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# Separation and subsequent determination of low radioactivity levels of radium by extraction scintillation

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#### Abstract

A method is developed for separation and subsequent determination of low <sup>226</sup>Ra levels based on its extraction efficiency by various organic extractants followed by direct interaction with mixed scintillation cocktail (SC) in toluene as the most suitable solvent. Three organic extractants including Tricaprylmethyleammonium chloride (Aliquat-336), triphenylphosphine sulphide (TPPS) and tri-*n*-octylphosphine oxide (TOPO) are individually embedded in 1-phenyl,4-phenyloxazole (PPO) as a primary scintillator and 1,4-di-2-(4-methyl, 5-phenyl oxazoyl) benzene (POPOP) as a second scintillator. Different parameters affecting the extraction process including shaking time, type and concentration of extractant, aqueous/organic volume ratio as well as various levels of <sup>226</sup>Ra are individually investigated. Based on the optimized condition, it was found that the extraction of <sup>226</sup>Ra by Aliquat-336 is highly selective with efficient separation capability from <sup>133</sup>Ba, which is necessary to determine the yield and recovery of <sup>226</sup>Ra in related measurements. The combination of extraction with direct scintillation processes is mainly elaborated to overcome the heterogeneity problem and hence the slow scintillation rate that often exists in conventional liquid scintillation counting especially with low radioactivity levels.

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## 1. Introduction

Analysis of radioactive species in radioactive wastes is essential for safe and economic disposal of wastes. <sup>226</sup>Ra being one of the naturally occurring alpha emitters and a member of alkaline earth metals is bone seeker [1], and dangerous due to its radio-toxicity and long half life. The radon daughter of radium is also an alpha emitter that can decay and deposit in the respiratory system causing serious injury leading lung cancer. Several countries use the specific activity of <sup>226</sup>Ra and/or the gross specific activity of <sup>226</sup>Ra and <sup>228</sup>Ra as basis for legislation and control of natural radioactive levels.

Several methods are reported for quantitative separation of <sup>226</sup>Ra from different environmental samples by acid digestion of test samples and subsequent precipitation as barium–radium sulfate after being separated from both uranium and thorium

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fractions [2,3]. Radiochemical separation of radium as Ra–Ba sulfate from other naturally occurring radionuclides is generally performed by methods involving iron-hydroxide precipitation and TBP extraction [4]. The methods mostly based on separation of both uranium and thorium by co-precipitation using iron hydroxide at pH 9 leaving both radium and barium in solution.

The chemical yield of <sup>226</sup>Ra radionuclide is based on using <sup>133</sup>Ba as non-isotopic radiotracer [4].

Extensive attention has been paid to the separation of radium from barium because of the close similarity in the chemical behavior of both elements. A cation-exchange separation using ethylendiamine-tetraacetic acid (EDTA), ammonium citrate, and ammonium lactate or ammonium formate eluents has been used [5]. However; complete separation could not be achieved when dealing with high barium to radium ratios. This becomes very critical due to the fact that 10  $\mu$ g of Ba can result in a 50% reduction in the recovery of Ra in electrodeposition steps [6]. Thus, in spite of the high sensitivity of  $\alpha$ -spectrometry, these procedures have been less developed for the determination of low-levels of <sup>226</sup>Ra, mainly because of the difficulty in preparing thin counting sources and the tediousness of related radiochemical procedures. By electrodeposition, any barium contained in the sample causes both incomplete Ra plating and a poorly resolved alpha particle spectrum. For this reason, complete separation of barium and radium is very difficult, although some success resulted by using cation and anion exchange resins [7,8].

Leason [9] reported that cation-exchange chromatography using cyclohexane-diaminetetraacetic acid (CyDTA) allows an excellent separation of barium from radium. This finding made the measurement of extremely low-level radium activity in minerals and environmental samples by  $\alpha$ -spectrometry less difficult [10,11].

In literature [11], radium was preconcentrated from water samples by coprecipitation with BaSO<sub>4</sub>, while thorium with iron hydroxides. However, it was observed that a part of thorium was coprecipitated with iron hydroxide and an important part still remains in the BaSO<sub>4</sub> precipitate [11]. In order to improve the separation condition, both thorium and radium were coprecipitated as sulphates and hydroxides together in the preconcentration step [12]. After dissolution of the precipitate in 8 M HCl, the solution is passed through a Microthene-TOPO column. An alternative method, [13] free from these problems, involves the use of La<sup>3+</sup> as holdback carrier for Th<sup>4+</sup> during precipitation of Ba(Ra)SO<sub>4</sub> [14]. Precipitation of BaSO<sub>4</sub> is used for complete separation of  $Ra^{2+}$ , while the use of La<sup>3+</sup> prevents co-precipitation of Th<sup>4+</sup>. High separation yields of radium (80-90%) are expected when the concentrations of barium carrier are not significant, and fall drastically for barium concentrations slightly greater than 0.10-0.15 mg of Ba.

An extraction chromatographic method based on microporous polyethylene (Microthene) supporting tri-*n*-octylphosphine oxide (TOPO) was used to separate uranium and <sup>226</sup>Ra from phosphorites and their industrial derivatives [15]. TOPO is a good extractant for uranium in 2MHNO<sub>3</sub>, while alkali metals, alkaline earth metals, iron, aluminium, are not extracted [16,17].

Extractive scintillating resins are still under development. They mainly used for simultaneously separation and quantification of some radionuclides from aqueous solutions [18]. Extensive interest has been done to simplify or modify radiochemical separation procedures that could be completely automated for routine measurements [19]. The extractive scintillating used consists of a fluor 2-(1-naphtyl)-5-phenyloxazole) ( $\alpha$ -NPO) and the extractant is a mixture of trioctyl and tridecyl methyl ammonium chlorides (Aliquat-336) co-immobilized within an inert macroporous polystyrene resin [7].

In this study, radio-chemical separation of radium from barium is modified to compete with the most commonly used procedures based on precipitation, solvent extraction, extraction chromatography and/or by using extraction scintillation resins. The suggested procedure is based on selective separation of Ra–Ba followed by extraction of Ra from Ba using aliquat-336 and subsequent determination by a suitable immobilized liquid scintillating cocktail.

## 2. Experimental

#### 2.1. Reagents and solutions

All chemicals and reagents used are of analytical grade quality and used without further purification. Toluene was provided from BDH, 1-phenyl,4-phenyloxazole (PPO), 1,4di-2-(4-methyl, 5-phenyl oxazoyl) benzene (POPOP) and Tricaprylmethyleammonium chloride (Aliquat-336) from Merck. Triphenylphosphine sulphide (TPPS) is produced by Aldrich and tri-*n*-octylphosphine oxide (TOPO) by Cytec, Canda. Ultima Gold (UG) the scintillation cocktail and the glass vials are supplied by Packard (USA). Stock solutions of 0.3 M of each of Aliquat-336, TOPO and TPPS are prepared by dissolving the corresponding weights in 100 ml toluene. 4.0 ml volume portions of these solutions are used for each extractant.

## 2.2. Apparatus

A Tri-Carb 2770 TR-LSC Analyzer with Pulse Shape Analysis (PSA) and Multichannel Analyzer (MCA) supplied from Canberra-Packard, USA is used for radium measurements whereas barium measurements are carried out using NaI Gamma-detector.

## 2.3. Radioisotopes

Stock standard solutions of <sup>133</sup>Ba (41 Bq/ml) and <sup>226</sup>Ra (1.806 Bq/ml) radionuclides were obtained from International Atomic Energy Authority, IAEA. The <sup>133</sup>Ba measurements in aqueous phase were performed by gamma spectrometry (NaI crystal) within a channel number range from 0 to 200. Each sample of both blank and related standard are counted for 3600 s after shaking for 1 h. <sup>226</sup>Ra standards in aqueous phase were prepared by adding various volumes from <sup>226</sup>Ra stock standard (1.806 Bq/ml) to double distilled water then mixed with 14 ml of (UG) reference scintillation cocktail. These standards were measured by LSC using cpm counting mode. All samples were measured within counting time 90 min after 1 h shaking time.

## 2.4. Separation method

Radiochemical separation method was developed to separate <sup>226</sup>Ra from <sup>133</sup>Ba in the standard prepared solutions using different organic extractants such as Tricaprylmethyleammonium chloride (Aliquat-336), triphenylphosphine sulphide (TPPS) and tri-*n*-octylphosphine oxide (TOPO) that are individually embedded in organic solution containing 1phenyl,4-phenyloxazole (PPO) as scintillator.

Standard solutions of both <sup>226</sup>Ra and <sup>133</sup>Ba were prepared individually by taking various volumes (100–1000  $\mu$ l) from each stock solution that contain radioactivity level of 1.806 Bq/ml for radium and 41 Bq/ml for barium. Each solution was transported to 20 ml glass vial and completed to 1.0 ml using DDW. 14.0 ml of UG organic scintillator was added to the standard solution containing <sup>226</sup>Ra and directly measured by LSC after background correction while the vial containing <sup>133</sup>Ba (1.0 ml

Table 1	
Measurements of the percentage uptake of <sup>133</sup> Ba and <sup>226</sup> Ra by different extractants using NaI and LSC detectors, respective	ely <sup>a</sup>

Sample	Net count rate (C/S)		Uptake %	
	Aqueous phase	Organic phase	Aqueous %	Organic %
<sup>133</sup> Ba <sup>b</sup>				
<sup>133</sup> Ba Standard	$10.48 \pm 0.29$	$6.105 \pm 0.28$	_	_
SC (only)	$10.61 \pm 0.28$	BG	-100	-0
TPPS + SC	$10.39 \pm 0.29$	BG	-100	-0
Alq + SC	$10.75 \pm 0.30$	BG	-100	-0
TOPO + SC	$10.63 \pm 0.30$	BG	-100	-0
<sup>226</sup> Ra <sup>c</sup>				
<sup>226</sup> Ra Standard-UG	$74.2 \pm 3.19$	$94.2 \pm 3.3$	_	_
SC (only)	$59.0 \pm 2.95$	$6.96 \pm 1.92$	72.1	20.5
TPPS + SC	$58.0 \pm 2.9$	$7.91 \pm 1.95$	71.1	21.8
Alq+SC	$42.0 \pm 2.65$	$31.04 \pm 2.47$	46.5	43.4
TOPO + SC	$62.0 \pm 3.0$	$3.9 \pm 1.84$	75.4	16.5

<sup>a</sup> Concentration of each extractant is kept at 0.1 M, the shaking time 1.0 h, the radioactivity level for radium is 0.3612 Bq, and the Aq/Org ratio was 1/14. Abbreviation: SC (Scintillation Cocktail), TPPS (Triphenylphosphine sulphide, Alq (Aliquat-336), TOPO (Tri-*n*-octylphosphine oxide).

<sup>b</sup> The radioactivity level of <sup>133</sup>Ba in Bq was corrected after background substraction.

<sup>c</sup> The radioactivity level of <sup>226</sup>Ra in dpm was corrected considering that Ultima Gold cocktail (UG) as blank.

aqueous standard) was measured by NaI gamma detector after background corrections.

A series of the above standards were mixed with 4.0 ml of known concentrations of organic extractants (Aliquat-336, TPPS, TOPO). Each organic extractant was dissolved in toluene as the most suitable solvent. Finally 10.0 ml of the mixed scintillation cocktail (SC) containing 1-phenyl,4-phenyloxazole (PPO) as a primary scintillator and 1,4-di-2-(4-methyl, 5-phenyl oxazoyl) benzene (POPOP) as a second scintillator was added to each vial.

Each vial was then shacked and 1.0 ml of the aqueous solution was removed using adapted automatic pipette and transferred directed to be measured by gamma spectrometry using NaI detector. The measurement was double checked by LSC after adding 14.0 ml of a fresh UG organic scintillator. The organic phase containing the extractant and the mixed (SC) was measured by LSC to evaluate the extraction efficiency and the uptake percentage of <sup>226</sup>Ra and <sup>133</sup>Ba, as illustrated in Table 1.

A series of experiments were carried out using different concentrations of each extractant ranged from 0.07 to 0.25 M, to study the effect of concentrations of different extractants on the extraction percent. Simillarly, the expraction kinetics was tested at different shaking time ranged from 5.0 to 180 min at the other optimal experimental parameters. Using Aliquat-336, the effect of <sup>226</sup>Ra radioactivity level was studied within the range from 0.1807 to 1.807 Bq.

Using the optimized conditions, confirmatory test was performed to check the selective separation of <sup>226</sup>Ra from <sup>133</sup>Ba in their mixed standard solution by Aliquat-336.

#### 3. Results and discussion

In this study, we outline the possibility of using extraction scintillation system with application of various cationic (Aliquat-336) and basic (TPPS) and neutral (TOPO) extractants for separation and extraction of Ra from Ba. Hence, no application to "real" sample was attempted, as the intention was to define the optimum conditions for a suitable extraction scheme.

## 3.1. Effect of extractant

Table 1 illustrates the extraction behavior of <sup>133</sup>Ba and <sup>226</sup>Ra by different organic extractants in addition to (SC) cocktail. For <sup>133</sup>Ba, the data shows that the net count rate of each extractant is very close to that of the <sup>133</sup>Ba standard. i.e. insignificant extraction efficiency of <sup>133</sup>Ba (insignificant uptake percentage) from aqueous phase using the three extractants was observed.

For <sup>226</sup>Ra, the results revealed a significant uptake of <sup>226</sup>Ra (43.4 %) by mixture of 0.1 M of Alq-336 with the scintillation cocktail (SC), obviously exceeding its extraction by both of (TPPS + SC) and (TOPO + SC) at the same experimental conditions. In such cases, extraction of <sup>226</sup>Ra with both extractants is almost nil. The three investigated extractants proved to have insignificant effect on <sup>133</sup>Ba extraction while Alq-336 has superior extraction capability over TOPO and TPPS towards <sup>226</sup>Ra.

#### 3.2. Effect of extractant concentration

The dependence of the extractants concentration in organic phase on the extraction efficiency of both Ba and Ra is shown in Fig. 1.

For <sup>133</sup>Ba, the data revealed that the extraction efficiency is not enhanced by raising the concentration of the three investigated extractants from 0.07 to 2.0 M. This means that Ba ions are not capable to form metal complexes with the three investigated extractants even at relatively high extractant concentration.

Similar extraction behavior was observed for <sup>226</sup>Ra ion by TPPS and TOPO at various concentration ranges from 0.07 to 0.20 M of each extractant. The uptake percentages are close to that of the scintillation cocktail (SC) itself.

Promising achievement in the extraction capability of <sup>226</sup>Ra ion was observed by changing the Alq-336 concentration in the



Fig. 1. Effect of extractant concentration on the percentage extraction of radium and barium.

organic phase from 0.07 to 0.15 M which then decreases by further increase in Alq-336 concentration from 0.15 to 0.25 M. Maximum extraction efficiency (E %) reached to 67.7% at 0.15 M of Alq-336 concentration and the given constant experimental conditions similar to that previously shown in Table 1.

Moreover, it is important to point out that the transport of  $^{226}$ Ra ion is based on the spontaneous physical diffusion in addition to the particular chemical interaction due to complex formation mechanism with the embedded Aliquat-336 in the organic phase.

The extraction efficiency increases to the optimal extractant concentration value (0.15 M), where further increase in the extraction efficiency is not observed. This interesting phenomenon is apparently caused by two competing factors: the concentration gradient of the Ra-complex, and the viscosity of used organic phase. As applied by Dzygiel and Wieczorek [20], it is known that the flux (*J*) of the species through an interface layer of thickness (*dl*) is related to its diffusion coefficient *D* and related concentration gradient (*dc*), following Fick's first law:

$$J = -D\frac{\mathrm{d}c}{\mathrm{d}l}\tag{1}$$

The high fluxes can be obtained when a large chemical potential (concentration gradient) and diffusion coefficient are maintained. Nevertheless, the diffusion coefficient depends on the viscosity of extractant in the organic solvent ( $\hat{\eta}$ ) at temperature (T) and the radius (r) of the migrated species through Stokes–Einstein relation:

$$D = \frac{KT}{6\pi \eta' r} \tag{2}$$

From equations (1 and 2), the relation between the viscosity variation and concentration gradient of Aliquat-336 can be derived as follows:

$$\frac{\mathrm{d}c}{\mathrm{d}l} = \left(\frac{-6\pi r J}{KT}\right)\eta' \tag{3}$$

According to Eq. (3), the viscosity of the extractant seems to have direct relationship with its concentration gradient. An increase in Alq-336 concentration leads to growth in the complex



Fig. 2. Illustrative scheme for separation and subsequent determination of radium using Aliquat-336 + SC extraction scintillation system.

flux, however, at concentrations (over 0.15 M) the viscosity of the solution could have a significant effect and might retard the mass transfer of Ra–Alq-336 complex at the interface due to the increases in layer thickness. Thus, by raising the concentration of Alq-336, the amount of  $^{226}$ Ra complex that could be extracted into the organic phase tends to increase, Fig. 1.

In general, the extraction process of all alkaline earth cations including radium is particularly depend on the ionic hydration size of each cation. Ions of smaller hydrated radious tend to displace ions of larger hydrated radius and hence, the extraction affinity series obeys the following sequence [21]:

$$Ra^{2+} > Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+} > Be^{2-}$$

The hydrated ionic radii  $(A^0)$  of Be<sup>2+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup> and Ra<sup>2+</sup> are 4.59, 4.28, 4.12, 4.12, 4.04 and 3.98, respectively.

Based on the previous postulates, the mechanism of the transport of  $^{226}$ Ra ion is proposed in Fig. 2 and can be described as follows:  $^{226}$ Ra in the aqueous media interacts with dissociated chloride ions to form the hydrated chloride complex in the form RaCl<sub>2</sub> 2H<sub>2</sub>O [22]. This hydrated complex is transported by a driving attraction force between the anionic hydrated ion [RaCl<sub>2</sub>(OH)<sub>2</sub>]<sup>2-</sup> and the cationic species of Aliquat-336. The proposed mechanism is quantitatively supported as in the data illustrated in Table 1 which illustrates the extraction uptake of  $^{226}$ Ra using Aliquat-336 (43.4% in organic phase) rather than the other extractants when using the same and/or optimum experimental conditions. However, it seems important to determine complex formation constants for the proposal so far postulated.

Basically, at the interface between aqueous and organic phases, <sup>226</sup>Ra-complex and alq-336 form an ion-pair complex, which becomes neutral. Then, the ion-pair complex diffuses through the interface layer between aqueous and organic phases. Furthermore, Aliquat-336 acts as cationic carrier for <sup>226</sup>Ra ion-pair complex. The carrier–counter–ion complex diffuses completely to the pure organic phase that contains the scintillation cocktail. A total effect of counter-coupled transport process is diffusion of <sup>226</sup>Ra from aqueous phase to organic phase.

# 3.3. Effect of shaking time

Increasing the shaking time may increases the driving attraction force and in turn higher extraction may be achieved. Attempt to check the impact of shaking time on the <sup>226</sup>Ra extraction was



Fig. 3. Effect of shaking time on the percentage extraction of radium and barium.

tested. The concentration of Aliquat-336 extractant was kept at 0.15 M. Radioactivity level for radium was kept at 0.3612 Bq where the Aqueous/Organic ratio was kept at 1/14 ml. Shaking time was changed from 5 to 180 min.

Fig. 3 reveals the effect of shaking time on the extraction behavior of  $^{226}$ Ra using SC alone and its mixture with 0.15 M of Aliquat-336. The data demonstrated a significant enhancement in uptake percentage of  $^{226}$ Ra with increasing the shaking time from 5.0 to 180 min. Maximum uptake percentage was attained after 60 min equilibration time. This may be due to the gradual in-growth in the counter-ion complex till 60 min that may be then dissociated with further shaking time.

## 3.4. Effect of radioactivity levels of <sup>226</sup>Ra

Trials have been performed to test the reliability of the proposed procedure at various radioactivity levels of  $^{226}$ Ra ranging from 0.1806 to 1.806 ml Bq. The data presented in Fig. 4, shows that the maximum standard deviations of the net counting rate in CPM not exceed than 2% particularly at high radioactivity level (1.806 Bq). At low radioactivity level of  $^{226}$ Ra (0.1806 Bq), the calculated standard deviation was 5.0%. These results confirmed



Fig. 4. Effect of Ra-226 radioactivity level on the percentage extraction of Ra by Alq-336.



Fig. 5. Effect of aqueous/organic ratio on the precent extraction of radium.

that the proposed procedure provided high reproducibility and precision with relatively low (acceptable) standard deviation for both high and low radioactivity levels of <sup>226</sup>Ra.

However, gradual decrease in extraction percent was observed, the amount of the corresponding extracted radium increases with the increase of <sup>226</sup>Ra radioactivity level. This is highly dependent on the specific extraction efficiency of the Alq-336 rather than the dependence on the radioactivity level of the available radionuclide radium. i.e. some of radium radionuclides may remain in aqueous phase.

## 3.5. Effect of phase ratio

The area of the interface layer is expected to have an important role affecting the migration flux of  $^{226}$ Ra from the aqueous phase to the organic phase. In this respect, various volume of aqueous phase was mixed individually to the organic phase to get various aqu/org phase ratios. The Aqu/org ratio was changed from 1/14 to 4/11 ml. The data in Fig. 5, show that the uptake percentage increases by increases in the volume of aqueous phase from 1.0 to 3.0 ml then decreases using 4.0 ml. This means that the maximum uptake 78.9 % was achieved at 3/15 phase ratio at which maximum migration flux was obtained.

# 3.6. Selective separation of <sup>226</sup>Ra from <sup>133</sup>Ba

To check the selective capability of alq-336, a mixture of barium and radium was tested under the previous all optimized conditions. Aqueous and organic phases measurements were simultaneously performed to ensure the extraction capability in the organic phase. As shown in Table 2, the extraction percent of alq-336 for both for radium and barium, in organic phase reaches to 74.4 and 0.0 %, respectively. These results are in a good agreement with the corresponding extraction percentages in aqueous phase measurements.

Looking at the literature, it was found that simultaneous determination of  $^{226}$ Ra and  $^{210}$ Pb by LSC was described by Yong-Jae et.al. [23]. Radium and lead were separated together as Ba(Ra)·PbSO<sub>4</sub> co-precipitate, which was dissolved with 0.1 M EDTA solution (pH 9.0). Radium was separated as Ba(Ra)SO<sub>4</sub> co-precipitate by adding ammonium sulfate and adjusting the pH of the solution to 4.2. Lead remaining in the solution was

Table 2		
Selective separation of	of <sup>226</sup> Ra from	<sup>133</sup> Ba

Sample	Net count rate (C/M)	Extraction %	Sample	Net count rate (C/S)	Extraction %	
<sup>226</sup> Ra measurements			<sup>133</sup> Ba measurements	<sup>133</sup> Ba measurements		
Aqueous phase measuremen	nts					
Standard <sup>226</sup> Ra	$74.2 \pm 3.19$	-	Standard <sup>133</sup> Ba	$9.72 \pm 0.29$	-	
Standard. 133Ba	$412.6 \pm 6.6$	-	Standard <sup>226</sup> Ra	N.A	N.A	
Alq <sup>226</sup> Ra/ <sup>33</sup> Ba	$431 \pm 6.8$	24.6 ( <sup>226</sup> Ra)	Alq- <sup>226</sup> Ra/ <sup>33</sup> Ba	$9.74 \pm 0.29$	100 ( <sup>133</sup> Ba)	
Alq - <sup>133</sup> Ba	$411 \pm 6.6$	0.0	-			
Organic phase measurement	ts					
Standard <sup>226</sup> Ra-UG	$94.2 \pm 3.3$	-	UG- <sup>133</sup> Ba-St	$6.105 \pm 0.28$	_	
Alq- <sup>226</sup> Ra/ <sup>133</sup> Ba	$69.9 \pm 3.15$	74.2 ( <sup>226</sup> Ra)	Alq- <sup>226</sup> Ra/ <sup>133</sup> Ba	N.A	0 ( <sup>133</sup> Ba)	
Alq- <sup>133</sup> Ba	$0.7 \pm 1.7$	0.74 ( <sup>133</sup> Ba)	Alq- <sup>133</sup> Ba	N.A	$0(^{133}Ba)$	

Alq (Aliquat-336) concentration of was kept at 0.15 M, Shaking time was kept at 1.0 h, Radioactivity level of radium was kept at 0.3612 Bq. Aq/Org ratio was kept at 3/12 ml.

separated as PbSO<sub>4</sub> precipitate by adding 9 M sulfuric acid. Ba(Ra)SO<sub>4</sub> and PbSO<sub>4</sub> precipitates were suspended in the scintillation gel, and measured. Two different liquid scintillation cocktails, Instagel<sup>®</sup> XF and UltimaGold<sup>TM</sup> AB were used for counting the samples [23].

Another method for the determination of Ra-isotopes has been developed by Manjn et al (1997). Ra is co-precipitated with Ba as sulphate. The precipitate is then dissolved with EDTA and counted with LSC after mixing with a scintillation cocktail. The study of the temporal evolution of the separated activity gives the isotopic composition of the sample, i.e. the <sup>224</sup>Ra and <sup>226</sup>Ra contribution to the total activity was evaluated [24].

The advantages of the modified method elaborated in present work rather than the commonly used methods [23,24] are attributed to the relatively short time with one chemical step for extraction of radium compared with the long term chemical procedures of the other reported method. Selective separation for radium using Aliquat-336 is a considerable advantage over the radium/barium co-precipitation method. The proposed procedure offers directly quantitative measurement of the separated radium by the direct interaction with the internal scintillation cocktail. From the measuring point of view, the separation of <sup>226</sup>Ra from <sup>133</sup>Ba is considered of great advantage during the radiochemical measurements of radium by liquid scintillation counter (LSC) especially when using <sup>133</sup>Ba as yield tracer for radium because <sup>133</sup>Ba interferes with radium.

## 4. Conclusion

Chemical separation steps of radium from barium are still unavoidable for most of measuring techniques; therefore, selective separation followed by subsequent determination of radium by Alq-336 provided a new concept for reliable analytical scheme. The advantages of the modified method are attributed to the relatively short time with one chemical extraction step of radium. The proposed procedure offers directly quantitative measurement of the separated radium by the direct interaction with the internal scintillation cocktail. The combination of extraction with direct scintillation processes solves the heterogeneity problem that often encountered in conventional liquid scintillation counting especially with low radioactivity levels. From the measuring point of view, the separation of <sup>226</sup>Ra from <sup>133</sup>Ba is considered of great advantage during the radiochemical measurements of radium by liquid scintillation counter (LSC) especially when using <sup>133</sup>Ba as yield tracer for radium because <sup>133</sup>Ba is usually interferes with radium.

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