}Y $E_{maxi} = 2.3$ MeV.

(2) Yttrium separation is a relatively simple and quick chemical procedure.

(3) ^{90}Sr activity determination by ^{90}Y is possible since ^{85}Sr can interfere in direct activity determination of ^{90}Sr.[20]

(4) As most environmental samples contain large amounts of potassium, and the resin also retains small amount of potassium, TBP-extraction is usually preferred.[5]

(5) In an investigation of old fallout, there is no need to wait for 14 days as ^{90}Sr and ^{90}Y are already in equilibrium.[3]

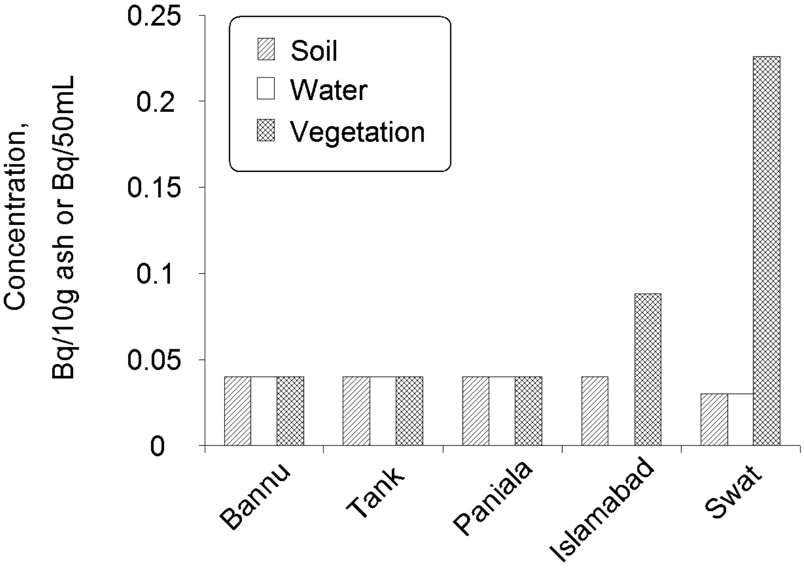

Fig. 4. Comparison of ^{90}Sr concentration in different environmental media with other areas of Pakistan

Detection limit

The lower limit of detection (LLD) was calculated as given below by taking into account the blank count rate, counting time, the counting efficiency of instrument and the chemical yield:[21]

$$\mathrm{LLD} = \left[\frac{2.71 + 4.66\sqrt{i_{bg}}}{t \times \varepsilon \times \eta}\right] \tag{4}$$

where ε is the efficiency, t is the counting time, and η is the chemical yield.

The LLD for ^{90}Sr was found to be 0.03 Bq.

Conclusions

This work provides the distribution of ^{90}Sr in environmental samples of the study area using combined TBP solvent extraction Cerenkov radiation. The activity concentration is found below the lower limit of detection (0.03 Bq) in most of the cases except in few vegetation samples with average value of 2.86±1.7 Bq·kg^{-1} of dry weight. The results are found on lower side as compare to other parts of world and almost similar within the Pakistan. However, the presence of ^{90}Sr in some vegetation samples of swat requires further investigation.

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