

SNO-SIR-94-025

An investigation of the SUF of radium using different membranes.

Gareth White

August 2, 1994

Introduction

Energy freed by nuclear reactions at the centre of the sun takes a million years to reach the solar surface, in which time it loses all information about how it was formed. By contrast neutrinos interact so weakly with matter that they travel directly from the sun to earth at the speed of light, taking 8 minutes. Detectors already built have shown that the measured flux is about half the theoretically predicted figure. The SNO project hopes to explain this solar neutrino problem, but even the thousand ton tank full of heavy water will only pick up about ten events per day. Hence backgrounds events need to be kept to a minimum. This requires that the D₂O and surrounding H₂O be purified with respect to ²²⁸Th and ²²⁶Ra. One method employed for purification is extraction of the radioactive species using ultrafiltration membranes.

The aim of these experiments was to compare the filtration of three membranes. In order to compare the membranes fairly, certain parameters were set equal for all three. These were the HTiO concentration on the membrane surface, and the permeate rate per area of membrane. During all filtrations the permeate and retentate rates were set equal.

There were two types of experiment performed on each membrane. The first, type A, used 1 liter of water spiked with a ²²⁶Ra source. Feeds, permeates and acid elutions for these experiments were all γ -counted. The specific activity of each sample was used to calculate the decontamination factor for the experiment and the recovery of ²²⁶Ra, using the following definitions:

- $DF = \text{Specific activity of feed} / \text{Specific activity of permeate}$
- $\text{Percentage extracted} = (1 - 1/DF) * 100$

- Recovery = (Total recovered activity in eluates / Total feed activity) * 100

Titanium recovery was also calculated by analyzing the HTiO solution before and after priming and the acid elutions.

The second type of experiment, type B, filtered 100 litres of water spiked with a ^{224}Ra , ^{212}Pb equilibrium mixture. These sources were made from ^{228}Th -free ^{224}Ra sources. The source was then left for two days for the ^{212}Pb to grow into equilibrium with the mother ^{224}Ra . The 50 ml feed source was then γ -counted before dilution into 100 litres. After dilution the feed was too weak to be γ -counted and so the feeds and permeates were counted using the β - α coincidence counter. The acid elutions could be γ -counted since the washes had a volume of only 250 ml. These were counted 1-3 hours after the experiment and again 2-4 days later. From the ^{232}Th decay chain it can be seen that the first count gives the ^{212}Pb activity and the second gives that of the ^{224}Ra . These counts are thus used to give the recoveries. The DFs for these experiments came from fitting the data from the β - α counter to give the activities of ^{212}Pb , ^{224}Ra in the samples.

Both types of experiment were essentially the same. The membrane was initially "primed"-coated with HTiO. It was intended that a surface concentration of 0.1 g/m^2 Ti in HTiO be used for all three membranes. Priming was done by recirculating the HTiO solution for about 1 hour. Then the spiked solution was filtered at a rate of 20 l/min/m^2 , so as to compare fairly the filtration efficiency of the membranes. Then the HTiO was washed off the membrane using 0.5 M HCl , recirculating for about 1 hour. Two acid washes were followed by one water rinse. The three membranes are best described in table 1.

Individual experimental results.

There follows a precis of the experiments carried out:

- Experiment 1 - Type A with Filtron Mini-Ultrasette

The membrane was primed with 0.2 g/m^2 HTiO. This HTiO had been made about 4 months previously and had clearly reacted in some way to produce a white solid which was insoluble in 1.5 M HCl . The measurements of Ti concentration from the spectrophotometer decreased with time and depended on how well the cuvettes were shaken. If the test tubes were left to stand for about an hour then a fine white solid settled out. This was suspected to be TiO_2 , formed from a water elimination reaction of HTiO.

Membrane	Type	Surface area m ²	Pore size KD	Max.pressure psi	Permeate Rates l/min	
					Before	After
Filtron Mini- Ultrasette	Flat bed	0.005	300	60	0.22@ 30 psi	0.07@ 42 psi
Amicon H1 P30-20	Hollow fibre	0.06	30	25	0.55@ 6 psi	0.40@ 25 psi
Filtron Minisette	Flat bed	0.07	100	60	1.65@ 20 psi	?

Table 1: Membrane descriptions. The permeate rates refer to the rates immediately after the glycerol had been washed off and that recovered consistently by cleaning after a number of experiments.

If this was the case then it would explain the dramatic drop in permeate rate observed at the start of the first acid wash. One explanation is that the acid dissolved most of the HTiO, but not the TiO₂, which settled on the membrane and clogged the pores. It was concluded that a new batch of HTiO should be used for further experiments. This new batch, "C2", was used for all other experiments.

- Experiment 2 – Repeat of experiment 1 using C2 HTiO

This time only 0.1g/m² of the new HTiO was used to prime the membrane. Whereas in EX1 three different permeate rates were used, the maximum permeate rate was now 0.07l/min so only this one rate was used. Again the permeate rate dropped suddenly at the start of the first acid wash. Washing after the experiment restored it to 0.07l/min.

- Experiment 3 – Type B using Filtron Mini-Ultrasette

The filtration of 100l was to be left overnight and should have taken ≈24 hours at 0.07l/min. However, by the next morning only 25l had been filtered, as the permeate rate had dropped to 0.013l/min. The experiment was stopped at this point. It was suggested that the cause of the continual drop in permeate rate was bacteria growing on the membrane, from the RO water supply. The membrane was washed and backflushed with NaOCl to kill the bacteria. This

failed to restore the permeate rate and so this was the last experiment using the mini-ultrasette.

- Experiment 4 - Type A using Amicon H1 P30-20

This and all subsequent experiments were carried out using Millipore water, to stop any possible bacteria problem. This experiment went to plan and gave good results.

- Experiment 5 - Type B using Amicon H1 P30-20

This experiment went well and gave instructive results about the decrease in DF during the experiment.

- Experiment 6 - Type B using Amicon H1 P30-20

This was intended to be a repeat of EX5, but the membrane was only primed with $\approx 0.04\text{g/m}^2$ HTiO instead of 0.1g/m^2 , due to confusion as to the concentration of the C2 stock being used. This confusion continued through experiments 7,8,9 before it was realised and corrected. Consequently the results are completely different and the DFs much lower.

- Experiment 7 - Type B using Amicon H1 P30-20

The membrane was primed with 0.05g/m^2 HTiO. The filtration is different from EX5,6 in that it is dead end, with the permeate side of the membrane filled with fluid at the start of the experiment. This again gave poor DFs, and some unexplainable Ti analysis.

- Experiment 8 - Type B using Amicon H1 P30-20

The acid washes show that the membrane was primed with 0.25g/m^2 HTiO.

- Experiment 9 - Type A using Filtron Minisette

The membrane was primed with $\approx 0.05\text{g/m}^2$ HTiO. Consequently the DFs are very poor.

- Experiment 10 - Type A using Amicon H1 P30-20

The membrane was purposely primed with 0.05g/m^2 , to compare the DFs with those obtained in EX4. However, the exact effect of insufficient priming cannot be deduced from this experiment alone since it was also discovered that the Millipore water now had a much lower resistivity: $1\text{M}\Omega\text{cm}$ instead of the $18\text{M}\Omega\text{cm}$ it should be. This was surmised to have affected the DFs in EX9 (and possibly EX8) as well as the priming.

- Experiment 11 - Type A using Amicon H1 P30-20

This was an exact copy of EX4, to check that the membrane was behaving as it did at the start of the experiments.

- Experiment 12 - Type B using Amicon H1 P30-20

A general conclusion of the previous experiments was that more HTiO should be used on the membrane. Hence $0.5\text{g}/\text{m}^2$ HTiO was used. The membrane was primed overnight so that during priming as much water was filtered by the membrane as in the actual experiment.

- Experiment 13 - Type B using Amicon H1 P30-20 and RO water

Since EX12 gave good results, it was decided to investigate the effect on DF of the quality of the water used. Hence EX12 was repeated, using RO water instead of Millipore.

- Experiment 14 - Type A using Filtron Minisette

The membrane was primed with $0.5\text{g}/\text{m}^2$ HTiO. Instead of the usual ^{226}Ra source used for type A experiments, a cocktail of ^{228}Th and ^{226}Ra was used. Hence the experiment yielded three DFs and recoveries.

Results

The results are shown in table 2.

Conclusions

There are a few points which should be noted for further work:

- Water quality is a very important parameter for the effectiveness of HTiO. It is more important for the filtration of Ra than Pb, but nevertheless important for Pb. The evidence for this comes from comparing experiments 12 and 13, which differ only by the quality of water used. Experiments 4 and 10 also bear this out, since they differ in water quality and HTiO concentration but it is clear that the former is the dominant factor. The poor results of experiment 8 can also be attributed to the $1\text{M}\Omega\text{cm}$ Millipore water used.
- At the start of this set of experiments it was anticipated that $0.1\text{g}/\text{m}^2$ HTiO would be sufficient for good DFs but it is clear that $0.5\text{g}/\text{m}^2$ gives better DFs which are constant throughout the 100 litre experiments. Much time was spent in establishing these first two conclusions, but they are now well known.

A : 1 liter
 B : 100 liters, Ra, Pb sp

Exp.	Type	HTiO g/m ²	DF values	Activity recovery %	Titanium recovery %
1	A - Mini Ultrasette	0.2	>370, >84, >103 >98, >373, >187	105±6	89±5
2	A - Mini Ultrasette	0.1	>200	95±9	
4	A Amicon	0.1	260±44 >250	101±1	97±5
5	B Amicon	0.1	²¹² Pb-P1=87, P2=16, P3=16 ²²⁴ Ra-P1=1300, P2=7.3, P3=3.9	77±5 110±5	107±5
6	B Amicon	0.05	²¹² Pb-P1=20.8, P2=4.8, P3=2.4 ²²⁴ Ra-P1=4.4, P2=1, P3=1	59±6 10±4	?
7	B - Dead End Amicon	0.05	²¹² Pb-P1=4.1, P2=1, P3=1 ²²⁴ Ra-P1=3.9, P2=1, P3=1	44±2 25±2	?
8	B Amicon	0.25	²¹² Pb-P1=4.3, P2=5.2, P3=5.2 ²²⁴ Ra-P1=1.7, P2=1, P3=1		
9	A Minisette	0.04	1.35±2.3 1.25±2.1	40±2	103±5
10	A Amicon	0.05	20.2±7.4 18.2±10.3	95±2	
11	A Amicon	0.1	630±210 160±40	100±1	
12	✓ B Amicon	0.5	²¹² Pb-P1=35, P2=19, P3=15 ²²⁴ Ra-P1=95, P2=69, P3=54	81±4 103±6	
13	✓ B Amicon	0.5	²¹² Pb-P1=14.2, P2=7.5, P3=8.4 ²²⁴ Ra-P1=42, P2=8.0, P3=5.8	89±6	
14	A Minisette	0.5	²²⁶ Ra-P1=1.00, P3=1.01 ²¹² Pb-P1=4.44, P3=3.39		

7.11.06
 2MSD water

88.8, 94.94
 100, 86.3, 75

MSD
 EX 4

7.11.06
 20 water

97, 95, 93
 88, 88.5, 88
 83, 86.6, 88
 87.5, 83

Table 2: Results of ultrafiltration experiments

Flow 0.5 g/l m²
 105 g / 100 liters | 0.06 m² | 30 l/min @ 600 psi
 108 g / 5 m² | 150 l/min

(1 - 1/DF) * 100

SMD 6

- Of the three membranes, the Amicon was most used since it gave good DFs and had a steady, reproducible permeate rate of 30l/min/m² at 60 psi back pressure. Of the Filtron flat bed membranes the mini-ultrasette gave good DFs but had a very poor permeate rate which worsened with each experiment. The miniset's permeate rate was not as good as expected to start with and the DFs obtained were very poor. This may be due to the fact that it is a low binding membrane. It is possible that the HTiO collects in parts of the circuit during priming rather than sticking to the membrane, consequently giving low DFs.
- It is recommended that the combination of 18M Ω cm water, 0.5g/m² HTiO and the Amicon H1 P30-20 membrane be used, which gives excellent DFs and recoveries. If these scale linearly to the size of the SNO assembly then they will allow the assay of ²¹²Pb, ²²⁶Ra and ²²⁴Ra in the detector.