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Applicability of layered metal sulphide for estimation of Sr concentration in groundwater

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ABSTRACT

A layered metal sulphide reported in the literature was synthesized in the laboratory and characterized. Its applicability for selective uptake of strontium was studied. The experimental conditions for efficient uptake were standardized. The applicability of the metal sulphide for Sr removal/collection from ground water was tested. This method offers the option of lesser analysis time and removes the interferences of Ca.

Keywords: Strontium; Groundwater; Interference; Cation; Distribution coefficient; Cherenkov counting; Metal sulphide

1. Introduction

Nuclear power has played important role in meeting the power demand of India. The safe and effective management of radioactive waste is a major priority of any nuclear energy programme. ^{90}Sr is a major fission product with a relatively long half life of 28 y that is generated in the nuclear fuel cycle and has to be separated from nuclear waste before its disposal in the environment. The activity of ^{90}Sr in the effluent is monitored at various stages of the waste treatment process before it is discharged into the environment. Once the effluent has been discharged tracing its pathways becomes even more essential due to the chemical similarity of Sr to Ca, an essential nutrient for plants and an important component of the bones [1]. Thus in countries that produce nuclear energy, regular environmental surveillance is carried out near nuclear waste disposal sites and other facilities to demonstrate good compliance with regulatory limits on the concentration of ^{90}Sr in the water (5 Bq l^{-1}) and food (100 Bq kg^{-1}), set by international bodies like the World Health Organisation (WHO) [2] to ensure the protection of the general public. This surveillance requires processing and analyzing a large number of samples annually.

Strontium is an alkaline earth metal and the environmental samples of groundwater, soil, sea water etc. contain natural Sr and other alkaline earth metals like Ca and Ba in large amounts. In contrast the radioactive strontium content that typically accumulates in the above materials through the normal operations of a nuclear power plant is orders of magnitude lower. Analysis of ^{89,90}Sr radioisotopes is conventionally carried out by radiochemical separation followed by beta counting [3]. Radiochemical separation procedures are often based on selective precipitation and complex formation. The major aim of radiochemical processing is the separation of Sr isotopes from alkaline earth matrix components and alkaline earth radionuclides, for example, ^{133}Ba, ^{140}Ba, ^{226}Ra, ^{228}Ra and several other possible interferences [4].

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A series of selective precipitation reactions is traditionally used for the separation of Sr from other alkali earth metals, yttrium and other interferences, for example, lead. Because of the limited selectivity, precipitation steps have to be repeated many times. The two major isotopes of strontium ^{89}Sr and ^{90}Sr produced in nuclear fuel cycle are both pure beta emitters. ^{90}Sr is more hazardous due to its longer half life as compared to ^{89}Sr, which generally decays by the time it reaches the environment. ^{90}Sr is estimated by the ingrown ^{90}Y to estimate correctly the dose due to ^{90}Sr. This makes the conventional procedure very tedious and introduces the need to shorten the analytical procedure and estimation time.

A number of rapid estimation techniques like non-destructive Cherenkov assaying (NDCA) and techniques involving separation using crown ether based ion extraction chromatography and polymer inclusion membranes have been reported recently [4–9]. These techniques are advantageous compared to the conventional radiochemical separation scheme. NDCA is the fastest method of analysis but is suitable mostly for effluent samples. Ion chromatographic techniques using crown ether followed by Cherenkov counting [6–8] are also very convenient and involve a short chemical separation procedure.

A new layered metal sulphide KMS-1 has been reported to be very efficient in Sr uptake from waste effluents under all conditions [10]. Strontium is selectively exchanged and concentrated on a solid material by ion exchange, even in the presence of enormous amounts of Na and Ca. The layered metal sulfide, KMS-1, is made of potassium, manganese, tin and sulfur, which targets only strontium. Sulfur, a component of KMS-1, attracts heavier ions with higher charge. Because strontium is a heavier ion than calcium, and has a charge of +2 as compared to +1 for Na strontium is selectively exchanged. The layered metal sulphide used for this study was synthesized in the laboratory as per the procedure in Ref. [10] and characterized using X-ray powder diffraction. Its suitability for selective uptake of Sr in environmental samples was studied. The method was used for analysis of ^{90}Sr in ground water and compared with the conventional radiochemical method and NDCA method of analysis for ^{90}Sr.

2. Experimental method

2.1. Synthesis of KMS-1

Fig. 1. SS autoclave fabricated for reaction.

Of the three methods reported by Manos et al. 2008 for the synthesis of KMS-1, the hydrothermal method was adopted. A mixture of pure AR grade Sn (60 mmol), Mn (30 mmol), S (180 mmol), K_2CO_3 (30 mmol) and water (40 ml) was put in a Teflon container, sealed and placed inside a stainless-steel autoclave (Fig. 1). The autoclave was kept in a box furnace maintained at 200°C and left undisturbed at the constant temperature for 4 d. After 4 d the autoclave was allowed to cool to room temperature. The brown polycrystalline product was washed several times with water, acetone and ether, filtered and dried. About 11.5 g of product was obtained in the first attempt and after several attempts involving proper premixing of the solid reactants the reported yield (14.30 g, yield ≈81%) could be achieved. The structure of the metal sulphide was confirmed with X-ray powder diffraction analysis. The XRD pattern of the prepared KMS-1 sample is shown in Fig. 2. The formation of the desired compound was confirmed by comparing these data to those reported in Ref. [10]. The diagnostics peaks for the identification of KMS-1 are marked in Fig. 2. Peaks that could not be identified are attributed to an unidentified secondary phase. Intense peaks observed at 39° and 47° and 67° are attributed to a platinum sample holder used to record the XRD data.

A similar XRD pattern for a Sr saturated sample is shown in Fig. 3. From this figure, a clear low angle shift of peaks indicates the expansion of the crystal lattice due to Sr^{2+} incorporation.

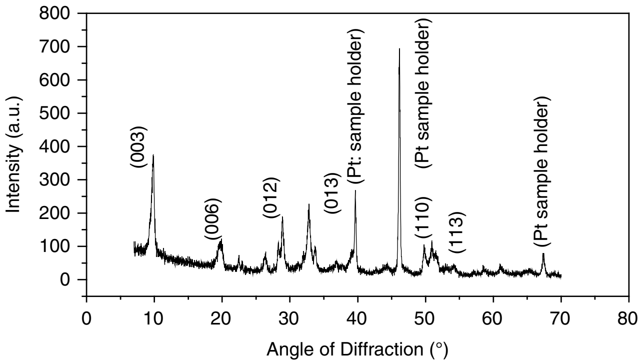

Fig. 2. X-ray diffraction pattern of KMS-1.

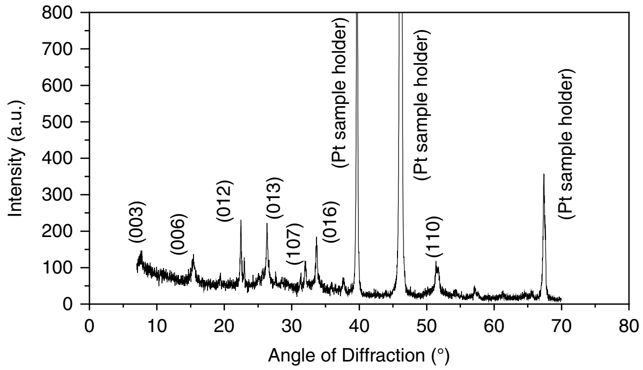

Fig. 3. Sr saturated XRD pattern of KMS-1.

3. Adsorption studies

Experiments were carried out to standardize the parameters for efficient adsorption of Sr by KMS-1. ^{85}Sr tracer ($t^{1/2}$ = 64.84 d, γ = 514 keV) obtained from the Board of Radiation and Isotope Technology, India was used for the standardization experiments.

The adsorption studies were carried out using a batch equilibration technique with a V/m ratio of 1000 ml g^{-1}, at room temperature (27°C). ^{85}Sr activity was spiked in distilled water (1000 ml) and the solution was well stirred. Next, one gram of KMS-1 compound was added to the solution and stirred mechanically for 15 min at room temperature using a magnetic stirrer. The turbid solution obtained was allowed to settle. The clear supernatant liquid was siphoned off and the remaining solution was centrifuged at high speed (2000 rpm) to separate the KMS-1 solid from solution. The KMS-1 solid and the supernatant were both counted to estimate the amount of radioactive ^{85}Sr adsorbed from solution and the total activity added was determined. ^{85}Sr was estimated using a 54 cc coaxial HPGe detector with 15% relative efficiency and resolution of 2 keV at 1332 keV of ^{60}Co.

The distribution coefficient (Kd) that determines the affinity of an element for any adsorbent was calculated for Sr on KMS-1 by the equation:

$$Kd = (V[(C_0 - C_f)/C_f])/(m)$$

where C_0 and C_f are the initial and equilibrium concentration of M^{n+} (ppm) in solution respectively; V is the volume (ml) of the solution, and m is the amount of the ion exchanger/adsorbent (g) used.

The following experiments were carried out to standardize the conditions of efficient adsorption. These studies were conducted in triplicate.

3.1. Standardization of pH

The effect of pH on adsorption of Sr by KMS-1 was studied to establish the pH range in which maximum adsorption of Sr occurs. Experiments were carried out over a pH range of 2–10. The pH values of the solutions were adjusted down or up with concentrated HNO_3 or NH_4OH, respectively. ^{85}Sr activity was spiked in distilled water (1000 ml) whose pH had been adjusted after which 1 g of KMS-1 compound was added to the solution which was then stirred mechanically for 15 min with 1 g of KMS-1 compound. The KMS-1 solid and the supernatant were both counted to estimate the amount of radioactive ^{85}Sr carried.

3.2. Standardization of required quantity of KMS-1

Experiments were carried out with 0.1, 0.2, 0.3, 0.4, 0.5 and 1, 2 and 2.5 g of KMS to standardize the amount of KMS-1 required for optimal adsorption. The experimental procedure as described above was followed for different quantities of KMS-1 at pH 7 and both the supernatant and KMS-1 compound were counted to estimate the activity carried.

3.3. Kinetics and optimization of exchange time

Experiments with various time intervals of adsorption were carried out to study the time dependence of sorption and to standardize the time needed for optimum uptake. Ten samples of distilled water spiked with ^{85}Sr activity were shaken with 0.5 g KMS-1 for time intervals of 1, 2, 3, 4, 5, 8, 10, 12, 15 and 20 min. Similar experiments were repeated for ground water samples spiked with ^{85}Sr.

3.4. Maximum loading capacity of the ion exchanger

Experiments using spiked activities over a wide range from 2 to 5,505 Bq were carried out to study the maximum loading capacity of the exchanger using the above mentioned procedure.

3.5. Effect of interfering cations

The main interference encountered in the analysis of Sr was caused by the large quantities of Ca in the samples. Another source of interference was ^{137}Cs a major fission product and beta emitter that has to be separated from Sr before beta counting. The effect of Ca and Cs on adsorption of Sr by KMS-1 was studied by spiking 5–150 mg of Ca and Cs in 1000 ml of distilled water with a fixed activity of ^{85}Sr.

3.6. Analysis of ground water samples

Ground water samples were collected from a depth of 8 m and filtered through 0.42 μm filter paper. ^{85}Sr activity was spiked in 1 l of ground water to which 10 mg of stable Sr carrier was added. The solution was stirred well and allowed to stand for 2 d to achieve equilibrium. The adsorption analyses were carried out by adding 0.5 g of KMS-1 to the solution and stirring for 30 min. The sample was left undisturbed and allowed to settle for one hour. KMS-1 with adsorbed ^{85}Sr was separated from the supernatant by centrifuging. Both the supernatant solution and solid KMS-1 adsorbent were analyzed for ^{137}Cs and ^{85}Sr activity. The estimation of ^{85}Sr and ^{137}Cs was carried out using a 54 cc coaxial HPGe detector with 15% relative efficiency and a resolution of 2 keV at 1332 keV of ^{60}Co. The adsorption of Sr from actual ground water in presence of all other cations of an environmental sample was studied. The experiment was carried out to distinguish selectivity in adsorption of Sr and the main interfering beta emitting fission product Cs.

3.7. Estimation of ^{90}Sr in ground water samples

During estimation of the beta emitter ^{90}Sr in environmental samples, beta emission interference from $^{137/134}$Cs is possible. This interference has to be removed along with that of Ca as mentioned earlier. Pre-concentration of Sr from water samples onto KMS-1 is a suitable method as Sr is selectively adsorbed and interference of Ca is removed. Experiments with spiked $^{137+134}$Cs showed that if sufficient stable Cs carrier was present, some Cs activity was also carried on KMS-1. The sorption of Cs onto KMS-1 has been reported to be one order of magnitude lower than that for Sr [11]. Additional purification steps would be required for estimation of ^{90}Sr if samples contain Cs activity. The separation and estimation of ^{90}Sr in ground water was carried out using three methods to compare their applicability: (i) sorption onto KMS, (ii) NDCA, (iii) conventional radiochemical analysis (RCA).

3.7.1. KMS-1 method

Water samples (1 l) collected from bore wells were filtered through 0.42 mm filter paper acidified with nitric acid (2 ml l^{-1}) to prevent hydroxide precipitation and adsorption onto the walls of the containers. Twenty milligram of cesium and strontium carrier were added to the solution which was stirred well to reach equilibrium. Carriers are stable isotopes of radioactive elements, added to reduce the loss of a radionuclide during radiochemical separation especially when they are present in trace concentrations in the sample. Next 200 mg l^{-1} of ammonium molybdophosphate (AMP) was stirred into the solution to collect Cs. After one hour of stirring the solution was allowed to settle and AMP carrying the Cs was separated from the supernate containing Sr [12]. The pH of supernate was adjusted to a pH 6 after which 0.5 g of KMS-1 was stirred in for 30 min. The KMS-1 carrying ^{90}Sr was collected and digested in concentrated HNO_3. The in-grown ^{90}Y in this solution was scavenged by precipitating ferric hydroxide. Five milligram of ^{89}Y carrier was added next and the sample was allowed to sit for 15 d to establish equilibrium between ^{90}Sr and ^{90}Y. After 15 d, yttrium oxalate was precipitated and counted in a GM counter to estimate ^{90}Sr.

3.7.2. Non-destructive Cherenkov assay

This technique is analogous to γ-spectrometry without any chemical separation even in the presence of γ-emitters. A 15 ml aliquot of filtered sample was put into a glass vial of low K-content and subjected to Cherenkov assaying in a liquid scintillation analyser. The commonly found γ-emitters such as ^{137}Cs, ^{134}Cs, ^{60}Co, ^{58}Co, ^{40}K and traces of other radionuclides in addition to ^{89}Sr and ^{90}Y all emit Cherenkov radiations. The Cherenkov emission efficiency of ^{90}Y is around 50% but for ^{137}Cs is only around 2.4%. The β-particle of ^{90}Sr has low energy (E_{max} = 546 keV) and does not produce Cherenkov radiation. However ^{90}Y is always in secular equilibrium with ^{90}Sr and therefore estimation of ^{90}Y by Cherenkov radiation can be related to ^{90}Sr. The only limitation of this technique is that the counts due to ^{90}Sr should be at least three times the standard deviation of counts due to all of the γ-emitters. The activity due to ^{90}Sr was computed by subtracting the activity due to other radionuclides estimated by γ-spectrometry from the total activity obtained by Cherenkov counting.

3.7.3 Radiochemical analysis

The ground water samples were also analyzed using conventional radiochemical separation followed by beta counting of the daughter ^{90}Y. Fig. 4 gives the flowchart for conventional radiochemical separation (RCA) and the KMS-1 analytical scheme followed for isolation of ^{90}Sr from a water sample.

4. Results and discussion

4.1. Effect of pH

Studies on the effect of pH on the exchange of Sr on the metal sulphide KMS-1 indicated an increase in adsorption from 30.5% at pH 1 to as high as 98.4% at pH 7, a slight reduction to 97% at pH 9 and still lower to 88.8% at pH 10. The results show that KMS-1 has good capacity for taking up Sr over a wide pH range and is

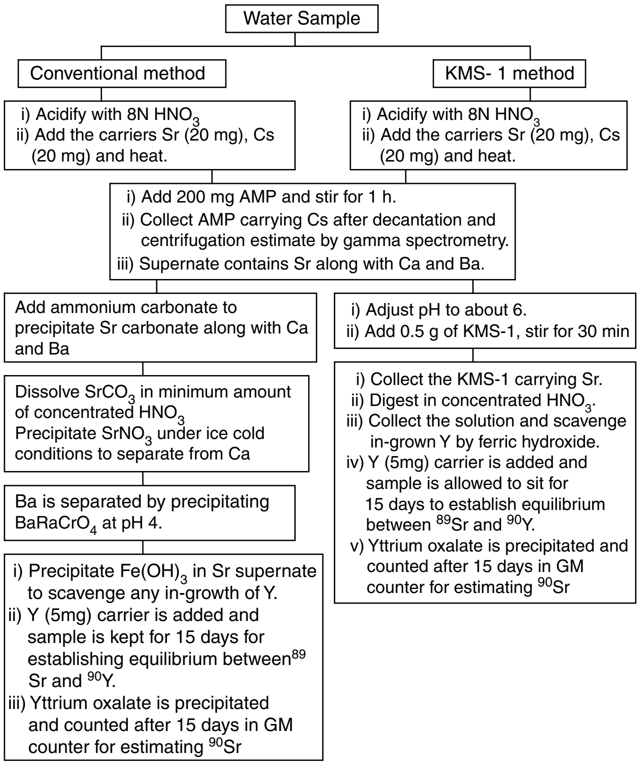

Fig. 4. Separation scheme of ^{90}Sr from water sample by the conventional and the KMS-1 methods.

suitable for working in both alkaline and acidic mediums, that is, it can be used for effluents or acidic extracts as well as environmental water samples. The variation in uptake with pH is shown in Fig. 5.

Kd values ranged from $8.77 \times 10^2 – 1.23 \times 10^5$ ml g^{-1} depending on the pH as shown in Fig. 6. The maximum distribution or adsorption onto KMS-1 was obtained at pH 7. Kd in the pH range of 4–9 was also high of the order of 10^4. The adsorption reduced at pH 10 to Kd of 1.53×10^4 as compared to $\sim 6 \times 10^4$ at pH 6, 8 and 9. Thus the groundwater pH need not be adjusted for efficient uptake of Sr.

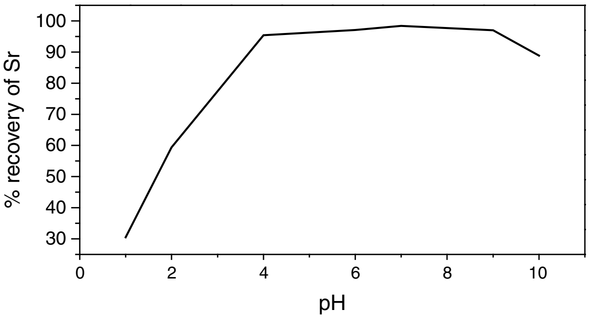

Fig. 5. Effect of pH on Sr recovery.

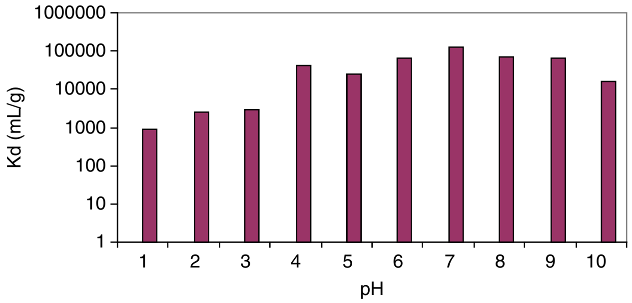

Fig. 6. Effect of pH on Kd.

4.2. Effect of quantity of adsorbent

The efficiency of sorption was good with even a small quantity of KMS-1. It was observed that as little as 0.1 g was sufficient for 95.4% adsorption of the spiked ^{85}Sr which was comparable to the efficiency shown by 5 g of the compound. Therefore after several experiments, 0.5 g was decided to be a suitable amount for efficient recovery of Sr from 1 l water. This quantity was also confirmed for solutions at pH 7–8, which is a common pH range of ground water. If the sample size were increased, the amount of sorbent could be increased proportionately.

4.3. Optimum exchange time

The optimum exchange time in distilled water samples was observed to be about 5 min for 90% sorption. The efficient exchange of spiked Sr in ground water samples took about 15 min. Hence the ground water samples were stirred for 30 min with KMS-1 to ensure sufficient exchange time.

4.4. Loading capacity

The adsorption of Sr was high and ranged between 79% and 98% in solutions containing a wide range of activities between 2 Bq and 5505 Bq of Sr. Analyses for higher Sr activity were not performed as environment levels are unlikely to exceed the above levels. Evidence for exchange capacities above 77 mg g^{-1}. has not been found in the literature, so this method should also be suitable for matrices with high stable Sr levels.

4.5. Effect of interfering cations

The recovery of ^{85}Sr on KMS-1 at various concentrations of Ca and Cs (5–150 mg l^{-1}) is shown in Fig. 7. Adsorption of Sr was not significantly reduced by concentrations of Ca and Cs of up to 100 mg l^{-1}.

Efficiency of ^{85}Sr adsorption: Table 1 gives the recovery of ^{85}Sr and ^{137}Cs from ground water on KMS-1. ^{85}Sr

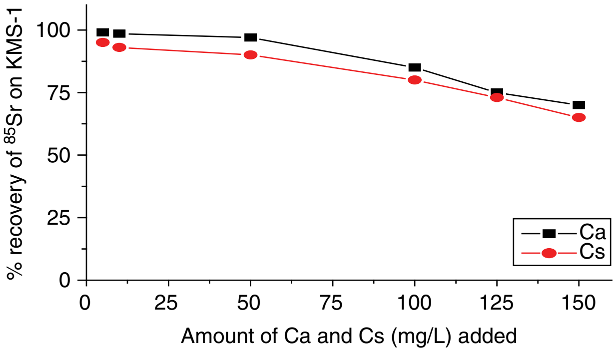

Fig. 7. Effect of added Ca and Cs (mg l^{-1}) on % recovery of ^{85}Sr estimation of activity in ground water.

Table 1
Efficiency of ^{85}Sr adsorption from ground water and separation from ^{137}Cs

	^{85}Sr spiked (Bq)	(%) of ^{85}Sr adsorbed on KMS-1	^{137}Cs in sample (Bq)	% of ^{137}Cs adsorbed on KMS-1
1	1000	99.0	3.6	2.2
2	500	99.2	3.2	1.2
3	250	97.2	6.3	2.0
4	88	93.5	50.1	25
5	86	95.6	5.8	1.8
6	30	97.5	29.5	6.8
7	20	95.5	12.7	15.0
8	10	92.5	9.4	11.0
9	5	96.7	6.3	1.5
10	2	88.5	2.1	2.0

Table 2
Activity (Bq l^{-1}) of ^{90}Sr in bore well water obtained using the three techniques

Sample No.	Activity using radiochemical separation	Activity using NDCA	Activity using KMS-1 as adsorbent
1	55.11 ± 2.0	57.46 ± 0.25	54.21 ± 0.45
2	52.67 ± 1.3	48.9 ± 0.22	45.77 ± 0.36
3	39.14 ± 1.5	41.35 ± 0.22	38.67 ± 0.35
4	35.28 ± 1.5	36.57 ± 0.25	37.65 ± 0.48
5	26.35 ± 1.2	24.23 ± 0.23	24.63 ± 0.52
6	15.27 ± 1.2	13.89 ± 0.38	15.12 ± 0.44
7	3.17 ± 0.4	5.56 ± 0.1	4.34 ± 0.32
MDA	<0.25	<3.2	<0.25

recovery on KMS-1 ranged from 88% to 99.2%. Adsorption of ^{137}Cs appeared to be lower (2–25%) compared to Sr. This could be due to lower sorption of Cs by KMS-1 (38%) at V/m ratio equal to 1000 ml g^{-1} [11]. The observation in this study could well be due to the loss of some radioactive atoms of ^{137}Cs in ground water, relative to other more abundant elements as no stable Cs carrier was added to reduce this loss. Similarly, the recovery of ^{85}Sr observed in ground water was not as efficient as in distilled water due to matrix interferences. The recovery of ^{85}Sr improved only after the groundwater was spiked with mg levels of stable Sr.

The results of ^{90}Sr activity in the ground water samples using the three methods discussed above are shown in Table 2. The radioactivity contents obtained by the three methods are comparable and differences among them are not statistically significant. NDCA has an advantage of being the fastest method for analysis of ^{90}Sr. The method excludes tedious chemical separation and is suitable for direct analysis of liquid or effluent samples though soil samples need first to be chemically digested. The method is also suitable only for samples in which counts due to ^{90}Sr are at least three times greater than the standard deviation of counts due to all the γ-emitters.

RCA has the advantage of eliminating interferences of all the γ-emitters and β-emitters. However the procedure is time consuming and lower yield is obtained. A number of hazardous chemicals are also used during the procedure.

In comparison to the above two methods, separation of Cs by AMP followed by Sr adsorption and separation by KMS-1 is a better-suited option. It reduces the analytical steps involved in purification of Sr. ^{90}Sr counting by a combination of liquid scintillation and Cherenkov measurement can reduce the estimation time for ^{90}Sr, but has not been applied in this paper. A lower detection limit (<0.25 Bq l^{-1}) could be achieved in both the RCA and KMS-1 methods as sample size were increased. The sample size in NDCA can be increased by evaporating a larger quantity of water and thus reducing solution volume but evaporation may cause the dissolved solids content to increase enough to cause self attenuation during Cherenkov counting.

5. Conclusions

The classical method of radiostrontium determination has been replaced by simpler, more selective and faster methods. NDCA is the fastest method of analysis but is suitable mostly for effluent samples. KMS-1 is a suitable material for Sr determination and it can be synthesized easily in a laboratory. It has good selectivity for Sr over wide pH ranges even in the presence of other common cations. It shows very high Kd values for Sr on the order of 10^5 even at neutral and alkaline pH. Ground water samples need not be pretreated or adjusted for pH before analysis using KMS-1. It shows a high Kd (order of 10^4) in acidic pH and can be used for Sr determination in effluents and acid extracts. The proposed procedure for Sr separation using KMS-1 is suitable for pre-concentration of Sr from water samples and can be applied to other environmental matrices. It reduces the tedious chemical separations involved in the conventional radiochemical method while achieving a similar detection limit. Concentration of ^{90}Sr in the range of 0.22–55 Bq l^{-1} in ground water samples could be accurately determined and compared well with the other analytical techniques. The estimation time for ^{90}Sr in ground water samples can be further reduced by estimating ^{90}Sr activity with a combination of liquid scintillation and Cherenkov counting after separation using KMS-1.

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