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HTiO: Sorption and Elution

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Preparation of HTiO

The recipe used recently for making HTiO is:

250 ml 15% w/v $Ti(SO_4)_2$ solution

750 ml molar NaOH + ≥ 1.5 L water

The HTiO solution is added rapidly to the sodium hydroxide solution, which is well stirred during addition. The resulting precipitate is centrifuged and then washed twice with deionized water. The pH of this slurry (made to Ca. 4 litres) is slowly adjusted, over the course of a day, from pH 9.3 to 7.0 by the dropwise addition of dilute HNO_3 . This suspension is then centrifuged, washed again and then diluted to taste. Good DF's have been achieved with this preparation.

Elution of HTiO

There is some interest as to whether lead can be both extracted by HTiO and consequently eluted from it. Previous studies (see attached report by Heidi) have only been concerned with the elution of radium and thorium from HTiO. Due to the relatively easy susceptibility of HTiO to attack by acids, the aim of the elution studies was to elute the maximum quantity of radium or thorium with the minimum dissolution of the HTiO. The results obtained show that elution efficiencies for ^{226}Ra can be $> 90\%$ whilst at the same time having $< 5\%$ dissolution of the HTiO by using 0.03M nitric acid and a contact time of > 20 min. The elution of ^{228}Th is more difficult but by using 0.05M sulphuric acid 90% elution can be achieved with 25% HTiO dissolution. In order to determine whether lead can be eluted from HTiO simple batch experiments have been performed using nitric, sulphuric and acetic acids.

Elution of lead using acetic acid no good

As HTiO cannot be removed whole from ultrafiltration membranes in a solid form, it is desirable that the chosen acid can elute the HTiO *in situ* yet be compatible with the membrane material. Acetic acid was investigated as an eluant because of its compatibility with polysulfone membranes. Acetic acid solutions of

25 and 50% were investigated using HTiO loaded with ^{228}Th and ^{226}Ra which was monitored by γ -counting (for method see below). It was found that only 3% of ^{228}Th and none of the ^{212}Pb was eluted using either concentration of acetic acid.

Elution of lead using HNO_3 and H_2SO_4

*Ti is dissolved.
Cut Pb off, have to dissolve till Ti*

HTiO loaded with ^{228}Th was eluted with both HNO_3 and H_2SO_4 to determine if ^{212}Pb is eluted. 60 ml aliquots of a stock solution containing 1000 ppm HTiO and 7 Bq/ml ^{228}Th were shaken for 10 min with an equal volume of acid of twice the intended final concentration. The suspensions were filtered by 0.2 μm Mediapak filter and the ^{212}Pb content of 50 ml aliquots of the filtrates were determined by γ -counting. The filtrates were then measured by γ -counting two weeks later to determine thorium content. Unfortunately the wrong sulphuric acid concentration was used (0.1M instead of 0.05M) so the quantity of thorium eluted and consequently the amount of HTiO dissolved (Ti analysis not performed yet) are both greater. It seems likely that the amount of lead "eluted" by the sulphuric acid is directly related to quantity of HTiO dissolved.

	^{212}Pb c/s	% ^{212}Pb eluted	^{228}Th c/e	% ^{228}Th eluted
^{228}Th stock (after x2 dilute)	2.34		0.67	
0.03M HNO_3 (a)	0.35	15	0	0
0.03M HNO_3 (b)	0.42	18	0	00
0.1M H_2SO_4 (a)	0.81	35	0.63	95
0.1M H_2SO_4 (b)	0.82	35	0.63	95

However, since these elution experiments were performed, a change has occurred in the low-level counting technique proposed for the analysis of eluants. Originally, the eluants were to be concentrated to < 10ml and then a sample could be evaporated onto a planchette which could be placed in a α -spectrometer. However, by using Norm's liquid scintillator β - α coincidence technique (see attached report), 10 ml aliquots of aqueous solutions can be assayed, making the analysis somewhat easier and removing a concentration stage. For small-scale elutions, 1 foot membranes for example, an aliquot of the acid eluant may be counted directly providing the acid is compatible with the scintillator. Dissolved HTiO will have no effect on this

100 g/l \rightarrow 10 liter of acid \rightarrow 200 liter solution

method. Thus for small scale elution, effort need only be made to use the smallest volume of acid. The liquid scintillator used at present is compatible with both 0.1M H₂SO₄ and HNO₃ and may be compatible with higher strengths. As good elution figures have been obtained for both ²²⁸Th and ²²⁶Ra with lower acid strengths it seems from the results above that almost complete elution of these radionuclides may be achieved. Lead may only be monitored if the HTiO is completely dissolved.

For larger scale experiments, it will be necessary to perform a number of elution-precipitation steps to concentrate the radionuclides. Whilst this may be achieved for ²²⁸Th and ²²⁶Ra, a method has yet to be devised for lead. How interested are we in lead assay? At present it seems that simple acid elution will not work for lead. Elution of lead (and ²²⁸Th) might be possible with a hot EDTA solution at pH 2-3.

Hot EDTA + acid? not tried yet

Batch Extraction Experiments With MgCl₂ Solutions

It was desirable to know whether HTiO can extract ²²⁸Th and ²²⁶Ra from strong MgCl₂ solutions. To test this, a number of 100 ml MgCl₂ solutions were prepared, each containing 500 ppm HTiO and a mixture of ²²⁸Th and ²²⁶Ra (neutralised to pH 7). The magnesium chloride used for this experiment was Merck Analar MgCl₂·6H₂O. The solutions were shaken for 15 min and then filtered using 0.2 μm filter. The activity of 50 ml aliquots of these solutions was measured by γ-counting. The results are summarised below.

Sample	²²⁶ Ra c/a	error ± %	DF	²²⁸ Th c/s	error ± %	DF
Stock	3.66	2.92		2.56	2.6	
0% MgCl ₂	0.08	7.60	46	<0.007	*	>366
5% "	<0.01	*	>366	<0.006	*	>427
10 "	<0.018	*	>203	<0.009	*	>284
20 "	0.02	23.14	183	<0.006	*	>427
25 "	0.04	50.88	91.5	<0.01	*	>256

big excess of HTiO₂ compared to solution
10mg HTiO₂ to 50 liter H₂O

DF = Decontamination Factor * = 95% Confidence limit

$\frac{1}{DF} = \text{how much comes through}$

It can be seen that good DF's (>100) are obtained with all of the samples, with the notable exception of some radium appearing in the filtrate of the solution containing no MgCl₂. However, it seems quite clear that sorption of ²²⁶Ra and ²²⁸Th by HTiO is, to the measurement limits of this experiment, unaffected by

the presence of "pure" MgCl_2 . This experiment was repeated with a 25% solution of Merck "Technical" grade anhydrous MgCl_2 . The filtrate obtained from this single batch contact contained no measurable ^{228}Th and only 0.02 c/s ^{226}Ra .

Benchtop Ultrafiltration Experiments

A series of benchtop seeded UF experiments have been performed using a 1 ft Amicon HIP30-20 loaded with 50 μg of HTiO. The purpose of these runs was to obtain finer and more realistic measurements of the sorption properties of HTiO than can be obtained with batch experiments. In each experiment 40-50 litres of feed were passed through the HTiO-loaded membrane, with samples of permeate taken at intervals. 10 ml aliquots of the permeate were measured using the β - α coincidence scintillation apparatus. This technique, which records the $^{212}\text{Po} \rightarrow ^{208}\text{Pb}$ transition, has a counting efficiency of 50% (allowing for the branching ratio). As the ^{228}Th permeate will not be in equilibrium after being passed over the HTiO, the count rate observed from these samples will, of course, vary with time. Initially, for the first day, the majority of the activity present will be a result of the decay of ^{212}Pb ($t_{1/2} = 10.6$ h). As the ^{212}Pb lead decays, the ensuing activity will be as a result of the 3.66 day ^{224}Ra and finally, after 2 weeks, equilibrium with ^{228}Th will have been established.

HTiO blank

40 L of 2 M Ω R.O. water was passed through the membrane.

Samples of permeate below limit of scintillator detection.

Eluted HTiO with 100 ml of 0.1M HNO_3 . Activity of eluant (same day) = 40 c/l = 2.2 mBq/ml. Activity

- Techniques!

Run 1

12 KBq of ^{228}Th in 40 L of R.O. water (0.3 Bq/ml). pH = 4.5.

Performed to gain experience.

Permeate after 10 L.

counted same day = 0.1 c/s \approx 0.02 Bq/ml ^{212}Pb . DF = 15.

after 12 days = 50 c/h = 3 mBq/ml ^{228}Th . DF = 100.

Run 2

Repeat of Run 1.

Perm 1, after 5 L.

Counted after 20 h = 124 c/h \approx 7 mBq/ml ^{212}Pb . DF = 43.

After 18 days = 41 c/h \approx 2 mBq/ml ^{228}Th . DF = 150.

Perm 2, after 15 L.

Counted after 24 h = 128 c/h \approx 7 mBq/ml ^{212}Pb . DF = 42.

After 1 week = 130 c/h = 7 mBq/ml ^{226}Ra . DF = 42.

After 18 days = 95 c/h \approx 5 mBq/ml ^{228}Th . DF = 56 (?)

repeat = 115 c/h.

Perm 3, after 40 L.

Counted after 1 h = 650 c/h \approx 0.036 Bq/ml ^{212}Pb . DF = 8.

After 16 h = 341 c/h \approx 0.018 Bq/ml ^{212}Pb . DF = 17.

After 18 days = 64 c/h \approx 3.5 mBq/ml. DF = 86.

As a check, 50 ml of the feed solution was measured by γ -counting during Run 2 by looking at the ^{208}Tl line (583 KeV).

Activity recorded = 0.42 c/s. Assuming 3% GeLi efficiency (including branching ratio) = 14 Bq/50 ml = 0.28 Bq/ml. This agrees with the expected activity. However, recently (3/12/93), the activity of this sample of feed was re-measured. The activity recorded = 0.07 c/s = 2.26 bq/ 50ml = 0.045 Bq/ml.

Thus more than 80% of the ^{228}Th must have plated out on the side of the feed tank, whilst the lead and probably the radium were unaffected. Therefore, the true DF's for the samples counted after 18 days are:

Perm 1 = 22.5, Perm 2 = 9, Perm 3 = 12.8

Run 3

12 KBq of ^{228}Th in 45 L of 10% MgCl_2 (Merck Technical grade anhydrous used). pH of MgCl_2 solution = 8.68. before the addition of ^{228}Th to the feed, ran 2 L of feed through membrane to load the HTiO with Mg. The pH of the feed solution after addition of 30 ml of 0.1 HNO_3 ^{228}Th solution = 6.7.

Perm 1, after 5 L.

Counted after 5 days = 370 c/h = 0.021 Bq/ml. DF = 13

After 10 days = 336 c/h = 0.019 Bq/ml. DF = 14.

After 17 days = 32 c/h = 3 mBq/ml of ^{228}Th . DF = 89

Perm 2, after 20 L.

After 6 h = 370/h = 0.021 Bq/ml. DF = 15.

After 17 days = 460 c/h = 12.8 Bq/ml ^{228}Th . DF = 20

The activity recorded from both 50 ml feed samples after 3 weeks was 0.18 c/s. Assuming a 3% counting efficiency (as before), Activity = 6 Bq/50 ml = 0.12 Bq/ml

This implies that 60% of ^{228}Th is missing. Therefore the true DF's for ^{228}Th are:

Perm 1 = 40, Perm 2 = 11

As can be seen, the final DF obtained during Run 3 implies that ^{228}Th was no longer being extracted after 20 L of MgCl_2 solution. Batch experiments have shown that, with a relatively large amount of HTiO , good DF's can be obtained with from MgCl_2 solutions prepared from both anhydrous MgCl_2 and "Analar" $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. A cursory inspection of MgCl_2 solutions prepared from Merck "Technical" grade MgCl_2 reveals an appreciable quantity of undissolved crud. Efforts were made during the run to prevent particulate matter entering the HF membrane by ensuring that the feed pipe was 15 cm above the bottom of the tank and also by installing a coarse filter in the feed pipe. It may be that the Technical grade anhydrous MgCl_2 is chemically too impure, in terms of soluble and insoluble species, and the HTiO is simply loaded with chemical impurities rather than the radioisotopes of interest. Efforts are being made to procure a "clean" source of anhydrous MgCl_2 .

Conclusions

- More work needed (*surprise*).
- desirable to obtain a chemically clean source of $MgCl_2$ which is affordable.
- Need more β - α coincidence chambers.
- Better "accountancy" of radioisotopes in future experiments needed.

APPENDIX

NaCl v. MgCl₂

MgCl₂ is preferred to NaCl because the latter, outside the Acrylic Vessel, will acquire a significant 15 hour ²⁴Na activity from neutron capture, and the ²⁴Na decay releases a 2.75 MeV γ ray which can photodisintegrate deuterium and give rise to a neutral current background. It also happens that the MgCl₂ sample which has been checked has lower thorium content than NaCl samples.

There are however some potential difficulties with MgCl₂, which do not occur for NaCl:

- (1) It is necessary to use the 2 tons of MgCl₂ in the anhydrous form since the lowest hydrate, MgCl₂·2H₂O, would degrade the 1000 tons of D₂O by 758 ppm.
- (2) The quality of commercial anhydrous MgCl₂ is poor, as it can only be obtained at a purity level of 98%. Solutions of \approx 5% MgCl₂ prepared from the anhydrous reagent have a pH > 8.5 probably because it contains MgO. Examination of MgCl₂ solutions reveals the presence of insoluble "dirt". Preliminary evidence from ion exchange experiments (see attached report) suggests that soluble contaminants present in the MgCl₂ loads up and impairs the efficiency of H₂TiO. Thus it may be necessary to refine the MgCl₂ before purification can occur. Additionally, the use of appropriate quantities of deuterated hydrochloric acid to obtain the optimum pH might be required. NaCl is available as a high purity chemical.
- (3) The heat of solution is about 140 KJ mol⁻¹ of MgCl₂, sufficient to make a 20% solution boil. The dissolution of 2 tons of anhydrous MgCl₂ will require the removal of 3 giga Joules of heat. By contrast NaCl has a heat of solution of -2.4 KJ mol⁻¹.
- (4) For the same concentration of chloride an MgCl₂ solution has a substantially higher viscosity than a NaCl, about 63% higher for a 5M chloride solution and consequently filtration rates are lower.
- (5) The D₂O can be recovered from a MgCl₂ solution by evaporation, but only down to the level of MgCl₂·2D₂O. Recovery of the last 0.8 tons of D₂O may be difficult. NaCl can, of course, be completely dehydrated.

Summary

	For	Against
NaCl	<ul style="list-style-type: none"> -Cheap -Dehydrated easily -Purification may be easier -Lower chemical impurities 	<ul style="list-style-type: none"> -Na Neutron activation problem -Potassium present
MgCl ₂	<ul style="list-style-type: none"> -No activation problem -Less mass needed <p style="text-align: center;"><i>less potassium</i></p>	<ul style="list-style-type: none"> -Cannot be completely dehydrated, ∴ extra chemical processing for recovery -Large heat of solution -May need "course" purification -Relatively expensive