DETERMINATION OF RADIUM IN WATER BY GAMMA SPECTROMETRY USING COMMERCIAL CATION EXCHANGE RESINS: COMPARISON AND VALIDATION

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A series of laboratory tests have been conducted to evaluate the quantitative retention of $^{226}\text{Ra}$ by three different strong cation exchange resins under varying conditions. The influence of the maximum flow rate, which could be obtained with the extraction chromatography columns, was tested. The Radium Selective Complexer (RSC) showed a relatively higher adsorption capacity for radium with an average $^{226}\text{Ra}$ recovery of 96.4%. The effect of increasing the amounts of the competing Ca and Mg ions on the uptake of $^{226}\text{Ra}$ by the three types of resins has been evaluated. The Purolite resin showed a relatively higher adsorption capacity for radium in water samples that have Ca and Mg ions as high as 3000 mg/L. The average radium recovery achieved by the Purolite resin was 90.7%. The influence of Iron (III) on the recovery of radium using the three types of resins was significant. The maximum $^{226}\text{Ra}$ recovery obtained was 89.9% using the Purolite resin. A groundwater sample was analyzed for $^{226}\text{Ra}$ and measured by gamma spectrometry using the three types of resins, and also analyzed by alpha spectrometry and a radon detector (RAD-7) for comparison. The recoveries of $^{226}\text{Ra}$ achieved by the three types of resins were comparable, and the results of comparison with the different techniques were very encouraging for the use of such water softener resins in the extraction of radium isotopes from large number of groundwater samples, when rapid and inexpensive method is needed.

Key words: Radiation Measurements, Radium, Groundwater, Gamma spectrometry, High TDS, Cation Exchange Resin, Saudi Arabia.

1. INTRODUCTION

There has been a growing interest in the development of improved methods for the detection of radium isotopes in water. Radium is usually found in trace amounts in water. So the determination of radium initially requires preliminary
separation and/or preconcentration steps in order to remove elements which might interfere with those processes and also to purify the sample with respect to large quantities of inactive substances [1]. An initial step in radium assay, therefore, is to preconcentrate radium by a variety of techniques including MnO₂ and/or BaSO₄ co-precipitation [2, 3, 4, 5, 6]. Ion exchange and extraction chromatographic resins can also be used for the chemical separation of radium from various sample matrices [7, 8, 9, 10].

Ion exchange resins are polymers that are capable of exchanging particular ions within the polymer with ions in a solution that passes through them. Generally, water purification aims at either to soften the water or to remove the mineral content altogether. The water is softened by using a resin containing Na⁺ cations which in turn binds Ca²⁺ and Mg²⁺ more strongly than Na⁺. As the water passes through the resin, it pulls out Ca²⁺ and Mg²⁺ and releases Na⁺ resulting in a 'softer' water. These resins are mainly used to remove divalent calcium and barium from water. Since radium has the largest ionic radii among unhydrated ions, it is the most preferred among the alkaline earth metals. Accordingly, they are preferentially arranged in the following order: Ra²⁺ > Ba²⁺ > Sr²⁺ > Ca²⁺ > Mg²⁺ [11].

The need to determine radium isotopes in large number of groundwater samples has provoked the necessity to examine and evaluate the use of inexpensive water softeners to analyze a large number of groundwater samples within a short time without tedious radiochemical separation steps. The groundwater might have a high TDS, which contain high concentrations of divalent alkaline earth ions (Ca²⁺, Mg²⁺, etc.) in addition to high iron (III) content. This evaluation was based mainly on the maximum radium recovery that could be achieved by these resins when loading four liters of groundwater sample that contains high concentrations of Ca²⁺, Mg²⁺ and Fe³⁺ with a maximum flow rate through the standard extraction chromatography columns (BIORAD ECONO Columns of 0.9 cm).

2. EXPERIMENTAL WORK

Unless otherwise indicated, all references to water will refer to double distilled water (DDW). The research reported in this study deals with the radium preconcentration on a cation-exchange resin regardless the gamma-ray spectrometric measurements.

2.1. REAGENTS AND ANALYTICAL EQUIPMENTS

Three types of selected commercial resins have been tested during this study. First, Purolite C-100 (Pur.) is an inexpensive strong acid cation exchange resin, with a high capacity crosslinked polystyrene divinylbenzene matrix, and has a high capability for removing Ca, Mg, Mn and Fe ions from influent waters. A package of 30 kg of the resin, in the Na form, was supplied by Veolia Water Company.
Second, Tulsion (Tul.) is a strong acid cation exchange resin, a polystyrene matrix resin with a sodium sulfonate functional group having excellent resistance to oxidizing agents for use in industrial water softening, demineralization. A package of 25 kg was purchased from Thermax Company, India. Third, Radium Selective Complexer (RSC) is barium salt complexed with a styrene-divinylbenzene matrix with BaSO₄ on the polymer adsorbent support. A package of 50 kg was supplied by DOW chemical Company.

Slurry of 12 cm length from each resin was packed into a Biorad Glass Econo column of 0.9 cm diameter, together with polypropylene funnels and Teflon end fittings connected with plastic taps.

All other acids and reagents used in this research including CaCl₂, MgCO₃ and HCl were of analytical grade. Radium extractions were carried out in a column mode using BIORAD Glass Econo columns of 0.9 cm diameter, together with polypropylene funnels and Teflon end fittings connected with plastic taps. Both pH and Total Dissolved Solids (TDS) were monitored using a multi-parameter TDS and pH meter (HACH HQ40). For gamma measurements, standard plastic containers of 60 cm height and 5 cm diameter were used. The radium solution standard was supplied by the National Institute of Standards and Technology (NIST)-(SRM 4967A), and the ¹³³Ba standard solution was supplied by North American Technical Services (NATS)-(EZ-83879-767).

### 2.2. INSTRUMENTS

During the course of this work, all the gamma measurements were carried out using Canberra HPGe coaxial detector (Model GC4020) with a 40% relative photopeak efficiency and 2.0 keV energy resolution at 1332.5 keV energy. The detector is associated with preamplifier model 2002CSL and cryostat model. The detector was connected to a CANNBERA Digital Spectrum Analysis model DSA-1000. The detector is mounted on a vertical cryostat model 7935SL-7 with liquid nitrogen Dewar and surrounded by a lead shield which is internally surrounded by a copper layer. The alpha spectrometric analysis were carried out using a Canberra Alpha Analyst, with a chamber containing a passivated implanted planar silicon (PIPS) detector with an active area of 450 mm². The efficiency of the detector was calibrated against a standard alpha multi-source (67970-121, Analytics Co.). The radon measurements were carried out using a silicon semiconductor detector (RAD7) supplied by Durridge Co.

### 2.3. TESTS METHODOLOGY

Standard resins were prepared by spiking DDW samples with known amount of ²²⁶Ra. The extraction columns were packed with resins, and the sample solutions were allowed to pass through the resins in columns with a fixed flow rate of
2 mL/min, determined with the use of a stop watch and measuring cylinder. This flow rate was determined based on a series of previous tests [12]. In order to ascertain that all the radium has been retained by the resin, the load solution from the first column was allowed to pass through a second resin column to detect the presence of radium by comparison with a similar amount of pure resin. The resin was transferred into a standard plastic counting containers with the help of DDW from a wash bottle, sealed using epoxy and kept aside to achieve secular equilibrium between $^{226}$Ra and its respective progenies for four weeks.

The effect of the flow rates for Purolite resin has been already assessed [12]. In that study, the highest performance was achieved via lowest flow rate (2mL/min), while slightly lower performance was achieved via a 24 mL/min flow rate. For the three types of resins, the effect of maximum obtainable flow rate (about 24 mL/min) on the radium recovery has been assessed. This flow rate was chosen in order to propose the worst case scenario needed for such highly needed production rate. This was performed via using no tap at the end of the column (about 24 mL/min). Double distilled water samples spiked with the same activity of $^{226}$Ra were allowed to pass through the resin columns and the resins were then transferred into the standard counting containers following the standard resin preparation steps.

The effect of the presence of high concentrations of Ca$^{2+}$ and Mg$^{2+}$ was also evaluated. Samples with the same amount of radium activities and TDS value of 3000 mg/L were prepared using tap water, 74% CaCl$_2$ and MgCO$_3$ solutions, and then allowed to pass through the three types of resins in columns. The resins, after the extraction of radium, were then treated similar to the standard resins.

Occasionally, groundwater samples show higher iron content, where particulate Fe in water has the ability to adsorb radium, resulting in an incomplete adsorption onto the cation exchange resin [13]. In order to study the effect of excess iron content in water on the retention of radium by the three different resins, ferric chloride was added to one liter tap water samples spiked with the same $^{226}$Ra activity to have 2 mg/L Fe$^{3+}$ solution. Each sample solution was allowed to pass through the resin columns, and the resins were transferred to the counting containers.

In order to achieve an optimal Standard resin samples were prepared, transferred into the 250 mL standard bottle provided with the RAD-7 equipments, tightly closed and kept in refrigerator at 5°C for four weeks to achieve secular equilibrium. The radon in the samples was measured and the efficiency was determined. Groundwater sample GW30 was vigorously bubbled by aeration to drive off the initially contained radon gas, transferred to the standard 250 mL glass bottle, kept at 5°C for four weeks for the ingrowth of radon daughters and counted. The average net count rate was recorded to determine the $^{226}$Ra activity concentration in the sample.
2.4. QUALITY ASSURANCE AND VALIDATION

Blank samples were prepared and analyzed along with each set of resin samples in order to assess both the potential for sample contamination during analysis and background estimation. Standard samples were also prepared and measured by the radon detector. Accuracy was determined by testing the closeness of the measured samples to its reference values.

A selected groundwater sample coded (GW30) was analyzed to compare between different techniques. One liter of the sample was analyzed for $^{226}\text{Ra}$ using the resins under study by following the same method and measured by gamma spectrometry.

The sample was also analyzed for $^{226}\text{Ra}$ using an alpha spectrometric method described by S. Nour et al., 2004 [5]. In this approach, radium and Ba-133 tracer were co-precipitated with MnO$_2$, dissolved in 2M HCl, loaded into a Diphonix resin column to eliminate other interfering radionuclides and the collected Ra/Ba fraction was then precipitated using BaSO$_4$ micro-precipitation. The filter was mounted on a disk, counted by gamma for Ba-133 recovery and the $^{226}\text{Ra}$ was assessed by alpha spectrometry. The sample GW30 was also analyzed for Ra-226 using RAD-7 detector.

Errors were propagated due to nuclear counting statistics, tracer and volume. Precision was determined by estimating the errors associated with a series of repeated measurements of the standard resins, and was calculated as 2 sigma of the mean of 3 replicates.

3. RESULTS AND DISCUSSION

Radium preconcentration onto a strong acid cation exchange resins was studied at various conditions. The pH of the test solutions was maintained at 1.7 to simulate acidified groundwater samples. The specific activity determinations were basically performed using a comparison method:

$$A_{unk} = \frac{A_{std}}{CR_{std}} \cdot CR_{unk} \quad (1)$$

where;
$A_{unk}$ is the calculated activity of the sample;
$A_{std}$ is the activity of the standard resin;
$CR_{std}$ is the counting rate for the standard resin; and
$CR_{unk}$ is the counting rate of the unknown sample.
3.1. THE EFFECT OF MAXIMUM FLOW RATE ON THE RADIUM RECOVERY

The recovery of $^{226}\text{Ra}$ with respect to the maximum flow rate has been studied for the three different resins. At a maximum flow rate of about 24 mL/min, the Purolite resin showed an average radium recovery of 93.6±3.5%. The Tulsion resin showed an average recovery of 94.6±4.0% while the RSC resin showed a radium recovery of 96.4±4.5% as shown in Table 1 and Fig.1. Although the lower flow rates are rather favorable as they allow the radium to be adsorbed more readily by the resin, good results may still be obtained at much higher flow rates. This is encouraging for laboratories which are obligated to process large numbers of samples within short periods. On the other hand, higher radium recoveries may also be achieved by increasing the amount of resin.

Table 1

<table>
<thead>
<tr>
<th>Resin type</th>
<th>Max flow rate</th>
<th>High TDS</th>
<th>High Fe$^{3+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purolite</td>
<td>93.6 ± 3.5</td>
<td>90.7 ± 3.7</td>
<td>89.9 ± 3.5</td>
</tr>
<tr>
<td>Tulsion</td>
<td>94.6 ± 4</td>
<td>88.5 ± 4.2</td>
<td>87 ± 4</td>
</tr>
<tr>
<td>Radium selective complexer</td>
<td>96.4 ± 4.5</td>
<td>89.2 ± 4.7</td>
<td>84.4 ± 4.5</td>
</tr>
</tbody>
</table>

Fig. 1 – Effect of different tests on the $^{226}\text{Ra}$ recovery, at 1σ uncertainties.
3.2. THE EFFECT OF HIGH TDS ON THE RADIUM RECOVERY

Cation exchange resins don’t have a degree of selectivity for radium over calcium and magnesium which might exist in excess amounts in groundwater with high concentrations. An important study in this research was to estimate the effect of increasing amounts of these two elements on the radium recovery. Results, as shown in Table 1 and Fig.1, demonstrate that the Purolite, Tulsion and the RSC resins had radium recoveries of 90.7±3.7%, 88.5±4.2% and 89.2±4.7% respectively. The influence of coexisting divalent cations to the preconcentration of radium by the resins is significant when the analyzed groundwater samples have a TDS value as high as 3000 mg/L. Increasing the exchange sites on the resin beads, by increasing the resin volume in column, may improve the radium recovery.

3.3. THE EFFECT OF EXCESS IRON (III) ON THE RADIUM RECOVERY

Table 1 and Fig.1 represent the influence of excess Fe$^{3+}$ to the recovery of $^{226}$Ra using the tested resins. The Purolite, Tulsion and the RSC resins had radium recoveries of 89.9±3.5%, 87.0±4.1% and 84.4±4.5% respectively. Ferric ion precipitant clogs the resin beads and causes a decrease in the resin uptake capacity. The addition of ascorbic acid, as a reducing agent, may reduce the Fe$^{3+}$ to Fe$^{2+}$, and increase the retention of radium by the cation resins [12].

3.4. QUALITY ASSURANCE AND VALIDATION

Standard resin samples were prepared and measured by the radon detector (RAD-7). The average activity concentration of $^{226}$Ra was 6.4 Bq/L for the three replicates, and the accuracy was 99.4 % with a standard deviation of the mean of 0.47 Bq. The precision, at 2 sigma for the three replicates, was found to be 0.95 Bq. The groundwater sample coded GW30, which was analyzed for $^{226}$Ra by the RAD-7, showed an average $^{226}$Ra activity concentration of 1.93 Bq/L as shown in Fig. 2.

The activity concentration of $^{226}$Ra in the groundwater sample GW30 analyzed by alpha spectrometry was found to be 2.32±0.16 Bq/L. The gamma spectrometry results performed by the three types of resins for the GW30 showed a good agreement with the alpha spectrometry method. While the alpha method employed is an established and reliable technique, it involves more analysis time and radiochemical separation steps than the gamma method, and the wet chemistry methods require skills to provide consistent and accurate results. Fig. 2 shows the $^{226}$Ra activities in GW30 analyzed by the different techniques.
4. CONCLUSION

The higher radium recovery with the RSC resin, compared with the other resins, may be explained by the presence of barium sulfate on the polymer adsorbent support. For a 12 cm height of the RSC resin packed into a 0.9 cm diameter column, the obtained 96.4 % radium recovery may agree with the 99% radium recovery reported in literature for 200 mL RSC resin and 2.5 cm column diameter [11]. Higher radium recoveries could be achieved by increasing the amount of resin in columns. This would increase the radium penetration distance through the resin bed.

The most significant limitation to the use of these water softener resins in the extraction of radium isotopes from large number of groundwater samples is the presence of excess Ca and Mg ions, and iron (III). This disadvantage can be controlled by optimizing the amount of resin necessary for radium pre-concentration. Tests may be conducted to determine the depth to which radium penetrates into the resin column. Also, a correction factor could be established using radium spiked solutions with different TDS values in order to correct for the recovery decline in relation with the TDS contents. The addition of ascorbic acid to the water sample before loading into the resin column may reduce Fe$^{3+}$ to the dissolved Fe$^{2+}$ [12], and groundwater samples should be routinely analyzed for
their iron content before conducting this procedure, in order to decide the need for ascorbic acid addition.

The $^{226}$Ra activities in the groundwater sample determined by gamma spectrometry were in good agreement with the alpha result. More groundwater samples should be analyzed by both techniques in order to validate the use of these resins in radium extraction.

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REFERENCES