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Th/ Ra/ Pb extraction onto MnO<sub>2</sub> resin  
and the effect of EDTA on the extraction

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The present study, carried at pH 7, is a follow up on a previous, similar study (July 1994 Water Meeting report) at pH values of 4-6. All of the reported tests were conducted by counting <sup>212</sup>Pb 239 KeV gamma rays on a germanium detector. Background at this energy is 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.

Slow and fast spikes-experimental procedures:

Slow and fast spike tests on the adsorption of <sup>228</sup>Th, <sup>224</sup>Ra and <sup>212</sup>Pb were conducted. 1.5 cc of CRPP-MnO<sub>2</sub> resin (prepared with KMnO<sub>4</sub>) were used for all tests, with a 6cm:0.6cm (l:d) column configuration. Column material is PC. Spike solutions were prepared in 500 cc HDPE bottles for fast spike studies and in a 60 cc teflon beaker for the slow spike studies. Water, 1 ppb, 10 ppb and 100 ppb EDTA solutions were tested, (prepared with EDTA-Na<sub>4</sub>). Slow spike studies were performed at 0.3 BVM (residence time of 180 sec.) with gravitational flow. The flow rate in fast spike runs was 33 BVM (residence time of 2 sec.), using an all teflon diaphragm pump.

The original stock spike was 10 cc at  $\approx 2000$ Bq/cc, in 1N HNO<sub>3</sub>. 60  $\mu$ litres of this stock solution were used as spikes. For each run two such solutions were prepared, one used to calibrate the spike activity and insure equilibrium of Th and daughters in the stock solution and one to spike the column.

The 500 cc solutions for the fast spike studies were prepared by placing 100 cc UPW in the (prewashed) bottle, adding the Th spike, placing on a magnetic stirring plate for 5-10 min. and then titrating to pH 7: this was accomplished by adding slowly, while stirring, about 350 cc of 20 micromolar NaOH solution (to a pH of 6.3) and then titrating to pH 7 by the dropwise addition of 50 micromolar NaOH. When EDTA solutions were to be studied, the procedure was as above but EDTA spikes from 0.5 and 30 ppm stock solutions were added to the water and mixed for 30 min. before spiking with Th. Slow spike solutions were prepared by placing 28 cc 2.2 mM NaOH in the (precleaned) 60 cc teflon beaker. The Th spike was then mixed in and pH was adjusted to 7 by the dropwise addition of 2.2 mM NaOH. EDTA spikes were added prior to the Th spike. All solutions were allowed to mix for 30 min. before the start of a run.

For both sets of tests the eluates were collected: in the slow spike case 30

cc of eluate were collected into a clean pp vial. In the fast spike case the 500 cc eluates were acidified to 1N HNO<sub>3</sub> and then evaporated down to 70 cc in a hood, by IR heat lamp+hot plate. 30 cc of the contents were then transferred into a 30 cc PP vial. These vials were then counted periodically for lead, radium and thorium (evaporation lasted 4-5 hours, only half of the pb212 half life.).

After the elutions the beads were rinsed by 30 cc UPW, transferred into a standard geometry column used for counting (see previous reports on CRPP beads) and counted periodically for lead, radium and thorium. The entire system (pump, tubes, empty column etc.) was then rinsed with 30 cc of 1% HNO<sub>3</sub> (of background radioactive levels) which were also collected in 30 cc PP vials for subsequent periodic counting. The teflon beaker used for holding the 'slow spike' solutions was filled up with 30 cc acid, left to mix for 15-20 min. and then the acid was also transferred in to a 30 cc PP vial and counted.

### Results:

Tables 1,2 include the calculated extraction efficiencies for the various columns and the experimental error. Also included are <sup>226</sup>Ra extraction results from previous studies, as well as the results of E. Ferraris (Oxford, Ph.D. thesis). Fast spike studies (table 1) with UPW (0 EDTA) runs are consistent with previous data (Ferraris for <sup>228</sup>Th and CRPP reports for <sup>226</sup>Ra data). About 30% of the lead is plated out (acid fraction). Pb and Th extractions are 10 and 20 % respectively, 3-5 times less than the extraction measured for Ra. Addition of 1 ppb EDTA does not affect the extraction efficiencies but has a slight reducing effect on Pb and Ra detected in the acid wash. 10 and 100 ppb EDTA reduced the lead extraction but did not affect the Th extraction. Conversely the addition of 10-100 ppb EDTA had a pronounced effect on the amounts measured in the acid fractions, for both Pb and Th, effectively reducing the plated out activity from these elements to zero. No effect on the Ra content in acid is observed. The mass balance (the sum of each element in the three fractions) is satisfactory for both Pb and Ra but not for Th. The process by which the eluate is concentrated, where 500 cc of 1N HNO<sub>3</sub> is evaporated to 70 cc (and acidity ≥7M), results in the formation of Th(NO<sub>3</sub>)<sub>6</sub><sup>-2</sup> complexes the solubility of which is not available at present. Thus it could be that the poor mass balance for Th reflects an improper evaporation procedure. Future studies will be conducted with lower eluate volumes so that evaporation is not necessary.

Two sets of slow spike studies are included in table 2. Two duplicates with UPW as well as two duplicates with 100 ppb EDTA resulted in a low Pb extraction (11-18 %) and lower Ra extraction than the value measured independently for <sup>226</sup>Ra under the same conditions (0.70, 0.86 vs. 1.00). Two single runs in UPW and 100 ppb EDTA yielded a high extraction of lead (65-72 %) and <sup>224</sup>Ra extraction compatible with <sup>226</sup>Ra extraction under the same conditions. An independent Pb extraction study was conducted using stable lead in UPW (6 ppm, 10 and 15 cc at pH 4.5-5, on 1.5 cc MnO<sub>2</sub> resin). Both the eluate and the acid wash fractions contained no lead, suggesting high extraction efficiency on the col-

umn. The instances of lower Ra extraction efficiency associated with the low Pb extraction might reflect irreversible formation of hydroxylated species during the titration. The small volume titrated in the slow spike studies (30cc) results in a lower buffering action during titration as compared with the fast spike studies, where large volumes and low NaOH concentration favour titration under close to equilibrium conditions. Thus the results for slow rate Pb extraction will have to be repeated using a modified titration procedure (e.g. use concentrated 3 micron spike at 0.1N HNO<sub>3</sub>, so that with the addition of 30 cc UPW pH will reach 5, and only minute amounts of diluted NaOH will be required to reach a pH of 7).

The extraction of Th for all slow spike runs is consistently higher than the values measured by Ferraris and close to the high values measured for Ra. At an average value of  $85 \pm 5$  % the extraction is 4 times higher than at 33BVM.

Mass balance calculations for the various elements indicate full recoveries (within the quoted errors). Again, the presence of EDTA significantly reduced lead levels in the acid wash, indicating no significant plate out at 100 ppb EDTA for any of the three isotopes.

#### Conclusions:

Small scale tests indicate that at 33 BVM Th extraction efficiency onto CRPP-MnO<sub>2</sub> at pH 7 is 20%, a third of the value measured for Ra under identical experimental conditions. EDTA at 1-100 ppb does not affect the extraction. Lead extraction is even lower, at 12%, and seems to further decrease with the addition of EDTA (down to 6% at 100 ppb EDTA).

At 0.3 BVM and pH 7 Th extraction is almost as efficient as that of Ra (80% and 100% respectively). The presence of 100 ppb EDTA does not affect the extraction. If the same efficiencies would have been measured on large scale tests, the implication would be that columns containing up to 60 litres of resin would be needed in order to efficiently remove Th from D<sub>2</sub>O at 20 LPM. Previous tests have indicated that large scale extraction efficiencies are higher than those measured in small scale tests due to improved column geometries. In that case the 1:3 extraction ratios for Th:Ra suggest a 2 L column would be sufficient for efficient Th removal at 20 LPM. It is thus desirable to check the Th extraction efficiencies at the 1 Tonne scale using 0.5 litre of beads, and at intermediate flow rates (e.g. 10 BVM).

Lead extraction results vary widely, for both UPW and 100 ppb EDTA, from 11% to 70%. Further tests have to be conducted in order to test whether these large fluctuations are related to the titration process employed. The presence of EDTA has practically reduced the plate out of lead to zero, in both sets of experiments.

#### Further studies:

- 1) In view of the large change in Th extraction efficiencies as a function of flow rate, tests at intermediate flow rates would be conducted.

- 2) As suggested above, titration procedures will be defined so that conditions at pH 7 will be most similar to those at SNO and reproducible results are achieved.
- 3) Large scale tests are to be conducted using  $^{228}\text{Th}$  spikes. In previous studies it was confirmed that Ra extraction at 33-40 BVM was improved when changing from the 1.5 cc scale column to the 500-1000 cc scale.
- 4) Further tests with stable lead will be conducted in order to confirm the radioactive species tests.
- 5) Future studies will be conducted using solid (Diakon) beads rather than porous (XAD 7) beads, since the solid beads are the favorable option for SNO.
- 6) The effect of  $\text{MgCl}_2$  (0.2-2 %) on the extractions will be investigated.

EDTA (ppb)	<sup>212</sup> Pb	<sup>224</sup> Ra	<sup>228</sup> Th	pH	<sup>228</sup> Th (Ferraris)	<sup>226</sup> 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 (pH 6)
(2) A	0.24±0.11	0.14±0.04	0.07±0.01			
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 1

EDTA (ppb)	<sup>212</sup> Pb	<sup>224</sup> Ra	<sup>228</sup> Th	pH	<sup>228</sup> Th (Ferraris)	<sup>226</sup> 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

Table 2