Th/ Ra/ Pb extraction onto Diakon- MnO_2 resin and the effect of EDTA

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Study on Th/Ra/Pb extraction onto Diakon-MnO_2 resin is a follow up on a previous, similar study on CRPP-MnO_2 (SNO-STR-94-039). All of the reported tests were conducted by counting ^{212}Pb 239KeV(*) gamma as a function of time for 350 hours on a germanium counter. Background at this energy is measured at 0.05-0.1 cps. The data were then fitted using the relevant decay constants and PAW (D.Hunt, I.Blevis) to give the initial lead, radium and thorium levels in the various components measured. The present study was carried out at pH 7. The pH values were measured with an Accumet 915 pH Meter and Glass body combination electrode with Ag/AgCl reference (Fisher).

The previous CRPP resin study carried out in triplicate at slow spike was marked by large statistical variations (see table 1 in SNO-STR-94-039).This was attributed by us to the titration process used. In the present study this titration process was modified (see below).

EXPERIMENTAL PROCEDURE:

Extraction tests were designed at two flow rates: slow spikes were performed at 0.5 BVM (residence time of 120 sec) and fast spike runs at 10 BVM (residence time of 6 sec). 1.5 ml of Diakon-MnO_2 resin (prepared with $NaMnO_4$) were used for all tests, with a 6 cm x 0.6 cm (L x D) column configuration. Column material is PC.

The L (Length) $\geq$10 x D (column diameter) configuration is the standard recommended column geometry for column extraction. However, at 1.5 ml resin (the standard amount counted efficiently on the gamma counter (1990-1994) and resin diameter (Dr) of up to 800 μ, the ratio D/Dr is lower than 10, where D/Dr larger than 10 is the recommended ratio. Thus absolute extraction efficiency maybe improved by using more favorable column to bead diameter ratio.

Slow spikes:

The ^{228}Th source solution was 1 μCi in 1ml 0.1N HNO_3. The spike solution was prepared by pipetting 4 μl of the Th source solution into a 50 ml teflon beaker containing 10 ml of UPW to a pH of about 4. Use of a concentrated Th source (in comparison, 60 μl, 1N HNO_3 were used in previous CRPP resin study for the same activity) resulted in a less acidic solution and required less titration reagent-NaOH). A teflon coated magnetic stirring bar was placed in the beaker and contents were mixed for 5-10 min. About 20 ml of 0.1 millimolar NaOH were

then added in dropwise to achieve a pH 7 spike solution. The titration lasted about 10 minutes.

The spike solution was gamma counted before spiking as calibration. Then slow spike was conducted with gravitational flow. Eluate was collected in a 30 ml pp vial for gamma counting. The resin was then rinsed by 30 ml of UPW and transferred into a standard geometry column for counting.

In order to asses the plated out activities, 30 ml of 10% HNO_3 were placed in the teflon beaker used for holding the spike solution and mixed for 30 min. This acid was collected and counted. The column system was reassembled and 30 ml of 10% HNO_3 were poured into it. 30 min later, it was collected and counted.

When 100 ppb EDTA solution was tested, 100 μl of 30 ppm EDTA solution was mixed for more than 10 min with 10 ml of UPW in a teflon beaker before spiking with Th. The spiking procedure is the same as described above. All liquid fractions were counted in 30 ml pp vials which were standardized against the column geometry.

Fast spike:

The spike solution was prepared in a 125 ml pp vial: 6 μl of ^{228}Th source solution (as above) were added into 15 ml UPW in a vial which contained a teflon coated stirring bar. While stirring, 110 ml of about 0.03 millimolar NaOH solution were slowly added to obtain a pH 7 spike solution and the solution was then counted as a calibration.

The spike was passed through the column at 10 BVM, using an all teflon diaphragm pump. A clean 125 ml pp vial was used to collect the eluate (1 ml of concentrated HNO_3 was added in the vial in advance to acidify the eluate to about 0.1N and avoid plating out of activities) for counting. 100 ml UPW was pumped through the column after the run and the resin was transferred to a standard geometry column for counting. The entire system (pump, tubing and empty column) of about 50ml volume was then rinsed with 60 ml of 10% HNO_3 circulated for 30 min. Acid was collected in a 60 ml pp vial for counting. The 125 ml titration vial holding the spike solution was also rinsed with 30 ml 10% HNO_3 and acid was transferred into a 30 ml pp vial for counting. 100 ppb EDTA solution was also tested. 420 μl of 30 ppm EDTA solution was mixed with the 15 ml UPW before spike was added in.

All vials (30ml, 60ml 125ml) were calibrated against the column geometry for the purpose of comparing the measured activities.

RESULTS:

The recoveries (%) of Pb/Ra/Th for the various columns, eluates and acid rinses are presented in tables 1, 2. All activities were converted to "column equivalent" counts. Tables 3 and 4 are the same tables 1,2 of SNO-STR-94-039 which included previous results for CRPP-MnO_2 at pH 7.

In slow spike studies (table 1), with UPW (0 EDTA), Pb apparent extraction rate is about 20% which is similar to the CRPP resin under the same conditions. Th apparent extraction is slightly over 50% and is lower than 70% of CRPP. However, over 50% of Pb and about 30% of Th plated out (acid rinse fraction), compared with 24% and 7% respectively for the CRPP case. Thus the actual Th extraction on Diakon-MnO_2 at 0 EDTA is about 70% (similar to CRPP), while the Pb extraction is close to 50%. The extraction of Th for slow spike runs with 0 EDTA is in the upper range of the values measured by Ferraris (see table 3). 86% of apparent Ra extraction efficiency is again close to 100% after corrected for the acid fraction. It is similar to the value measured independently for Ra^{226} at pH 6 (Unpublished results, reported in April's water meeting). Addition of 100 ppb EDTA reduced Pb extraction (6%) but increased Th extraction to 90% on the column. This trend agrees with the CRPP resin test results. 100 ppb EDTA prevented plating out of Pb and Th (acid rinse fraction). This was also previously observed from the CRPP results (table 3,4). A slight increase of plated out Ra when EDTA concentration increased from 0 (14%) to 100 ppb (26%) is in disagreement with previous results for pH values of 4-7. (SNO-STR-94-039, SNO-STR-94-038, SNO-STR–94-001)**.

** If time allows, dependence of Ra/Pb/Th plate out on titration procedure should be investigated.

Table 2 presents the results from fast spike studies. Th extraction efficiency in UPW at 10 BVM, corrected for acid fraction is about 16%, which is close to the value for CRPP at 33 BVM. Pb extraction efficiencies in UPW are similar in both Diakon- MnO_2 and CRPP beads (approximately 20% when corrected for acid fraction). Ra has a higher extraction rate on Diakon-MnO_2 at 10 BVM than on CRPP at 33 BVM (74% vs. 57%, or 79% vs. 63% corrected for acid fraction). There was no measurement for Ra extraction onto CRPP at 10 BVM. When 100 ppb EDTA spikes were applied, Pb and Th extraction efficiencies were only slightly lower than in 0 ppb EDTA when corrected for acid fraction: 16% of Pb and 14% of Th. Ra extraction corrected for acid is 90%.

The plate out for Pb and Th (table 2) in UPW were 33% and 15% respectively, with standard deviation larger than for slow spike. In 100 ppb EDTA the plate out of Th was reduced (4 ± 4 %). A slight increase of Ra plate out from 0 ppb EDTA to 100 ppb EDTA and Pb decrease in plate out from 33% to 4% is in fact consistent with no increase at 2 sigma level.

CONCLUSIONS:

Small scale tests indicate that at 0.5 BVM, pH 7 thorium extraction efficiencies onto Diakon-MnO_2 are $\geq$ 70%, equivalent to those measured on CRPP-MnO_2 and slightly increase with addition of 100 ppb EDTA (about 90%). Conversely, EDTA seems to reduce the lead extraction efficiency. Radium extraction efficiency (100%) seems not to be affected by EDTA. At 10BVM, pH 7 UPW, thorium extraction dropped by x4, as compared with radium extraction which dropped by only about 20%. The presence of 100 ppb EDTA had little effect on the extraction

efficiencies of lead, radium and thorium, but evidently reduced the plate out of lead and thorium to less than 5%.

Thus the small scale study indicates that at 0 - 10 BVM, Diakon-MnO_2 is most suitable for radium extraction, from UPW and that at <1 BVM it is also suitable for thorium extraction. Both CRPP and Diakon-MnO_2 appear to be poor thorium extractors at >10 BVM flow rates. In the present experimental setup, lead extracts the least onto these two MnO_2 supports. The achievable lead extraction onto MnO_2 is quoted to be 100% in published literature (e.g. S. Krishnaswami et al., Si,Ra,Th,and Pb in seawater: In-situ extraction by synthetic fibre, EPSL 16(1972), 84-90). The lower value measured in our studies might reflect non-optimal column geometry as well as non-optimal spike preparation (e.g. titration). The addition of EDTA is beneficial both for the elimination of thorium and lead plate out as well as improving thorium extraction at low flow rates.

FURTHER STUDIES:

-In SNO, MnO_2 coated resin is designed to be used both as a monitor (about 0.5L at 40BVM) mostly for radium and as a purifying device (unidentified amount at 100/200 LPM) for thorium and radium. On small scale the Diakon beads seem to be appropriate for the first use but not for the second purpose, unless very large amount of beads are used (i.e.>50L). CRPP beads have yet be tested at 10 BVM to check thorium extraction efficiency. Large scale tests of Th extraction on Diakon-MnO_2 should also be carried out in order to eliminate the artifact associated with small column/large bead design.

-In some of the above tests, in the presence of EDTA, radium content in the acid fraction was $\geq$20%. This is in conflict with previous studies. Further investigation on titration process may be conducted.

-Low ^{212}Pb extraction efficiencies were not confirmed by test we performed with stable lead, where extraction efficiencies of larger than 80% at 0.3BVM. The discrepancy may be related to different lead amounts ($<<$ μg for ^{212}Pb, about mg level in the stable lead case), or difference in the lead speciation in the two spikes. Further investigation will follow.

(*): The counting ROI in our studies is from 234kev to 244kev. ^{212}Pb gamma at 239kev is 47% intensity and ^{224}Ra gamma at 241kev is 3.7% intensity. When the lead extraction is low and radium extraction is high, the ^{224}Ra peak becomes significant. Thus the actual lead extraction efficiency maybe lower than reported by as much as 40%.

Table 1: Diakon-MnO2 beads (Slow spike)

EDTA (ppb)	^{212}Pb	^{224}Ra	^{228}Th	pH
Extraction Efficiency (%/100) - "Slow" (0.5 BVM) Spike				
0 C	0.21±0.01	0.86±0.02	0.52±0.08	6.85±0.05
(2) A	0.54±0.04	0.14±0.02	0.28±0.06	
E	0.24±0.05	nd	0.20±0.01	
100 C	0.06±0.02	0.74±0.01	0.91±0.05	6.85±0.05
(2) A	0.04±0.01	0.26±0.01	0.01±0.003	
E	0.90±0.03	nd	0.08±0.04	

Errors reported are sigmas on duplicate runs. Systemetic errors (for single measurements) are 5%, as measured by reported counting of given samples.
C: column; A: acid wash; E: eluate; nd: not detected (<2%)
(#): number of duplicates

Table 2: Diakon-MnO2 (Fast spike)

EDTA (ppb)		^{212}Pb	^{224}Ra	^{228}Th	pH
Extraction Efficiency (%/100) - "Fast" (10 BVM) Spike					
0	C	0.14±0.05	0.74±0.07	0.14±0.04	7.00±0.05
(3)	A	0.33±0.14	0.06±0.02	0.15±0.03	
	E	0.52±0.15	0.20±0.05	0.71±0.01	
100	C	0.15±0.02	0.75±0.06	0.13±0.004	6.90±0.05
(2)	A	0.04±0.03	0.18±0.06	0.04±0.04	
	E	0.81±0.05	0.07±0.01	0.83±0.04	

Errors reported are sigmas on duplicate and triplicate runs.
Systemetic errors (for single measurements) are 5%
C: column; A: acid wash; E: eluate;
(#): number of duplicates

Table 3: CRPP-MnO2 (Slow)

EDTA (ppb)	^{212}Pb	^{224}Ra	^{228}Th	pH	^{228}Th (Ferraris)	^{226}Ra
Extraction Efficiency (%/100) - "Slow" (0.3 BVM) Spike						
0 C	0.18±0.09	0.70±0.06	0.72±0.03	6.81±0.05	0.38-0.54	1.00
(2) A	0.24±0.11	0.14±0.04	0.07±0.01			(pH 6)
E	0.46±0.23	nd	0.10±0.03			
0 C	0.72±0.07	0.96±0.08	0.80±0.07	6.84±0.05		
(1) A	0.11±0.02	0.07±0.02	0.06±0.01			
E	0.16±0.03	nd	nd			
100 C	0.11±0.01	0.87±0.1	0.88±0.03	6.81±0.05		
(2) A	0.03±0.02	0.06±0.04	0.07±0.04			
E	0.72±0.06	nd	0.08±0.03			
100 C	0.65±0.06	0.98±0.08	0.90±0.08	6.84±0.05		
(1) A	nd	nd	nd			
E	0.31±0.05	nd	nd			

Errors reported are sigmas on duplicate runs. Counting errors (for single measurements) are 5%
C: column; A: acid wash; E: eluate; nd: not detected (<2%)
(#): number of duplicates

Table 4: CRPP-MnO2 (Fast)

EDTA (ppb)		^{212}Pb	^{224}Ra	^{228}Th	pH	^{228}Th (Ferraris)	^{226}Ra
Extraction Efficiency (%/100) - "Fast" (33 BVM) Spike							
0	C	0.12±0.08	0.57± 0.01	0.18± 0.05	6.9±0.1	0.05-0.33	0.45±0.05 (pH=6)
	A	0.29±0.12	0.09±0.02	0.04±0.02			
1	C	0.12±0.01	0.58±0.01	0.24±0.01	6.9±0.5		
	A	0.17±0.03	0.08±0.03	0.04±0.02			
10	C	0.08±0.03	0.58±0.03	0.21±0.04	6.8±0.1		
	A	0.01± 0.01	0.11±0.07	0.1±0.02			
	E	0.79±0.07	0.19±0.02	0.34±0.02			
100	C	0.06±0.01	0.54±0.02	0.18±0.04	6.8±0.1		0.59±0.07 (pH 6)
	A	0.02± 0.01	0.12±0.03	nd			
	E	0.95±0.05	0.16±0.02	0.35±0.02			

Errors reported are sigmas on duplicate runs. Counting errors (for single measurements) are 5%
Eluate measured after acidification of 500 cc (1N nitric) and evaporation by IR lamp + hot plate down to 70 cc
Poor mass balance for Th may be related to above eluate evaporation procedure
C:column; A:acid; E:eluate; nd: not detected (<2%)
Column numbers are average on duplicates. Eluates, as well as acid wash for the UPW and 1 ppb EDTA are for single samples