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Determination of ^{226}Ra in water using ion exchange resin and alpha spectrometry study and validation.

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ABSTRACT

The determination of Ra-226 in groundwater samples after preconcentration of radium from the water samples and purification of the extracted radium using diphonix resin column was studied. Co-precipitation tests were carried out to optimize the efficiency of radium adsorption with manganese oxide (MnO_2) and calcium phosphate ($Ca_3(PO_4)_2$). It was found that high recoveries (99%) were obtained with both precipitates for DDW samples. For groundwater samples, the calcium phosphate co-precipitation showed a relatively higher recovery. The ^{226}Ra was efficiently extracted from other contaminants using the diphonix resin, co-precipitated with barium sulphate, filtered and measured by alpha spectrometry. The ^{226}Ra was also analyzed in these groundwater samples using strong cation exchange resin to extract the radium from four liters volume, and the resin was measured by gamma spectrometry. The results obtained showed that the activity concentrations of ^{226}Ra are comparable with those of the alpha method and within measurements uncertainties. For groundwaters, where considerable concentrations of calcium and magnesium ions would be expected, and in case of a large number of samples, the gamma method would be preferable and lower detection limits may also be obtained.

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INTRODUCTION

Ra-226 is an alpha-emitter with a long half-life of 1600 y., and closely follows calcium metabolism in human body with eventual deposition in bones. This might lead to the buildup of Rn-222 and related daughters, causing potential health implications and high degree of radio toxicity due to long exposure hazards. This importance has led to a growing interest in the development of improved methods for the detection of radium isotopes in water. Because low levels of radium are ordinarily encountered in environmental water samples, the determination of radium initially requires one or more preliminary separation and/or preconcentration steps, both to remove elements which may interfere with counting and also to purify the sample with respect to large quantities of inactive substances (Karamanis*et al.*,2006).Therefore, it is necessary to preconcentrate radium by different methods including MnO_2 co-precipitation and/or $BaSO_4$ co-precititation (Eikenberg*et al.*,2001),(Nour*et al.*,2004;Horwitz*et al.*,1993). Ion exchange and extraction chromatographic resins can also be used for the chemical separation of Ra from various sample matrices (Nour*et al.*,2004),(Horwitz*et al.*,1993; Kim *et al.*,2000; Burnett *et al.*,1997). The need to determine the ^{226}Ra in groundwater has provoked the necessity to examine and evaluate the radiochemical procedure reported by S. Nour*et al.* (2004) for the determination of radium in water using diphonix resin (Nour*et al.*,2004) and compare this method with another fast method for the determination of radium in water by gamma spectrometry (El-Sharkawy*et al.*,2013), as a part of an in-house quality assurance and method validation.

2. Experimental work:

2.1 Materials and Apparatus:

Radium extractions from water samples were carried out using Diphonix Resin (50-100 and 100-200 mesh), supplied from Triskem International, 35170 Bruz, France. Standard reference solutions of ^{226}Ra and ^{228}Ra were supplied by the National Institute of Standards and Technology (NIST), (SRM 4967A, SRM 4339B). The ^{133}Ba standard solution was supplied by North American Technical Services (NATS) (EZ-83879-767). The cation exchange resin was used in a column mode with BioRad Glass Econo columns of 0.9 cm diameter, together with polypropylene funnels and Teflon end fittings connected with plastic taps. All gamma radioactivity

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measurements were carried out using a Canberra HPGe coaxial detector with relative photo-peak efficiency of 40% for the 1332 keV line of ^{60}Co. The germanium detector was connected to a 8192 multichannel analyzer with counting capacity of 228 counts per channel. 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 mm^2. The efficiency of the detector was calibrated against a standard alpha multi-source (67970-121, Analytics Co.) using the certified activity of the measured radionuclides. All other chemicals used in this study, including $KMnO_4$, isopropanol, ammonium sulphate and different mineral acids were of analytical grade.

2.2 Co-precipitation with Manganese Oxide:

The preconcentration of radium (Ra-226) via adsorption onto MnO_2 has been carried out from five water samples (DDW) spiked with a fixed known amount of ^{226}Ra and ^{133}Ba using a calibrated micropipette. The $RaMnO_2$ precipitate was dissolved in HCl, and the solution was measured by gamma spectrometry to determine the radium recovery. The radium recovery was determined by the comparison of the net count rate from the sample at the 609 keV gamma energy line with that of a standard water solution spiked directly with the same amount of ^{226}Ra at the same conditions (container, volume of solution, detector and counting time).

2.3 Co-precipitation with Calcium Phosphate:

The preconcentration of radium (Ra-226) via adsorption onto $Ca_3(PO_4)_2$ has been carried out from five water samples (DDW) spiked with a fixed known amount of ^{226}Ra and ^{133}Ba using a calibrated micropipette. The water sample was poured into 2000 ml glass beaker and was acidified with 10 ml aliquot of Conc.HNO_3. The sample was stirred vigorously to remove CO2, and then the same known amount of Ra-226 and Ba-133, 1 ml of 1.25 M $Ca(NO_3)_2$ were added, and the beaker was covered with watch glass and boiled for 30 minutes with stirring. The sample solution was left to cool, 20 ml of 1:9 phosphoric acid were added and NH_4OH solution was added to precipitate the alkaline earth phosphates at pH=9 as shown in **Figure 1**. The precipitate was digested on a sand bath with slow stirring for 1hr, and then allowed to settle **Figure 2**. The supernatant was decanted, the precipitate was separated by centrifugation, dissolved in 1:1 nitric acid and transferred to the counting container, adjusted to the standard volume and measured by gamma spectrometry (Environmental Measurements Laboratory, 1997; Uranium and Thorium in Water,2011). The radium recovery was determined by the comparison with the standard radium solution as described in sections***3.1***, ***3.2***.

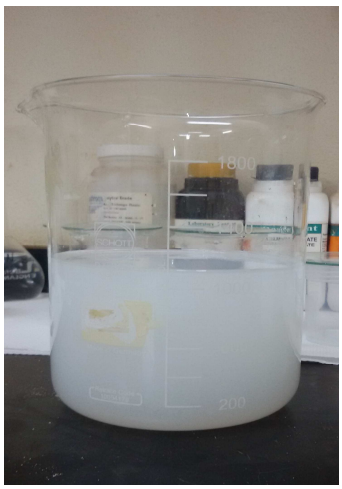

Figure 1Figure 2

Fig. 1 and 2: The calcium phosphate precipitate .

2.4 Comparison of Co-precipitations using Groundwater Samples:

In Saudi Arabia, groundwaters may contain high concentrations of divalent alkaline earth ions (Ca^{2+}, Mg^{2+}, etc.). The average value of total dissolved solids (TDS) in the investigated groundwater samples was 1984 mg/L, which may have some effects on the co-precipitation of radium. Three groundwater samples were used in this comparison test, where one liter of each sample was spiked with the same amount of ^{133}Ba that was used in the previous tests, and radium was co-precipitated with both methods by following the same procedure steps. The dissolved precipitates were transferred to the standard counting containers, measured by gamma spectrometry (HPGe detector), compared against a standard ^{133}Ba water solution and the ^{133}Ba yield was evaluated.

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2.5 Analysis of Groundwater samples using Alpha Technique:

Six groundwater samples were selected for the analysis of Ra-226 following the procedure described by S. Nour *et al*.(2004), with some modifications. In this approach, ^{226}Ra and ^{133}Ba tracer were co-precipitated with $Ca_3(PO_4)_2$ and dissolved in nitric acid, as described in sec.2.3. The dissolved precipitate was evaporated to dryness and wet ashed to white ppt. by the addition of 5 ml HNO_3 and few drops of H_2O_2 and evaporate to near dryness again. The residue was dissolved in 2M HCl and loaded into a Diphonix resin column to eliminate other interfering radionuclides, and the column was washed three times with 5mL of 2M HCl. The Ra/Ba fraction was collected and precipitated using $BaSO_4$ micro-precipitation by adding $(NH4)_2SO_4$ and isopropanol in a tube, mixed well and allowed to stand in an ice bath for 30 min before vacuum filtration (Maxwell and Culligan,2012). The filter was mounted on a disk, counted by gamma for the ^{133}Ba recovery and the ^{226}Ra is assessed by alpha spectrometry. The chemical recovery was determined from the ^{133}Ba yield using the 384 keV gamma energy line, and determined by comparison with a previously prepared standard Ba-133 under the same conditions (e.g. concentration, geometry, counting time).Ra-226 was determined by the formula:

$$A_{\text{Ra-226}} = \frac{N}{Eff \times Y \times V}$$

Where : N is the net count rate (cpm), Y = ^{133}Ba (Ra) yield expressed as a fraction, V is the sample volume.

2.6 Analysis of Groundwater samples using Gamma Technique:

The radium isotope ^{226}Ra was determined in the water samples using the procedure described by A.El-Sharkawy*et al*.(2013). Four liters of each sample were allowed to pass through the purolite resin packed columns, the resin was transferred to standard counting containers and the containers were tightly sealed for four weeks to allow secular equilibrium between ^{226}Ra and its decay products. The efficiency calibration of the germanium detector for the Ra-226 was carried out using standard samples. Known activity resins were prepared by spiking water (DDW) samples with known amount of ^{226}Ra. The spiked resin samples containing a known amount of the radionuclide of interest were used to provide an identical matrix with a known activity, and all other conditions were followed typically (flow rate, resin volume, counting time, geometry). The ^{226}Ra activities were determined via its daughters ^{214}Pb and ^{214}Bi through the gamma energy lines 295.22, 351.93 and 609.31 keV. The calculated specific activities were basically performed using a comparison method:

$$A_{unk} = \frac{A_{std}}{CR_{std}} \cdot CR_{unk}$$

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.

2.7 Quality Assurance:

For quality assurance and validation purposes, blank samples were prepared in the same manner as the corresponding samples, and measured for background estimation and detection of any contamination. Reference water samples were determined using the same analysis and measurement protocol, and were compared against their certified values to test the closeness of the measured samples to its reference values.

For the estimation of uncertainty, errors were propagated due to nuclear counting statistics, tracer and volume.

RESULTS AND DISCUSSION

In the following sections, the results of the co-precipitation tests, the alpha and the gamma measurements will be represented.

3.1 Results of Co-precipitation Tests:

The efficiency of co-precipitation (radium recovery) was estimated as the ratio of the ^{226}Ra average count rates in the 609 keV gamma energy line to those of DDW sample spiked with a typical ^{226}Ra activity in the same conditions (volume of solution, detector, counting time, measuring container). The average radium recovery was 99.5%, ranging from 99.27 to 99.75%, while for $Ca_3(PO_4)_2$, the average radium recovery was 99.3%, ranging from 99.11 to 99.59%, as shown in **Figure 3**.

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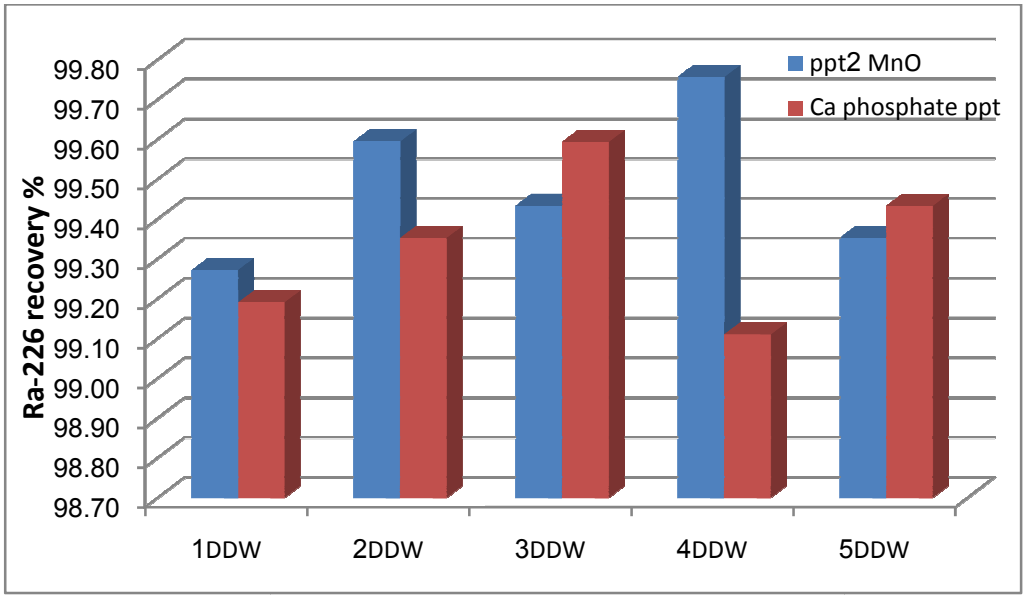

Fig. 3: Radium co-precipitation with MnO2 and $Ca_3(PO_4)_2$

3.2 Results of Comparison Tests:

The effect of calcium and magnesium ions in co-precipitation processes is much stronger when their concentrations exceed 1g/L which may result in lower radium recoveries (Bojanwski *et al*.,2005).

The primary focus of this test was to evaluate the co-precipitation of radium with both MnO_2 and $Ca_3(PO_4)_2$ from groundwater samples that contain different concentrations of TDS which may have an effect on the efficiency of co-precipitation due to matrix interferences in these groundwaters.The efficiency of co-precipitation (Ba-133 yield) was estimated as the ratio of the ^{133}Ba average count rates in the 384 keV gamma energy line to those of DDW sample spiked with a typical ^{133}Ba activity in identical conditions (volume of solution, detector, counting time, measuring container).

For the MnO_2 co-precipitation, the average Ba-133 recovery was 92.9% while for $Ca_3(PO_4)_2$, the average barium recovery was 98.1%, as shown in **Figure 4**.

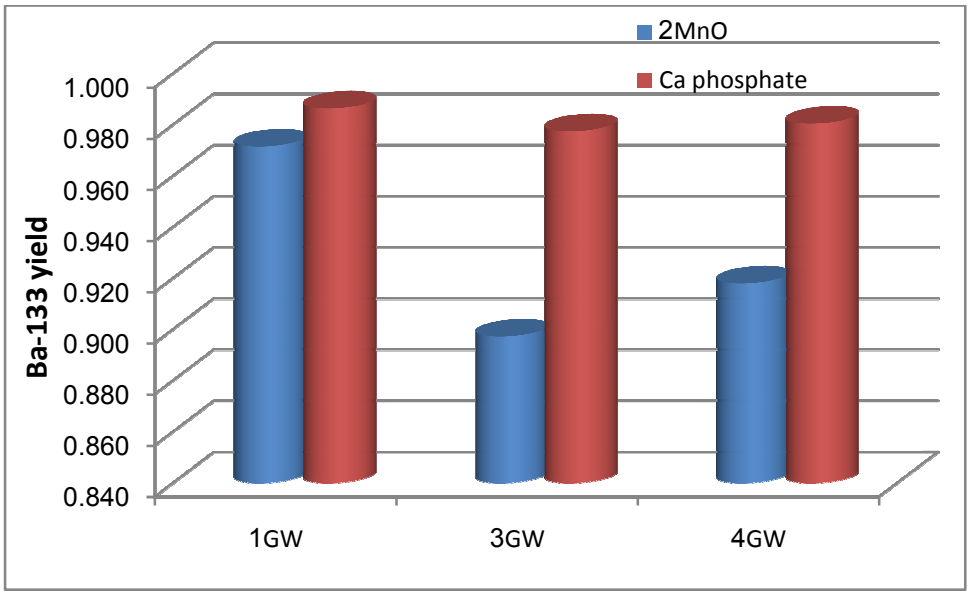

Fig. 4: barium-133 recovery from MnO2 and $Ca_3(PO_4)_2$ in groundwater samples

These results show that it would be more suitable to use the calcium phosphate co-precipitation for the preconcentration of radium in groundwater samples, as the presence of higher calcium and magnesium ions would have less effect on the efficiency of co-precipitation.

4.3 The Alpha and Gamma Analysis Results:

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Following the procedure described by S. Nour *et al*. (2004) , six groundwater samples (that have been used in the previous tests) were analyzed for Ra-226. The co-precipitation step was carried out using calcium phosphate, as a result of the obtained recoveries in sections ***3.1*** and ***3.2***. The sample solution in 2M HCl was allowed to pass through the diphonix resin, and the collected radium-barium mixture was precipitated with barium sulphate, filtered and measured by alpha and gamma spectrometry. Four liters from these groundwater samples were also analyzed for Ra-226 following the gamma method reported by A.El-Sharkawy*et al*.(2013), as described in sec.2.6. The Ra-226 activity concentrations obtained by both methods are presented in **Table 1**.

Table 1: Ra-226 activity concentrations in groundwater samples analyzed by alpha and gamma spectrometry with 1σ uncertainties.

	Alpha results		Gamma results	
	Ra-226 (mBq/L)	±	Ra-226 (mBq/L)	±
WG1	293.5	12.3	284.9	17
WG2	174.8	9	181.3	8.1
WG3	328.6	14.7	333.3	19.9
WG4	121.3	5.5	110	6.5
WG5	58.2	3.1	66.7	3.2
WG6	69.5	3.8	-	

As shown in table, the activity concentrations of Ra-226 analyzed by the gamma method are in good agreement with those analyzed by alpha spectrometry, as shown in **Figure 5**.

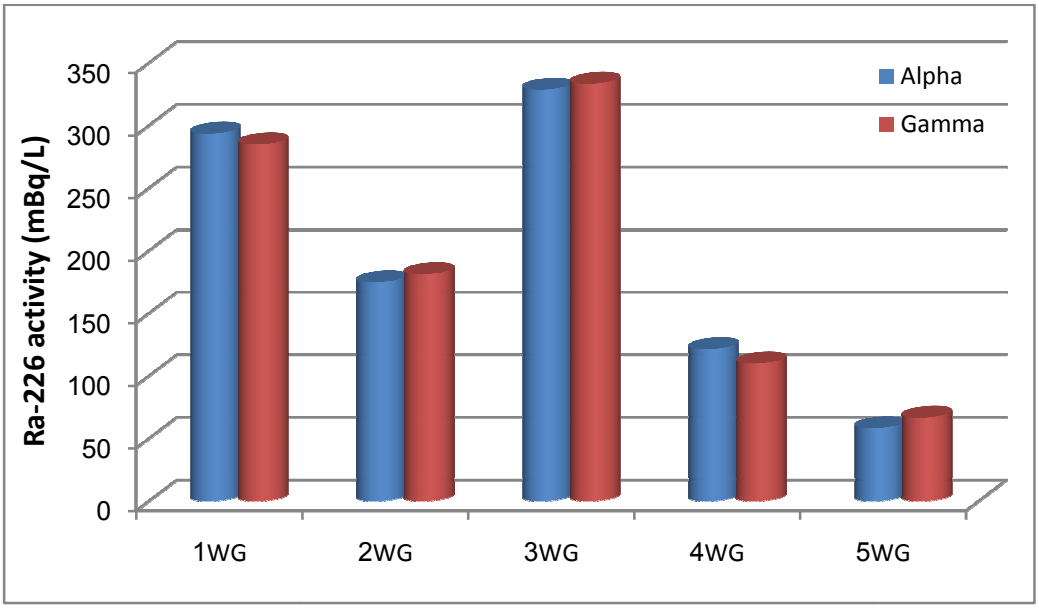

Fig. 5: Ra-226 in groundwater samples analyzed by Alpha and Gamma methods

5. Conclusions and recommendations:

- Co-precipitation tests were carried out to optimize the efficiency of radium adsorption with manganese oxide (MnO_2) and calcium phosphate ($Ca_3(PO_4)_2$). It was found that high recoveries (99%) were obtained with both precipitates for DDW samples. For groundwater samples, the calcium phosphate co-precipitation showed a relatively higher recovery.
- For the calcium phosphate, the precipitation process could be achieved by adding NH_4OH slowly until the white precipitate appears without the need ofa pH meter as in the case of MnO_2 precipitation steps , and thedecantation process could be done easier than that of the MnO_2.
- The radioanalytical techniques used for the analyses of radium isotopes and measurements by alpha and/or beta spectrometry require a considerable amount of time from the preconcentration of radium to the alpha or beta measurements, and depend on the analyst skills. In situations where a radiological monitoring is required, the number of samples acquired may be in the hundreds and the ability to provide accurate data for such a volume of potentially diverse samples in a short time period is diminished. So, this method for the determination of radium-226 by alpha spectrometry could be utilized only for a few samples.
- For groundwaters, where considerable concentrations of calcium and magnesium ions would be expected, the gamma analysis of radium isotopes using strong cation exchange resin to extract

the radium from four or five liters of the samples has shown a comparable results with those of the alpha method, and in case of a large number of samples it would be preferable, and lower detection limits may also be obtained.

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