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A rapid online estimation method for radiostrontium in soil samples using crown ether and supercritical fluid extraction

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ABSTRACT

Crown ethers dissolved in suitable medium are well known to promote the extraction of alkali (M^+) and alkaline-earth (M^{2+}) cations from aqueous to organic phases. Di-*tert*-butyl-cyclohexano18crown6 (DTBDCH18C6) has been identified as an effective and selective extractant for Sr(II) from nitric acid medium. An attempt was made to evaluate the feasibility of ^{85,89}Sr recovery from synthetic soil samples (0.5 g; particle size: <100 μm) by SFE route (pressure: 200 kg/cm^2; T: 40 °C) employing DTBDCH18C6 dissolved in methanol/nitric acid medium as phase modifier. The effect of various experimental parameters such as (i) dynamic/static mode of extraction, (ii) time of equilibration (15–150 min during static mode of extraction using 3 mL of modifier), (iii) nitric acid concentration (1–6 M), (iv) picrate as counter-anion, and (v) crown ether concentration in the modifier phase (2×10^{-4}–2×10^{-3} M) on Sr(II) extraction was studied. Based on these studies, 2×10^{-4} M DTBDCH18C6 dissolved in methanol/4 M HNO_3 was chosen as modifier and 30 min as equilibration time for batch mode employing 3 mL modifier solution in the static mode. Three successive batches employing 3 mL modifier solution (after each extraction stage) showed near quantitative recovery ($>95\%$) of ^{85,89}Sr from soil samples. Dynamic mode extraction using 2×10^{-4} M DTBDCH18C6 dissolved in methanol/4 M HNO_3 as modifier suggested that near quantitative recovery ($>95\%$) of ^{85,89}Sr could be achieved within 1 h. By contrast, ~10% ^{137}Cs extraction was observed from soil samples under identical experimental conditions. These studies demonstrate the potential of the SFE technique for the analysis of ^{90}Sr in different environmental samples.

1. Introduction

^{90}Sr ($T_{1/2}$: ~28.5 years, a pure β emitter) is one of the important long-lived fission products present in high level waste (HLW) solution generated during the reprocessing of spent nuclear fuel [1]. ^{90}Sr is also present in surface soil around the world as a result of fallout from past atmospheric nuclear weapons tests. A bone-seeker like ^{90}Sr, is readily incorporated into the bones and teeth, particularly of young children who have received milk from cows consuming contaminated forage. It may also become lodged in the lungs, where its intense local radiation can cause cancer or other damages. A recent Argonne National Laboratory report mentions that current ^{90}Sr levels in surface soil typically range from 0.01 to 1 pCi/g (picocurie per gram) , reflecting various rainfall and wind patterns, elevation, and terrain; most levels fall between 0.05 and 0.5 pCi/g, with 0.1 pCi/g as a general average. It is relatively mobile and can move down through soil with percolating water to groundwater. Its environmental transport is strongly influenced by the chemical form and it preferentially adheres to soil particles. Typically, the amount of ^{90}Sr in sandy soil is ~15 times higher than in interstitial water (i.e. water present in the pore spaces between soil particles). The US Environmental Protection Agency (EPA) has set the maximum contamination level for ^{90}Sr in public drinking water supplies as 36 pCi/L [2]. Therefore, it becomes essential to develop suitable techniques for the determination of ^{90}Sr content in different soils particularly the surrounding areas of nuclear installations. Conventional techniques for Sr determination in samples of different origins are complex multistep and often lead to the generation of large waste volumes. These include (i) coprecipitation using barium chloride/nitrate and sodium sulphate [3], (ii) ion exchange using resorcinol formaldehyde (RF) resin used for the recovery of Cs and Sr [4], and (iii) solvent extraction using various extractants such as di(2-ethylhexyl) phosphoric acid (HDEHP), chlorinated cobalt dicarbolide (CCD), polyethylene glycol (PEG) and crown ethers [5–9].

In this context, supercritical fluid extraction (SFE) of metal ions from such matrices appears an attractive option. The direct extraction of metal ions from various matrices may minimize the release of volatile organic carbon (VOCs). However, the

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supercritical carbon dioxide ($scCO_2$) needs suitable phase modifiers for the selective extraction of metal ions. The use of complexing agents in $scCO_2$ has been extensively explored for the extraction of metal ions and has become a growing field of research interest [10–15]. It is conceivable that selective extraction of metal ions in supercritical fluids may be achieved if the chelating agent possesses an ion recognition capability. Crown ethers are a class of selective ligands that form stable complexes with metal ions primarily based on the ionic radius-cavity size compatibility concept [16,17]. Wang et al. studied the solubility of a *tert*-butyl-substituted dibenzobistriazolo-crown ether in methanol modified CO_2 and used for the quantitative extraction of Hg^{2+} from sand, cellulose-based filter papers and aqueous samples [18]. Interestingly, it was pointed out that a small amount of water in the solid matrix is essential for the efficient extraction of the metal ion. Selectivity experiments suggested that other divalent metal ions like Cd^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, and Zn^{2+} were inextractable under the specified conditions. However, Au^{3+} could be partially extracted by the macrocyclic ligand. In addition, the extraction of Hg^{2+} from aqueous samples could be achieved using the macrocyclic ligand in methanol modified $scCO_2$. The formation of extractable metal chelates with the ligand at the pH defined by the CO_2–H_2O was identified as the important factor influencing the extraction efficiencies of the metal ion. Horwitz et al. as well as our research group evaluated dicyclohexanol18crown6 (DCH18C6) and it is di-*tert*-butyl derivative (DTBCH18C6, Fig. 1) as Sr selective extractants employing different diluents [9,19–21]. These 18 membered crown ethers (cavity radius = 1.45(± 0.15) Å) are reported to be selective complexing ligands for Sr^{2+} (ionic radius = 1.13 Å) and are, therefore, capable of replacing the water molecules present in the inner coordination sphere of the metal ion.

Solvent extraction studies have demonstrated that the transfer of cationic crown ether complex species across requires suitable counter anions in the organic phase. In this context, the large volume organophilic anions like picrate, tetraphenyl borate and chloroacetate have been evaluated. The general extraction equilibrium can be expressed as

$$Sr^{2+}_{(aq)} + 2NO^{-}_{3(aq)} + L_{(org)} + xH_2O_{(org)} \leftrightarrow SrL^{2+} \cdot 2(NO_3)^{-} \cdot xH_2O_{(org)} \tag{1}$$

However, the SFE studies add another dimension to the use of these novel ligands. The input of solubility data for different macrocyclic extractants in $scCO_2$ is critical for the extraction experiments. In this context, Shamshipur et al. reported the solubilities dibenzo-24-crown-8 (DB24C8), dibenzo-27-crown-9 (DB27C9), and dibenzo-30-crown-10 (DB30C10) in $scCO_2$ under varying experimental conditions of pressure and temperature [22]. The solubility of the crown ethers in supercritical carbon dioxide was found to vary in the order DB24C8 > DB27C9 > DB30C10. At a fixed temperature, there was an increase in the solubility of all these compounds with increasing pressure, and this influence was more pronounced at higher temperatures. These studies, however, suggested that the solubility of compounds was guided by their vapor pressure and molecular weights. Generally, the lesser the vapor pressure and the higher the molecular weight, the less soluble is the solute in $scCO_2$. On the other hand, several studies have been reported on the use of alcohols as modifiers in $scCO_2$ for extraction/recovery of metal ions from different matrices [23–28].

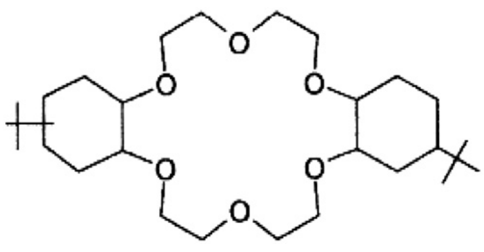

Fig. 1. DTBDCH18C6.

In the present work, an attempt has been made to evaluate the feasibility of $^{85,89}Sr$ recovery from synthetic soil samples by SFE route employing DTBDCH18C6 dissolved in methanol/nitric acid medium as phase modifier under varying experimental conditions such as (i) dynamic/static mode of extraction, (ii) time of equilibration (during static mode of extraction), (iii) nitric acid concentration, (iv) crown ether concentration in the modifier phase, and (v) picric acid concentration. The selectivity for $^{85,89}Sr$ over ^{137}Cs ($T_{1/2}$: ~30 years, a β/γ emitter) was also tested under identical experimental conditions. These studies demonstrate the potential of the SFE technique for the analysis of radionuclide in different environmental samples.

2. Experimental

2.1. Reagents

DTBCH18C6 (> 97%) was procured from Fluka Chemie AG, Switzerland and was used as received. A.R. grade methanol, procured from BDH, picric acid (extra pure) SD Fine Chemicals were used as received. $^{85,89}Sr$ tracer was procured from BRIT, Mumbai. All other reagents were of A.R. grade. Food grade CO_2 (99.99%) was used in the pressure range of 100–300 bar in the temperature range of 40–60 °C to be in the supercritical phase.

2.2. Preparation of synthetic soil samples

The synthetic soil samples (alluvial and loamy) were prepared by spiking known quantities of $^{85,89}Sr$ solution (specific activity: 2.6 mCi/g) and by drying under IR lamp to get soil samples with specific activities of ~70–1000 Bq/g (~10^{-6} M Sr in soil samples). These soil samples were sieved after thorough grinding in mortar and pestle and the particle size was ensured to be < 100 μm. After desired sample preparation, ~500 mg soil samples are taken for SFE experiments.

2.3. Instruments

2.3.1. Supercritical fluid extraction setup

SFE setup used in this study has been procured from M/s. JASCO International Co. Ltd. Japan, which consists of microprocessor controlled units such as a CO_2 delivery pump, a modifier pump, a thermostat, a back-pressure regulator and a collection vessel (Fig. 2). The technical specifications were as follows: (i) spiral tubes: inner diameter (0.25 mm), spiral diameter (40 mm), length (3.8 m), and material (stainless steel), (ii) mixing vessel: inner diameter (10 mm), volume (10 mL), and material (stainless steel). The sample was taken in the extraction vessel of 10 mL capacity (made of stainless steel) which is then loaded inside the thermostat. CO_2 is delivered to the extraction vessel at a desired flow rate using delivery pump. Simultaneously, the modifier pump is used to mix a desired percentage of the modifier (containing DTBDCH18C6, the extractant) to the CO_2 stream. In the present work, the extract collection port of SFE equipment was enclosed in a specially designed and fabricated acrylic containment to avoid any release of the activity. This was further certified by the health physicist of the laboratory.

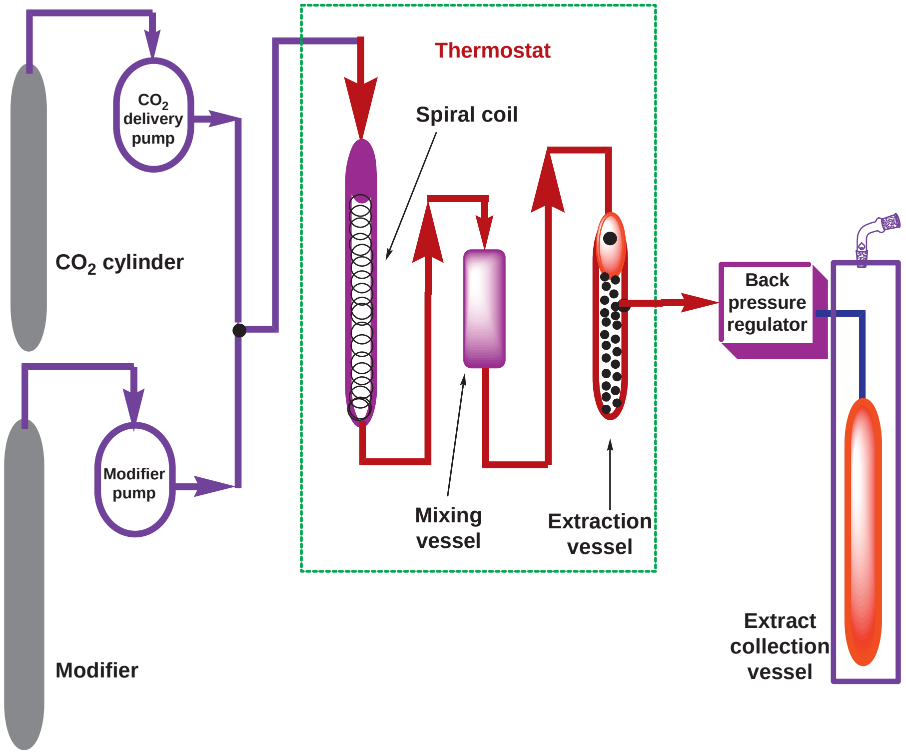

Fig. 2. SFE extraction setup used in the present study.

2.3.2. NaI(Tl) detector

All the samples containing $^{85,89}Sr$ and ^{137}Cs (soil or extracted fractions) were counted using multichannel NaI(Tl) scintillation detector. Care was taken to make samples of same geometry during the counting experiments. Each sample was counted for sufficiently long time to get better counting statistics and minimize the error. The collected data was analyzed by using a peak fit software PHAST [29].

2.4. Extraction experiments

The extraction studies of $^{85,89}Sr$ or ^{137}Cs from synthetic soil samples (0.5 g containing varying activities; particle size: $<100\ \mu m$) were carried out by the SFE route (pressure: 200 kg/cm^2; T: 40 °C; flow rate=2.0 mL/min CO_2; 0.2 mL/min modifier) by placing the sample in extraction vessels under varying experimental parameters such as (i) dynamic/static mode of extraction, (ii) time of equilibration (15–150 min during static mode of extraction using 3 mL of modifier), (iii) nitric acid concentration (1–6 M), (iv) crown ether concentration in the modifier phase (2×10^{-4}–2×10^{-3} M), and (v) picric acid concentration. Independent temperature variation experiments (40–60 °C) showed no significant effect on Sr(II) extraction under the conditions of this study. Similar observations were made during the recovery of uranium from different matrices [27,28]. The modifier comprised of the desired concentrations of DTBDCH18C6, nitric acid or picric acid dissolved in methanol. Each experiment was repeated at least three times and the reproducibility of the result was within ±10%. The extracted fractions were collected in glass collection tubes of 15 mL capacity for 15 min containing 1–2 mL ethanol as the trap solution. Several fractions were collected during these extraction experiments. After each extraction experiment, a small part from the collected fractions (0.5 mL) was taken for radiometric assay to quantify the recovery of $^{85,89}Sr$ (gamma energy: 514 keV) and ^{137}Cs (gamma energy: 660 keV) from the soil samples. This step was performed to match the geometry of the synthetic soil and residue (0.5 g) in gamma counting tube.

3. Results and discussion

3.1. Effect of modes of extraction

Two soil samples (0.5 g) with varying $^{85,89}Sr$ activities (250 and 682 Bq/g) were subjected to dynamic mode (no pre-equilibration) SFE experiments independently. These samples were kept in extraction cell (10 mL capacity) and $^{85,89}Sr$ recovery was monitored as a function of time employing 2×10^{-4} M DTBCH18C6 dissolved in methanol at 2 M HNO_3 as the modifier (Fig. 3). Other experimental conditions were as follows: pressure=200 kg/cm^2; temperature=40 °C, flow rate=0.2 mL/min (modifier), and 2 mL/min (CO_2). It is important to mention that modifier to CO_2 flow rate was maintained at 1:10 to ascertain the formation of single-phase supercritical fluid for extraction studies. The extracted activity was collected periodically at 10 min interval.

It is evident that major part of the activity could be recovered in the initial 30 min beyond which a saturation behavior was observed. However, the overall recovery of $^{85,89}Sr$ from these soil samples after 1 h of extraction under dynamic mode was ~89.5(±5.3) %. These studies, however, suggest that the quantity of $^{85,89}Sr$ activity used in the range of present work has no influence on its recovery.

Extraction studies were also carried out for the recovery of $^{85,89}Sr$ from 0.5 g soil sample (250 Bq/g) in static mode of extraction as a function of time of equilibration (15–150 min) employing 3 mL of the modifier solution (2×10^{-4} M DTBCH18C6 dissolved in methanol at 3 M HNO_3) at a pressure of 200 kg/cm^2, temperature of 40 °C, and flow rates of 0.2 mL/min (modifier) and 2 mL/min (CO_2). After desired duration of equilibration, the modifier solution and CO_2 were allowed to flow through the

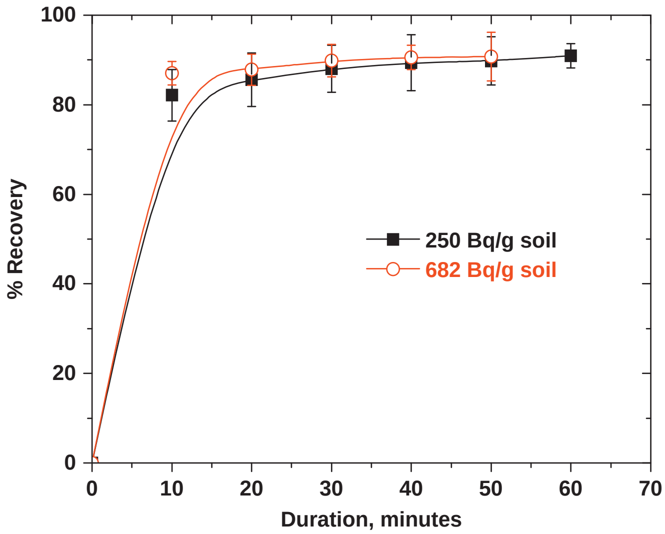

Fig. 3. Recovery of ^{85,89}Sr from synthetic soil samples in dynamic mode; modifier: 2×10^{-4} M DTBDCH18C6+2 M HNO_3 in methanol; temperature: 40 °C; pressure: 200 kg/cm^2; modifier flow rate: 0.2 mL/min.

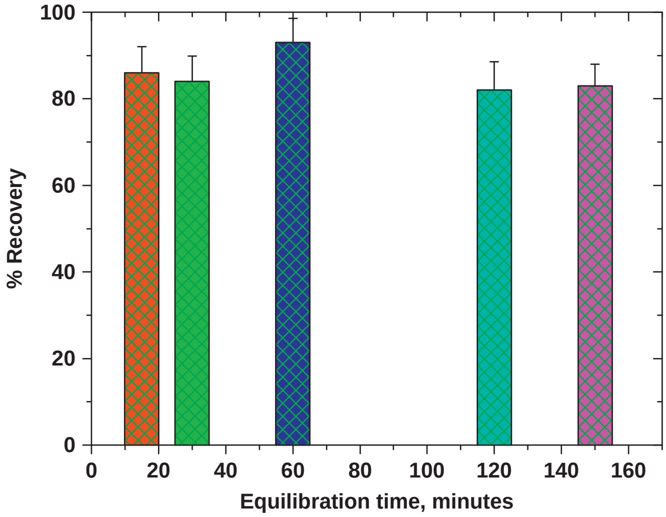

Fig. 4. Recovery of ^{85,89}Sr from synthetic soil samples in the static mode; modifier: 2×10^{-4} M DTBDCH18C6+3 M HNO_3 in methanol (3 mL added); temperature: 40 °C; pressure: 200 kg/cm^2; modifier flow rate: 0.2 mL/min.

extraction vessel. The extracts were collected for 15 min duration after each static mode of extraction (Fig. 4). There was a very small variation in the recovery of ^{85,89}Sr (85.6($\pm$ 5.8) %) under the conditions of these experiments, suggesting the time of equilibration does not have significant effect on the extraction process.

3.2. *Effect of nitric acid concentration*

As evident from extraction equilibrium (1), the presence of nitrate ions helps in the extraction of Sr(II) employing crown ethers as extractant. Based on this logic, it was of interest to investigate the effect of nitric acid concentration (1–6 M) in the modifier solution on Sr(II) recovery from soil samples. Fig. 5 shows gradual increase in the recovery of Sr(II) from 80% (1 M HNO_3) to 88% (6 M HNO_3) under these experimental conditions. These data indicate that the extraction equilibrium applicable for solvent extraction studies involving aqueous and organic phases is being followed under supercritical fluid conditions. Based on these observations, 4 M HNO_3 was chosen for further studies as it provided optimum recovery and would have less corrosion problems of the stainless steel tubings of the SFE machine.

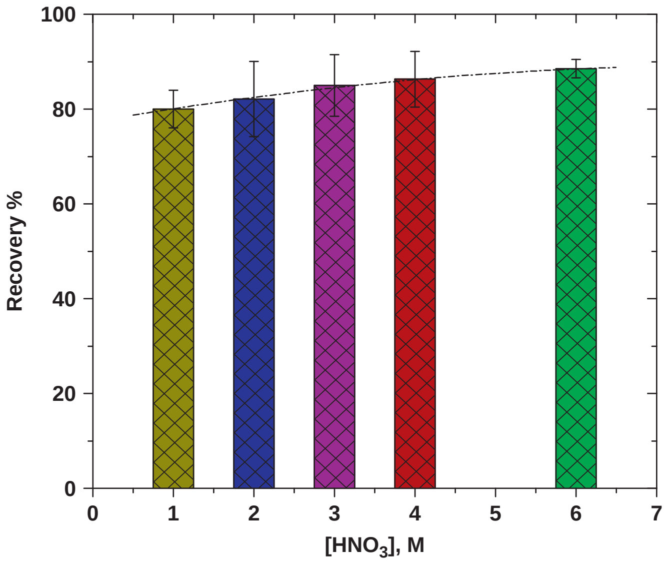

Fig. 5. ^{85,89}Sr recovery as a function of nitric acid concentration in modifier solution; [DTBDCH18C6]: 2×10^{-4} M; static mode; temperature: 40 °C; pressure: 200 kg/cm^2; modifier flow rate: 0.2 mL/min; equilibration time: 30 min; soil sample: 0.5 g; modifier volume: 3 mL.

3.3. *Effect of picrate as counter-anion*

Solvent extraction studies employing crown ethers have shown that counter-ions play an important role in affecting the efficiency and selectivity in liquid–liquid extraction or transport to classical organic solvents [30–32]. The anion hydration energy, lipophilicity, and its possible interactions with the crown ethers are responsible for remarkably different behaviors of counter-anions during extraction processes. Vayssière and Wipff reported molecular dynamic studies on the role of counter-anions (picrate and perfluorooctanoate) during supercritical fluid extraction of alkali and alkaline earth metal ions from aqueous solutions employing crown ethers as extractant [33]. These studies showed that surface active solutes involving metal and counter-anions, concentrate near the aqueous and supercritical interface and their extraction depends on the cation, counter-ion and extractant. Similarly, the extraction of Sr^{2+} was reported to be distinctly larger from HNO_3 medium as compared to that from HCl medium employing dicyclohexano18crown6 (DCH18C6) [20]. This behavior was attributed to the large number of water molecules associated with Cl^- which causes a decrease in the ionic potential of hydrated chloride anion to be lower than the corresponding nitrate anion thereby affecting the electrostatic interaction (ion pairing energy) between SrL^{2+} and the hydrated chloride ion adversely. Therefore, an attempt was made to investigate the recovery of ^{85,89}Sr recovery from synthetic soil samples by SFE route employing 2×10^{-4} M DTBDCH18C6 and varying concentrations of picric acid (1×10^{-5}–1×10^{-3} M) as counter anion dissolved in methanol as the modifier solution. Other experimental conditions used in these studies were as follows: 0.5 g soil (177 Bq/g); 200 kg/cm^2 pressure (P); 40 °C temperature (T); 2.0 mL/min CO_2 flow rate and 0.2 mL/min modifier flow rate. Soil samples were equilibrated with 3.0 mL of the modifier solution for 30 min followed by collection for 30 min after passing the modifier solution. This step was repeated three times for each soil sample and the cumulative recovery was calculated. There was marginal increase in the ^{85,89}Sr recovery from 10% (1×10^{-5} M picric acid) to 18% (1×10^{-3} M picric acid). These studies suggest that $^{85,89}Sr$ recovery from different environmental samples is not effective in picrate medium in contrast to that reported from aqueous medium [33]. Further studies were, therefore, carried out employing nitrate as counter-anions by using 4 M HNO_3 along with desired concentration of DTBCH18C6 in methanol.

3.4. *Effect of DTBCH18C6 concentration*

$^{85,89}Sr$ recovery from soil samples were also carried out as a function of crown ether concentration in the modifier phase (2×10^{-4}–2×10^{-3} M) at 3 M HNO_3 in methanol. There were minor variations in the recovery of $^{85,89}Sr$ (84($\pm$4)%) from different soil samples under the conditions of these studies. This behavior can be explained in terms of aggregation behavior of the crown ether molecules at the interface. Similar observations were reported in our earlier work on solvent extraction of Sr(II) employing dicyclohexano18crown6 (DCH18C6) in aliphatic alcohols as the solvent systems [20]. The aggregation tendency has been favored at higher ligand concentration and is influenced by the nature of ligand, solvent as well as nitric acid concentration. Even though the presence of alkyl substituents (viz. methyl- or *tert*-butyl-groups) on dicyclohexano crown ethers is reported to suppress the aggregation tendency, it appears that aggregation is favored under supercritical fluid conditions [33].

Based on these observations, further studies were proposed to be carried out using 2×10^{-4} M DTBDCH18C6 dissolved in methanol/4 M HNO_3 as the modifier and 30 min as the equilibration time (batch mode). However, it was realized that one has to carry out successive batch extractions (using 3 mL modifier solution) on soil samples in static mode (equilibration time: 30 min) in order to achieve near quantitative recovery of $^{85,89}Sr$ from such soil samples. $^{85,89}Sr$ extraction studies from synthetic soil samples showed $>95\%$ recovery in three batches employing 3 mL modifier solution after each extraction stage. On the other hand, it was noted that $^{85,89}Sr$ recovery from synthetic soil samples under dynamic mode employing 2×10^{-4} M DTBCH18C6 dissolved in methanol at 2 M HNO_3 as the modifier yielded ~90% recovery in 1 h. When similar exercise was performed employing 2×10^{-4} M DTBCH18C6 dissolved in methanol at 4 M HNO_3 as the modifier, the recovery became $>95\%$ in 1 h suggesting that higher nitric acid concentration favors the extraction as shown in the following scheme:

$$Sr^{2+} + 2NO^-_{3(SF)} + L_{(SF)} + xH_2O_{(SF)} \leftrightarrow SrL^{2+} \cdot 2(NO_3)^- \cdot xH_2O_{(SF)} \quad (2)$$

where $NO_3^-{}_{(SF)}$, $L_{(SF)}$, and $xH_2O_{(SF)}$ refer to nitrate ions, crown ether and water molecules (from modifier solution), respectively, present in the $scCO_2$ phase. The conditions for near quantitative extraction of $^{85,89}Sr$ from soil samples were optimized as 2×10^{-4} M DTBDCH18C6 dissolved in methanol/4 M HNO_3 (modifier), 30 min (equilibration time), 3 mL modifier solution (for each batch in static mode), 200 kg/cm^2 (pressure); 40 °C (temperature); 2.0 mL/min (CO_2 flow rate), 0.2 mL/min (modifier flow rate), and three successive batches (static mode extraction employing 3 mL modifier solution). As this study was intended for the estimation of radiostrontium in environmental/soil samples, these experiments were carried out using tracer concentrations of strontium.

3.5. *Selectivity experiments*

Selectivity for $^{85,89}Sr$ over ^{137}Cs ($T_{1/2}$: ~30 years, a β/γ emitter) was also tested under optimized experimental conditions.

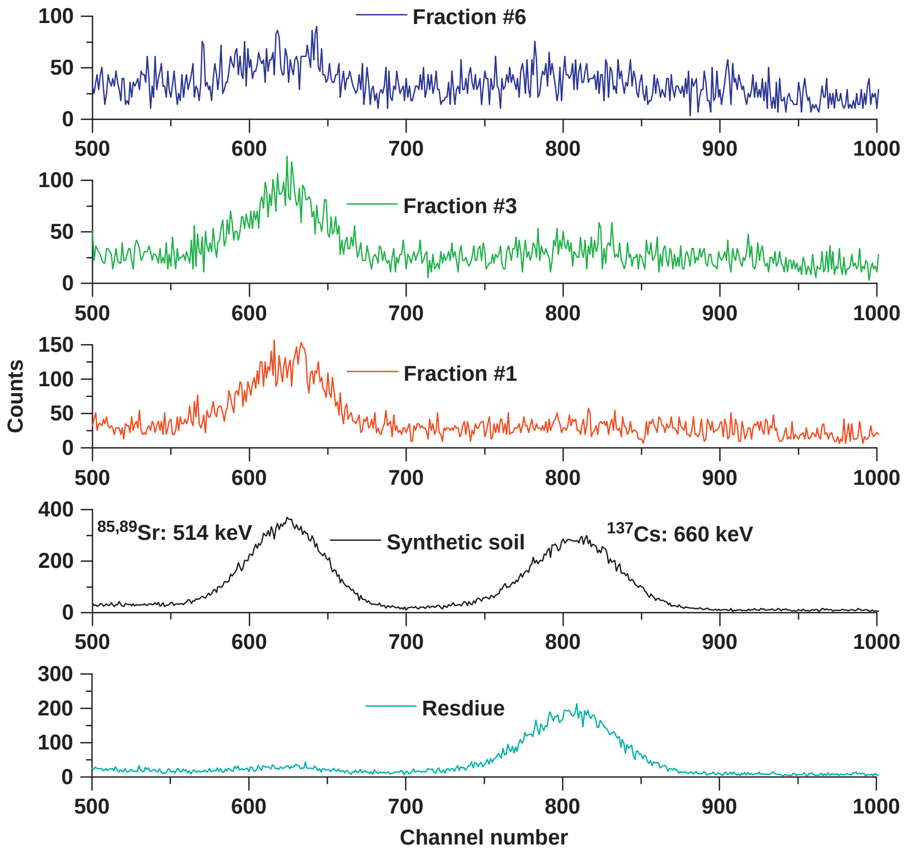

Fig. 6. Gamma spectra of different fractions collected during SFE (dynamic mode of $^{85,89}Sr$ and ^{137}Cs from synthetic soil sample); modifier: 2×10^{-4} M DTBCH18C6 in methanol at 4 M HNO_3; pressure: 200 kg/cm^2; temperature: 40 °C.

The soil samples were prepared by spiking known quantities of ^{85,89}Sr and of ^{137}Cs to get specific activities of ~500 Bq/g. The soil samples (0.5 g) were subjected to SFE experiments under dynamic mode using 2×10^{-4} M DTBCH18C6 dissolved in methanol at 4 M HNO_3 as the modifier and maintaining pressure = 200 kg/cm^2, temperature = 40 °C, flow rate = 0.2 mL/min (modifier) and 2 mL/min (CO_2). Sample collection was carried out at definite time intervals 5–90 min. A known volume of the collected fractions was counted in multichannel NaI(Tl) detector to measure the recovery of ^{85,89}Sr and ^{137}Cs from the soil samples. Fig. 6 shows the gamma ray spectra of the samples collected at different time intervals. Based on this study, it was demonstrated that near quantitative recovery of ^{85,89}Sr ($>95\%$) could be achieved within 60 min with $\leq 10\%$ contamination of ^{137}Cs in the extracted samples. These studies, however, demonstrate the potential of the SFE technique for the analysis of radionuclide in different environmental samples.

4. Conclusions

Di-*tert*-butyl-cyclohexano18crown6 (DTBDCH18C6) was evaluated as a selective extractant for ^{85,89}Sr recovery from synthetic soil samples under varying experimental conditions such as (i) dynamic/static mode of extraction, (ii) time of equilibration, (iii) nitric acid concentration (1–6 M), (iv) picrate as counter-anion, and (v) crown ether concentration in the modifier phase. The recovery of ^{85,89}Sr gradually increased from 80% (1 M HNO_3) to 88% (6 M HNO_3) indicating that the extraction equilibrium applicable under supercritical fluid conditions was same as that observed in solvent extraction studies. The presence of increasing concentration of picrate had marginal effect on ^{85,89}Sr recovery which is in sharp contrast that reported from aqueous medium. Similarly, minor variations in the recovery of ^{85,89}Sr (84($\pm$4)%) from soil samples under the conditions of these studies was explained in terms of aggregation behavior of the crown ether molecules at the interface. Based on these studies, 2×10^{-4} M DTBDCH18C6 dissolved in methanol/4 M HNO_3 was chosen as modifier and 30 min as equilibration time for batch mode employing 3 mL modifier solution in static mode. Three successive batches employing 3 mL modifier solution (after each extraction stage) showed near quantitative recovery ($>95\%$) of ^{85,89}Sr from soil samples. Selectivity for ^{85,89}Sr over ^{137}Cs ($T_{1/2}$: ~30 years, a β/γ emitter) was also investigated in dynamic mode extraction using 2×10^{-4} M DTBDCH18C6 dissolved in methanol/4 M HNO_3 as modifier. Whereas near quantitative recovery ($>95\%$) of ^{85,89}Sr could be achieved within 1 h, only ~10% ^{137}Cs extraction was observed from soil samples under identical experimental conditions. These studies demonstrate that the SFE technique can be employed for the analysis of contaminated soil samples.

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