Radium Removal/Monitoring in the SNO Experiment
Using MnO$_2$ XAD-7 Resin
Report on work done at CRPP

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INTRODUCTION

The SNO experiment requires that radium (Ra), both from the thorium-232 and uranium-238 chains, be removed and monitored. The most promising method appears to be trapping it in a columnar operation on an adsorber material such as MnO_2 coated resin beads. While the performance of MnO_2 coated fibres had been extensively demonstrated in both fresh water and sea water[1,2], the decision to use beads was based on work by B. Gershey[3] and A. Ferraris[4]. The beads they were using were manufactured by Seakem. It was found that the MnO_2 beads met most of the criteria for a suitable adsorber. One of the most desirable characteristics is a high affinity to the adsorbed component as compared to that of water ie: high distribution coefficient - K_D; where K_D is defined as :

$$K_D = \frac{V_w}{V_r} \times \frac{A_r}{A_w}$$, where V_w is the volume of

water, V_r volume of the resin, A_r activity of the resin and A_w activity of the water[5]. Other requirements are: a short time constant for essentially complete extraction (defined by residence time, calculated by dividing the total bed volume by the flow rate); efficient emanation of radon (^{220}Rn and ^{222}Rn); low background in terms of uranium and thorium; and the capability of extracting Ra from water in the presence of 0.2 - 2% NaCl or $MgCl_2$. This last characteristic is of particular importance in the SNO experiment

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where a chlorine source will be added to the water to enhance the neutral current reaction. At present, sodium chloride and magnesium chloride are being considered as chlorine sources.

This report discusses the preparation of MnO_2 XAD-7 beads as well as other experimental parameters which were established for optimum Ra extraction. Ra elution and Rn emanation off MnO_2 coated beads will be discussed in a separate report.

It was decided to prepare our own version of the resin (CRPP MnO_2) for many of the studies because of the high cost associated with Seakem resin ($2/gram). Also, preparing the resin inhouse allowed for better quality control. The method used to prepare the coated beads was adopted from B. Gershey (personal communication). He found that XAD-7 resin can be rapidly coated with a uniform and mechanically stable coating of 5% by weight MnO_2 upon treatment with potassium permanganate solution at room temperature. XAD-7 is a macroreticular resin, composed of a co-polymer of acrylic acid and divinyl benzene and is typically used for adsorbing non-polar organic compounds from aqueous systems. It contains no ionically functional groups[6] which makes it ideal for an oxidation reaction with $KMnO_4$. According to Gershey, these acrylic beads have uniform packing and flow characteristics, giving them a distinct advantage over the MnO_2 coated acrylic fibres. Electron microscope size distribution analysis performed at CRPP on 250 beads indicated a normal size distribution with an average diameter of 0.38 mm and a sigma of 0.04 mm.

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Studying Ra adsorption, Gershey used 95 mL of resin in a 33 cm x 1.9 cm column and a flow rate in the downward direction of 150 mL/min (1.6 bedvolumes per minute, residence time of 38 sec.). Other experimental parameters included a temperature of 20 °C, sample volume of 2 - 3 litres of water and a radium content of 4870 Bq (approx. 132 ng). Radium was completely recovered from the spiked freshwater samples within the first half (15 cm) of the column.

Ferraris used a two column procedure - the first contained 0.3 g of dry MnO_2 resin in a 5.85 mm x 130 mm column and the second contained 11 g of MnO_2 resin in a 18.37 mm x 220 mm column. The first bed performed the primary extraction while the second was used to act as a monitor of the effluent from the first bed. In all runs, 100 mL water was passed over columns, followed by a 100 Bq/L [228]Th spike solution and then another 100 mL of water.

When the spike was adjusted to pH 7 using potassium hydroxide and dilute nitric acid, 92% and 70% Ra extraction efficiencies were achieved at residence times of approximately 15 seconds and 1 second respectively. In another run, two sources were adjusted to a pH between 6.5 and 7.0 using sodium hydroxide; one contained 0.25% dissolved NaCl and the other did not. 100% and 75% extraction efficiencies were achieved for the no salt run at residence times of 6 seconds and 1 second respectively, somewhat higher than the previous run. With 0.25% NaCl, 93% extraction efficiency was achieved at 8 seconds but only 50% extraction

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efficiency was achieved at 1 second. These inconclusive results prompted us to do further investigations.

Ferraris also performed K_D studies in a batch style experiment where he established the K_D for water-MnO_2 to be about 10^5.

The work done in the CRPP laboratory has been carried out using both Seakem beads and the "CRPP" version in 1.5 mL and 1 L columns. Ultimately, the design calls for columns containing about 2 litres to achieve the greatest sensitivity of 1 disintegration per day per tonne of water. Since flow rates of 100 L/min are required it is imperative that the adsorber performs with an acceptable efficiency under these conditions. The first parameter to be established is the K_D value, both for water and for water containing a chlorine source. Other parameters to be studied have to do with kinetic effects: extraction of Ra onto a resin column at different flow rates, in different column geometries, in different directions through the column and at different levels of Ra. It is important that the material can be packed in such a configuration that will allow the extracted species to be adsorbed in a well defined region of the adsorber. Some points to consider are the length to diameter (L/D) ratio and the bead size to diameter ratio. The minimum length to diameter ratio should be 20:1[5] and the minimum bead size to diameter ratio should be 30:1 (personal communication with Bob Burk, Carleton University, Analytical Chemistry Center). In practical terms what is appropriate for optimal extraction kinetics (i.e. small particle

size for maximum surface area and a long column) is not the best choice for low impedance and good flow rates.

Radiation background was done on the MnO_2 resin at Guelph University and Queen's University. XJ. Wang (Guelph), using an electrostatic counter, analyzed the background for Seakem to be <23 ^{220}Rn per hour per kg and using NAA, found the background for CRPP to be <1 ^{220}Rn counts per hour per kg (<52 ppt ^{232}Th). The WET lab at Queen's (H. Lee) measured ^{222}Rn from Seakem to be <7.8 counts per hour per kg.

EXPERIMENTAL

Cleaning Procedure

All plastic and glassware used for Ra experiments were washed/sonicated using ≈1:20 Radiacwash solution for 1-2 hours. After a hot water rinse, non-nylon components were washed/sonicated in 10% HNO3 for about 30 minutes. The final rinse of all labware was with 18 Megohm water.

Reagents for Resin Preparation

- Amberlite XAD-7 resin 20-50 mesh (Rohm and Haas). The average particle diameter in dry form is 0.30 to 0.45 mm. The surface area is 450 square meters/gram and the average pore diameter is 80 Angstrom units. The values for hydrated beads will be different due to swelling. It is supplied as moist, fully hydrated beads and is used in this form for the preparation of MnO_2 beads.

- Amberlite XAD-8, (Rohm & Haas): same as above, but average pore size is 250 Å.

- Potassium Permanganate, analar grade (BDH)

- 18 Megohm grade water (Millipore or Biolab), referred to as UPW (ultrapure water)

Other Reagents Used

- Seakem MnO_2 XAD-7 resin

- NaCl Anachemia reagent grade

- $MgCl_2$ hexahydrate, BDH analar grade

- EDTA-Na4, BDH analytical grade

- ^{226}Ra 1 uCi source (Radio-isotopes) supplied in 1 N HNO3

This source was diluted to make an intermediate stock solution of $\approx$ 20,000 ng/L (pH $\approx$ 2.5) using UPW. The spiking was conducted after a further $\approx$ 1:100 dilution.

Counting Instrumentation

The counter used was a germanium gamma detector with a window diameter of 7.5 cm. In the early studies columns were allowed to stand for 10 days (for secular equilibrium to be achieved) and the spectrum analyzed for the 352 Kev ^{218}Pb to ^{214}Bi decay peak after counting for 3 hours. Later on in the experiments, in order to save time and because of the concern that the valves on the column were not leak tight (thus allowing Rn gas to escape), the columns were counted immediately for 24 hours at 185 Kev to analyze the ^{226}Ra decay peak directly.

For the K_D studies, a calibrated spike was not necessary since only relative activities were compared. However, for the fast spiking studies, a calibration spike was necessary so that the Ra extraction efficiency could be calculated. Since the gamma counter is sensitive to geometry, the spikes used for calibration had to be measured in a configuration similar to the columns we were using. Two sample holders (one from polycarbonate and one from teflon) were designed with the same geometry and dimensions as the 1.5 mL column to contain the spikes. The sample holder served both as a calibration for an absolute number for amount of Ra present and as a check on the variability of the counter. Typical numbers can be seen in the fast spiking results section, Table 9.

Except where otherwise noted, efficiencies for all fast spike experiments were calculated by dividing the column activity by the the activity of the calibrated spike (see Table 10). All activities (both fast spiking and K_D) were corrected for background. Background measurements were obtained by counting an unspiked MnO_2 resin column under identical conditions to the spiked column, then subtracting this value from the spiked value.

Preparation of MnO2 XAD-7 Resin

Method

1/ 1.25 kg of XAD-7 resin was placed in a 20 L polyethylene pail with the bottom cut out and a 0.0117" (0.3 mm) polypropylene sieve cloth placed on using the outside piece of the bucket to hold the sieve in place. The resin was then washed thoroughly

with ultrapure water (UPW) to remove fines and wash off any solvents the resin may contain.

2/   Without using any additional water, the resin was then transferred to a 20 litre polyethylene pail and 5 litres of 0.25 M $KMnO_4$ solution were added. The resin was stirred on an orbital shaker for 2 hours at 100 RPM.

3/   The mixture was returned to a clean 0.0117" sieve pail and rinsed with ultrapure water until the effluent became clear. This was achieved by lowering the sieve pail into a 50 L closed pail, covering the resin with a sufficient quantity water, then agitating the sieve pail in a washing-machine type motion. Water was continually added while the effluent was drained from the bottom of the pail.

4/   The resin was transferred to 2 x 3L and 2 x 2L pyrex glass baking dishes, spread out in an even layer no more than an inch thick and covered with aluminum foil cut with thin slits to allow moisture to escape. It was dried for approximately 16 hours at 80 °C.

5/   The material was sieved through a 0.029" (0.75 mm) sieve to remove large particles, then through a 0.0117" sieve to remove small particles and each fraction was weighed.

6/   The small fraction was discarded and the other fractions were
      stored separately in ziplock bags.

Notes about the resin

1/   If not properly mixed, the resin is not completely coated by
      MnO_2. This can be checked by cutting a bead in half and
      looking for a white center. This was experienced when a
      double batch was tried in the 20 L pail. The actual thickness
      of the MnO_2 coating on this particular batch was not measured.
      All other batches of MnO_2 resin were coated all the way
      through.

2/   The fraction used for our studies is 0.0117" - 0.029" (.3mm -
      .75mm) dry resin, which is the main fraction.

3/   The final yield of main fraction resin out of the total
      finished material is about 80% (Table 1).

4/   The resin should be stored dry because of possible microbial
      growth and leaching of MnO_2 into low ionic strength (ie
      ultrapure) water over time. Drying the beads may also enhance
      the strength of the bonding of the precipitate to the polymer
      (Gershey, personal communication).

5/   The resin swells when wet so it must be soaked in water for at
      least 2 hours before use. The expansion factor for dry volume

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to wet volume is 2.2. In terms of dry weight to wet volume
the expansion factor is 2.8.

TABLE 1

Yield of MnO$_2$ batches.

batch #	1	2	3	4	5	6
coarse	92g	101g	88g	108g	98g	114g
medium	472g	561g	441g	511g	457g	505g
fine	22g	18g	18g	18g	23g	21g
total	586g	635g	547g	637g	578g	640g
%yield of medium	81%	81%	81%	80%	79%	79%

Dry Resin Fractions

coarse > 0.029"
medium > 0.117", < 0.029"
fine < 0.0117"

K_D Studies

Outline of Study

A column (see preparation of columns for details) containing 1.5 mL wet resin was spiked with 2 ng of ^{226}Ra (about 1/10 of breakthrough capacity, Gershey)[3] and counted. Large volumes of water were then eluted through the column and the amount of activity left on the column was determined. While another option would have been to pass water from the spiked column through a second column to measure the activity, this activity would have been too low to measure on the available gamma counter. The amount of spike could not be increased by too much since we did not want to work at the saturation level of the resin.

Preparation of Columns

Both Seakem and CRPP MnO_2 XAD-7 were used for the study. Columns were prepared by placing 1.5 mL swelled resin in a polycarbonate column containing polysulfone frits to hold the resin in place and two polypropylene valves to control flow rates. The dimensions of the portion of the column where the resin resides were 1.5 cm in length and 1.1 cm in diameter. This particular geometry was designed to achieve maximum efficiency of the gamma counter for the 1.5 mL amount. The amount of ^{226}Ra used (2ng) was high enough to allow a less than 5 % counting error for 3 – 24 hours counting and small enough to be below the capacity of the

resin and to allow for easy disposal. The spike was prepared by diluting 100 μl of an intermediate stock solution of 20,000 ng/L in 30 mL of UPW. Spike was added to the column using a plastic syringe at a flow rate of 1-3 mL/min, then flushed with 30 mL UPW. This flow rate gave a residence time of 30 to 90 seconds which is well within the desired residence time of 15 to 20 sec based on the work of A. Ferraris. The amount of water put through the column varied between 20 L (ie. $MgCl_2$ study) up to 380 L for water.

Elution Set-up

Once spiked, water or potential interference solutions (NaCl, $MgCl_2$ or EDTA) were passed through the column in an upflow direction using either a teflon diaphragm pump or a peristaltic pump at approximately 6 mL/min to give a residence time of 15 seconds. The teflon pump is not designed for very low flow rates so the flow rate fluctuated from 6 to 10 mL/min. The column was checked for decreased activity after each 20 - 50 L elution cycle.

Seakem material was used to check the K_D with water, 1% NaCl, 1% $MgCl_2$ and 100 ppm EDTA. Three different batches of CRPP resin were checked only with water. For the water experiments, eluates from both Seakem and CRPP batches were analyzed for leaching of contaminants into the water by measuring Mn, K, pH, and electrical conductivity (EC). Elevated manganese levels would point to degradation of the resin. Potassium levels would indicate how well the resin was cleaned of potassium permanganate. In particular,

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the presence of ^{40}K is not desirable since it could act as a neutron capture source. A change in pH and EC would substantiate any breakdown in the resin. (Also, it was thought that MnO_2 would effect the pH of water passed over it.)

Small Scale Fast Spiking

This study was designed to look at Ra extraction efficiency at different flow rates. However, other parameters such as spike concentration (2-20 ng), direction of flow through column, column geometry (L/D of 1.4 vs L/D of 10) and interfering chemicals were also studied.

Method of Study

"Short" Columns

In this experiment, 1.5 mL wet resin was packed into regular geometry columns ("short" column, 1.5 cm x 1.1 cm, L/D of 1.4) and a spike solution of ^{226}Ra passed through either 1 column in an upflow or downflow direction or 2 columns placed in series in an upflow direction. The two column procedure was used to provide an alternative method for determining efficiency. This method is appropriate if the concentration of the initial spike solution cannot be accurately determined.

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Spike solutions were prepared in a polyethylene carboy by adding 1000 μl of a 20,000 ng/L intermediate stock solution of ^{226}Ra to 10 L of UPW. A teflon tube (1/4") was placed in the carboy and connected to a teflon diaphragm pump. Another teflon tube from the pump was connected to the bottom (input) of the column and a second tube was connected to the top (output) of the column. Two columns were tested in a downflow direction (input at top, output at bottom). All fittings used were 1/4" nylon Swagelok. The pump was then set for the desired flow rates. Once most of the solution had passed through the column, the carboy was tilted on its side so the remainder of the spike could be pumped. Then, 1 L of UPW was added to the carboy and pumped through the system at the same flow rate so that the lines, etc, could be rinsed of spike. Except for the spike amount, all fast spike experiments were set up in this fashion.

For experiments with one column only, flow rates of 5, 50 and 100 mL/min (3, 33, and 67 bedvolumes/min) were tested. Flow rates of 55, 100, 150, and 200 mL/min (37, 67, 100, and 133 bedvolumes/min) were used for the two column run.

"Long" Columns

Narrow geometry columns ("long" columns, 6 cm x 0.6 cm, L/D of 10) were packed with 1.5 mL wet MnO$_2$ resin. The spike solutions were prepared by adding 100, 500 and 1000 μl of 20,000 ng/L

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intermediate spike solution to obtain 2, 10 and 20 ng of ^{226}Ra in 10 L UPW. Flow rates of 2, 8, 30, 50 and 100 mL/min (1, 5, 20, 33 and 67 bedvolumes/min) were used. The 20 ng studies were conducted both in the upflow and the downflow mode.

MnO$_2$ beads from the narrow geometry column had to be transferred to the regular geometry column for counting purposes. This was achieved by removing valves and insert frits from the narrow geometry column and carefully transferring the resin to a regular geometry column.

MgCl$_2$ interference

A spike of 10 ng ^{226}Ra in a 1% MgCl$_2$ solution was passed through a narrow geometry column containing 1.5 mL wet MnO$_2$ resin in an upflow direction.

The ^{226}Ra solution was prepared by adding approx 8 L of UPW to the carboy, then adding 500 μl of intermediate ^{226}Ra solution (20,000 ng/L). To this, 427 g of MgCl2.6H2O (weighed out in a dry hood) were added. The solution was then made up to 10 L with UPW. The experiment was carried out at various flow rates; 8, 50, 100, 160 mL/min (5, 33, 67, 107 bedvolumes/min).

EDTA Interference

Solutions of 1ppm, 100 ppb and 1 ppb EDTA-Na4 in 10 L of water were spiked with 10 ng ^{226}Ra and passed through narrow geometry 1.5 mL MnO$_2$ columns at various flow rates. 1ppm was tested at 7, 50,

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100 mL/min; 100 ppb tested at 50 and 100 mL/min; and 1 ppb tested at 100 mL/min.

Variation to MnO$_2$ Beads

Two variations on the XAD-7 MnO$_2$ resin were also tested. XAD-8 MnO$_2$ resin, prepared in an identical fashion to the XAD-7 resin, was designed to check the effect of enlarging the pore size of the inner bead porosity on Ra extraction kinetics. Also, testing of the 0.0117"-0.0138" dry fraction of the regular CRPP resin was designed to check the effect of varying bead diameter/column diameter ratio on the Ra extraction efficiency. These two resins were tested only at one flow rate (100 mL/min) and one spike concentration (10 ng in 10 L).

Large Scale Spiking

Two columns were packed with 1 L of hydrated MnO$_2$ resin each and set up in series at the 1 tonne test facility (I. Blevis, unpublished report). Then, 1 tonne of water containing a spike of about 0.3 Bq Ra224 was passed through the columns at 4, 8, 12 and 24 L/min. The columns were counted on the TPC counter (I. Blevis).

The above [224]Ra spike was prepared by passing a 1 mL solution containing 1.98 Bq [228]Th in 7M nitric acid on an anion exchange resin: 1 mL of AG 1-X8 (100-200 mesh, hydroxide form) wet resin was packed into a column made from a narrow disposable plastic pipet. It was subsequently washed with 5 bed volumes of 1 M NaCl and 5 bedvolumes of 7 M nitric acid

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to convert it from the hydroxide form to the nitrate form.

Following the Th spike the column was eluted with about 5 bedvolumes of 7 M nitric acid to remove the 2 Bq of ^{224}Ra. Approximately 1.5 mL of this spike was used to spike the 1 tonne tank. This small volume of acid added to 1.tonne of UPW would not have any effect on the pH of the water.

RESULTS

K_D Studies

TABLE 2

Seakem MnO_2

Volume of Eluant	Counts/3 hrs
0 L	10585 ± 337
20 L	10942 ± 345
20 L	11284 ± 352
40 L	8916 ± 330
40 L	11428 ± 343
40 L	9978 ± 345
40 L	9735 ± 339
40 L	10250 ± 330
40 L	10430 ± 334
40 L	10080 ± 327
40 L	10504 ± 346
20 L	10342 ± 332

TABLE 3

CRPP MnO$_2$

Volume Eluant	Counts/24hrs		
	CRPP I	CRPP II	CRPP III
0	20267 ± 1384	18780 ± 1362	16682 ± 1341
20 L	23100 ± 1311	18661 ± 1203	18427 ± 1271
20 L	19819 ± 1264	16021 ± 1201	19985 ± 1167
20 L	23369 ± 1224	18517 ± 1217	20513 ± 1099
50 L	18462 ± 1224	18166 ± 1064	20712 ± 1083
50 L	223759± 1041	20503 ± 1078	20377 ± 1054
50 L			19100 ± 1100

TABLE 4

1% NaCl on MnO$_2$ column

Volume of Eluant	Counts/3hrs
0 L	11119 ± 300
20 L	12461 ± 313
20 L	10819 ± 317
38 L	12574 ± 333
40 L	10780 ± 666
20 L	11412 ± 677

TABLE 5

1% MgCl$_2$ on MnO$_2$ Column

Volume of Eluant	Counts/24hrs
0 L	20754 ± 830
20 L	20105 ± 945

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TABLE 6
100 ppm EDTA on MnO_2 Column

Volume of Eluant	Counts/24hrs
0 L	17630 ± 846
20 L	20159 ± 887

TABLE 7
Elution Results •

Version	20 L	20 L	20 L	50 L	50 L	50 L
CRPP I						
pH		5.9	5.3	5.2	5.1	
EC		40	1.5		3	
Mn		0.02	0.01	nd	0.01	
K		9.96	0.14	0.28	0.03	
CRPP II						
pH	5.8	5.7	5.4	5.4		
EC	10.4	2.5	0.8			
Mn	nd	nd	0.02	nd		
K	2.29	0.39	0.08	0.28		
CRPPIII						
pH	6.4	5.2	5.4			5.3
EC	2.9	1.8	1.14			
Mn	nd	0.02	0.02			nd
K	0.78	0.54	0.09			0.11
Seakem						
pH						5.3
EC						1.35
Mn						nd
K						0.11

nd = not detected
Mn and K values reported in ppm
EC - electrical conductivity measured in microsiemens

Calculation for K_D:

Since it is difficult to calculate the K_D without any noticeable trend in decrease of activity on columns, the average (â) and variance (σ) were calculated and these values used so that a minimum K_D could be determined.
The following equation was used to determine K_D; when σ was larger than the counting error:

$$K_D \geq \frac{\hat{a} - \sigma}{2\sigma} \times \frac{V_w}{V_r} ;$$

otherwise, σ', based on the counting errors, was computed and K_D similarly calculated.

TABLE 8

Minimum K_D Values

Run	V_w = 20 L	V_w = 160 L	V_w = 210 L	V_w = 380L
Seakem, water		0.6×10^5		1.8×10^6
CRPP I, water		0.6×10^6		
CRPP II, water		0.7×10^6		
CRPP III, water		0.9×10^6	1.0×10^6	
Seakem, 1%NaCl		0.8×10^6		
Seakem, 1%MgCl2	1.4×10^5			
Seakem, 100ppmEDTA	0.9×10^5			

TABLE 9

Spikes

2ng ^{226}Ra in polycarbonate spike holder		
Date	Counts/24hrs	Average
29.6.92	24820 ± 3.8%	22624 ± 6.1%
20.7.92	21768 ± 4.4%	
05.8.92	22589 ± 2.9%	
18.9.92	23291 ± 2.9%	
05.4.92	23675 ± 3.0%	
2 ng ^{226}Ra spike applied to columns at 1-2 mL/min		
Date	Counts	Average
11.6.92	20839 ± 4.1%	19948 ± 5.5%
20.6.92	19352 ± 4.3%	
25.11.92	21305 ± 2.2%	
24.4.93	19987 ± 2.4%	
15.3.93	21020* ± 2.4%	
10 ng ^{226}Ra		
Date	Counts	Average
10.6.93	137372 ± 0.7%	131877 ± 5.5%
06.8.93	137264 ± 0.7%	
30.6.93	122647** ± 1%	
20 ng ^{226}Ra		
Date	Counts	Average
03.2.93	198250 ± 0.6%	206424 ± 6.3%
03.3.93	229615 ± 0.7%	
17.2.93	210561 ± 0.8%	
28.1.93	202868 ± 0.5%	
16.3.93	193583** ± 0.6%	

* teflon spike holder was used

** Amount of source used for this spike solution was lower than for other spike solutions. Since the volume could not be measured accurately this value was used to calculate the approximate concentration of the spike. The spikes used from this batch were 1.8, 9 and 18 ng ($\pm$ 1 ng).

TABLE 10

^{226}Ra Extraction Efficiency
Using "Short" 1.5 mL Columns

Flow Rate (mL/min)	1 Column Recovered Fraction	
5	0.69 $\pm$ 0.11	
50*	0.38 $\pm$ 0.04	
100*	0.27 $\pm$ 0.03	
	2 Columns in Series Recovered Fraction	
	Based on 1 Column	Based on 2 Columns
55	0.34 $\pm$ 0.04	0.39 $\pm$ 0.07
100	0.28 $\pm$ 0.03	0.35 $\pm$ 0.07
150	0.25 $\pm$ 0.03	0.47 $\pm$ 0.06
200	0.20 $\pm$ 0.02	0.27 $\pm$ 0.08

- 20 ng spike used in 10L UPW
* downflow direction used

Formula for calculation based on 1 column: $\dfrac{A_1}{A_0}$

Formula for calculation based on 2 columns: $\varepsilon = \dfrac{A_1 - A_2}{A_1}$

A_0 is the activity of the calibration spike and A_1 and A_2 are the activities of the first and second column respectively.

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TABLE 11

Extraction Efficiency of ^{226}Ra at Different Feed Concentrations, on "Long"[1] 1.5 mL MnO$_2$ Columns

Flow Rate (mL/min)	Recovered Fraction			
	1.8 ng	9 ng[3]	10 ng	20 ng
1.5 - 2	0.94 ± 0.11			
8 ± 2	0.77 ± 0.09	0.55 ± 0.06		0.71[2] ± 0.09
30 ± 3				0.57[2] ± 0.06
50 ± 5	0.54 ± 0.06	0.44 ± 0.03		0.60 ± 0.07
100 ± 5			0.45 ± 0.05	0.50 ± 0.06

1 - Columns were 6cm x 0.6cm (L/D of 10:1)
2 - 18 ng was used
3 - spike not accurately determined

-Upflow and Downflow directions for 20 ng tests were identical at the one sigma level - an average of the two was taken

TABLE 12

Effect of MgCl$_2$ on ^{226}Ra Extraction Efficiency onto 1.5 mL "Long" MnO$_2$ Columns

Flow Rate (mL/min)	Recovered Fraction**	
	2% MgCl$_2$	UPW only
8 ± 2	0.90 ± 0.10*	0.55 ± 0.06
50 ± 5	0.44 ± 0.05	0.44 ± 0.03
100 ± 5	0.36 ± 0.04	
160 ± 10	0.35 ± 0.04	

* Average of 2 values
** approximately 9 ng spike used in 10 L of UPW (spike not accurately determined)

TABLE 13

Effect of EDTA (Na$_4$ form) on ^{226}Ra Extraction Efficiency onto 1.5 mL "Long" MnO$_2$ Columns

Flow Rate (mL/min)	EDTA Concentration	Recovered Fraction*	
		EDTA	UPW only
100	1 ppb	0.45 ± 0.05	0.45 ± 0.05
50	100 ppb	0.59 ± 0.07	
100	100 ppb	0.50 ± 0.06	0.45 ± 0.05
7	1 ppm	0.62 ± 0.07	
50	1 ppm	0.38 ± 0.04	
100	1 ppm	0.26 ± 0.03	0.45 ± 0.05

* 10 ng spike used in 10 L of UPW

TABLE 14

Variation to CRPP-MnO$_2$ Bead Manufacturing Procedure - Effects on
Extraction Efficiency of ^{226}Ra

Description	Flow Rate (mL/min)	Recovered Fraction*
XAD-8 MnO$_2$	100	0.46 ± 0.05
XAD-7 MnO$_2$, 0.0117 - 0.0138" bead size	100	0.74 ± 0.08

- the regular CRPP XAD-7 MnO$_2$ resin (fraction 0.0117" - 0.029")
gave an extraction efficiency of 0.45 ± 0.05
* 10 ng spike was used in 10L UPW

Large Scale Spiking Results

For all flow rates, >95% efficiency was achieved based on a
two column calculation (I. Blevis, unpublished report).

DISCUSSION

K$_D$ studies suggest that K$_D$ MnO$_2$-water is >10^6, higher than the
values inferred by A. Ferraris (10^5). A similar coefficient is
measured for a 1% NaCl solution. MgCl$_2$ (1%) and EDTA (100 ppm)
results are not significantly different from results for UPW at the
same scale (see 20 L K$_D$ for UPW, Table 8), suggesting that while
the measured minimum K$_D$ is 10^5, a higher K$_D$ may be achieved for a
higher volume of water.

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Small scale fast spike studies indicate that upflow and downflow directions did not affect Ra extraction. This is demonstrated by the results for single "short" columns (Table 10), where the upflow/downflow efficiencies agree well within the reported error. Thus, upflow/downflow results for "long" column experiments (Table 11) were averaged to a single value.

While the efficiencies calculated for a single column have small experimental error and show a clear trend of decreased efficiency with increased flow rate, the results for "two columns efficiency" (Table 10) do not show the expected efficiency:flow rate pattern. This, combined with the larger errors on the two column efficiencies, prompted us to restrict ourselves to a single column experimental mode.

Column geometry had a critical effect on the extraction efficiency where changing the L/D ratio from 1.4/1 to 10/1 resulted in an increase of 10 - 20% in the extraction efficiency for all flow rates (Tables 10 and 11). Experiments with 10/1 aspect ratio columns (Table 11) again indicate extraction efficiency decreased with higher flow rates, decreasing rapidly from 94% to 77% as the residence time decreased from 60 seconds to 11 seconds.

The effect of 1% $MgCl_2$ on Ra extraction efficiency is seen to vary with concentration (Table 12). The increased extraction efficiency at low flow rates in the presence of Mg might indicate a "salting out" effect on the Ra[7,8] and should be further investigated. This effect (essentially an equilibrium effect) is

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not apparent at higher flow rates where Ra in $MgCl_2$ and Ra in water solutions seem to behave in an identical manner.

Conversely, high concentrations of EDTA (100 ppm) distinctly decreased the extraction efficiency as compared with UPW. The effect was more pronounced at high flow rates, where the stable complexed Ra-EDTA (in the water phase) cannot achieve a new equilibrium distribution between the EDTA and MnO_2 due to the high flow rate. With decreased flow rates and decreased EDTA concentration the EDTA effect on Ra extraction onto MnO_2 disappears. At the EDTA levels suggested for SNO (0.1 - 1 ppb) no effect on the Ra extraction onto MnO_2 is to be expected.

Attempts were made to improve on column efficiency by modifying the resin manufacturing recipe. Using the XAD-8 resin (larger pore size than XAD-7) did not improve the efficiency at the 100 mL/min flow rate (Table 14). However, using a finer fraction of XAD-7/MnO_2 (increasing the bead diameter to column diameter ratio) did make a significant difference. A decrease by a factor of 1.6 in average nominal diameter of dry beads (a factor of 3 for wet beads) resulted in a 30% increase in Ra extraction efficiency at 100 mL/min (60 BVM, 1 sec residence time). This value is similar to the values measured by Ferraris for 1 sec residence time (where his column had a bead diameter to column diameter ratio of 1:6 but a L/D ratio of about 25). Thus, the low bead diameter to column diameter ratio in the 6 cm columns ("long" column experiments, Table 11) could account for the low efficiency of 70% at 7 mL/min (15 sec residence time).

When scaling up to a 1 L column the bead diameter to column diameter ratio will be significantly improved and the extraction efficiency is therefore expected to be higher than for small scale experiments. Several large scale experiments which have been conducted (I. Blevis) indeed indicate extraction efficiency larger than 95% even for a residence time of 3 seconds. The extremely high extraction efficiency, evidenced by the large scale studies, will be addressed in a separate report. These results, presently for 3 - 18 sec residence time, will be extended also to 1 sec residence time and less in order to determine the operative conditions in SNO for the Ra monitoring loop.

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