

The effect of EDTA on the absorption of ^{226}Ra , ^{212}Pb and ^{228}Th by HTiO

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Abstract

A study was made of the effect of the complexant EDTA on the plating and the extraction properties of ^{226}Ra , ^{212}Pb and ^{228}Th . Batch contact and seeded-ultrafiltration experiments demonstrated that, at the 1 ppb concentration proposed for the SNO experiment, EDTA is unlikely to have any effect on the extraction of the radionuclides of interest by HTiO. It was also found that at these levels the plating behaviour of the radionuclides was not significantly altered by the presence of EDTA. At higher concentrations of EDTA (1-10 ppm) the extraction efficiency of ^{212}Pb was significantly impaired, whilst those of ^{226}Ra and ^{228}Th were effected to a lesser extent.

Introduction

The Sudbury Neutrino Observatory (SNO) will study the solar neutrino flux by detecting the Cerenkov radiation emitted by the electrons produced on photodisintegration of deuterons by neutrinos. Since neutrinos interact only weakly with matter, in order that this reaction is not obscured by that due to the photodisintegration of deuterons caused by the 2.6MeV gamma rays emitted in radioactive decay chain of ^{228}Th , the D_2O must be purified to extremely low levels of radioactivity. Hydrous titanium oxide (HTiO) can be used to effect the removal of ^{228}Th and ^{226}Ra . The addition of Ethylenediaminetetra-acetic acid (EDTA) to the D_2O in order to complex Pb has been proposed, however it is not known exactly how this would effect the action of the HTiO. Thus, a series of Batch Contact experiments were carried out in order to investigate the effect of varying EDTA concentration, pH, and presence of MgCl_2 on the absorption of ^{226}Ra and ^{228}Th by HTiO.

^{212}Pb

^{212}Pb
1

119
231

General experimental procedure

Samples were prepared in plastic conical flasks, the pH of each component being adjusted separately and the total volume of each made up to 100ml with RO water. Typically 2ml of 740Bq/ml ^{226}Ra or ^{228}Th stock solution was used in each sample, the ^{228}Th stock solution being diluted before neutralisation to reduce plating out. A 20% MgCl_2 Aldrich stock solution, and HTiO stocks C1 and C2 (800ppm and 900ppm respectively) were used. EDTA solutions were prepared using the *di*-sodium salt, which was normally added to active stock solutions prior to neutralisation.

The bottles were agitated for ≈ 30 minutes and then 50ml of solution was withdrawn from each bottle, using a syringe, and forced through a $0.2\mu\text{m}$ hollow fibre filter. A stock radioactive sample was prepared in each experiment to allow the calculation of DF's¹.

The ^{226}Ra samples were gamma-counted on the day of preparation using the 185keV gamma line. The ^{228}Th samples were counted twice, using the 583keV gamma line; firstly several hours after filtering, allowing ^{212}Pb DFs to be calculated, and then after ≈ 14 days, once the decay chain had equilibrated, in order to calculate ^{228}Th DFs. Where possible counting durations leading to 1 sigma errors of $< 5\%$ in the count rate were used, however for samples with count rates only marginally above background this was not possible and hence variations in DF between such samples may not be statistically significant.

1000 counts
3%

In each experiment duplicates of several of the samples were prepared in order to ascertain the magnitude of the errors on the results obtained and to determine the accuracy of the experimental procedures.

The ^{226}Ra experiments

A) 80ppm HTiO, 0 and 10ppm EDTA, 0 and 0.2% MgCl_2 at pH7

These results in table 1 show that the presence of EDTA reduces the absorption of ^{226}Ra by HTiO, leading to lower DFs, however the addition of MgCl_2 reduces the effect. It is not possible to deduce whether MgCl_2 completely reverses the effect of the EDTA since all the DFs obtained are high and therefore differences between them are not particularly significant. The errors stated refer to the lower limit, calculated from the one sigma error, of the DF in this case.

B) 80ppm HTiO, EDTA 0,10,50,100 ppm, MgCl_2 0,0.2% at pH9

The results are shown in table 2. With the exception of sample B all samples had low count rates. The errors counted on the high DFs achieved refer to the lower limit

¹DF = Decontamination Factor = initial activity/final activity.

Sample	EDTA ppm	MgCl ₂ (by mass)	DF <i>²²⁶Ra</i>
A	0	0	168±58
B	0	0	224±92
C	10	0	96±18
D	10	0.2%	384±196
E	10	0.2%	168±48

pH 7

Table 1: Experiment A - ²²⁶Ra

Sample	EDTA ppm	MgCl ₂ (by mass)	²²⁶ Ra DF
A	0	0	209±71
B	0	0.2%	22±2
C	10	0	190±77
D	10	0	127±32
E	10	0.2%	263±105
F	50	0	63±9
G	50	0.2%	112±20
H	100	0	144±40
I	100	0.2%	310±101
J	100	0.2%	279±89

pH 9

Table 2: Experiment B - ²²⁶Ra

Sample	EDTA ppm	MgCl ₂ (by mass)	²¹² Pb DF	²²⁸ Th DF
A	0	0	88±14	56.5±5
B	0	0.2%	111±15	84±13
C	10	0	34±3	63±4
D	10	0	36±3	53±4
E	10	0.2%	16±1	92±4
F	50	0	4.6±0.1	42±2
G	50	0.2%	7.5±0.3	85±15
H	100	0	1.5±0.1	33±3
I	100	0.2%	6.1±0.3	59±3
J	100	0.2%	6.1±0.2	58±1

pH 9

Table 3: Experiment A - ²²⁸Th

found from the one sigma error. Error bars have been omitted from the graph since their inclusion would totally obscure the data points.

In each case the addition of MgCl₂ improves the DF, however even at high EDTA concentrations good DFs (>100) are still obtained. The anomalously high count rate for sample B suggests an error in its preparation i.e. contamination or addition of insufficient HTiO.

The ²²⁸Th experiments

A) 90ppm HTiO, EDTA 0,10,50,100 ppm, MgCl₂ 0,0.2% at pH9

The results are as in table 3. The ²¹²Pb DFs are greatly reduced by the addition of EDTA, with further reductions occurring with increasing EDTA concentration. In each case the presence of MgCl₂ improves the DF, but does not significantly reverse the effects of EDTA.

The same trends are present in the ²²⁸Th DFs, which are in general higher than the corresponding Pb numbers, the exceptions to this being samples A and B, which both had ²²⁸Th DFs lower than the 10ppm EDTA samples.

B) 90ppm HTiO, EDTA 0,10,50,100ppm, MgCl₂ 0,0.2% at pH7

As seen in table 4, the ²¹²Pb DFs obtained are all extremely low, however the trend for decreasing DF with increased EDTA concentration is still observed, along with a slight reduction of the effect on addition of MgCl₂.

In the case of ²²⁸Th larger DFs were found, those with MgCl₂ being significantly

Sample	EDTA ppm	MgCl ₂ (by mass)	²¹² Pb DF	²²⁸ Th DF
A	0	0	1.93±0.08	10.2±5
B	0	0.2%	3.71±0.17	48.7±13
C	10	0	1.60±0.05	10.8±4
D	10	0	1.67±0.06	9.6±4
E	10	0.2%	1.70±0.07	56±4
F	50	0	1.22±0.04	7.6±2
G	50	0.2%	1.37±0.04	57±15
H	100	0	1.11±0.04	6.8±3
I	100	0.2%	1.41±0.05	95±3
J	100	0.2%	1.32±0.05	38±1

pH 7

Table 4: Experiment B - ²²⁸Th

Sample	EDTA ppm	pH	²¹² Pb DF	²²⁸ Th DF
A	0	6	×26.1±2.9	24.7±1.6
B	0	6	25.4±2.7	22.8±1.4
C	10	6	4.4±0.3	15.8±1.0
D	0	7	×36.7±5.4	14.7±0.1
E	10	7	12.2±1.0	12.4±0.6
F	0	7	30.5±3.9	12.4±0.6
G	10	8	16.5±1.8	10.9±0.6
H	10	8	18.9±1.9	10.1±0.7
I	0	9	×63.5±12.0	11.8±0.8
J	10	9	25.7±2.9	10.4±0.5

Table 5: Experiment C - ²²⁸Th

larger than those without, however it is difficult to assess the exact effect of the EDTA due to the apparently anomalously low DF of sample A.

C) 90ppm HTiO, EDTA at 0,10 ppm at pHs 6,7,8,9

From the results in table 5, the ²¹²Pb DFs, in general, decrease with decreasing pH, with the addition of EDTA at each pH causing a significant decrease in DF.

Sample	EDTA ppm	pH	²¹² Pb DF	²²⁸ Th DF
A	0	6	14.6±1.1	18.9±1.1
B	0	6	11.6±0.8	18.0±1.0
C	10	6	1.5±0.1	11.1±0.4
D	0	7	9.4±0.8	6.0±0.3
E	10	7	1.9±0.1	5.8±0.3
F	0	7	8.9±0.6	3.3±0.2
G	10	8	2.5±0.1	3.2±0.1
H	10	8	2.8±0.1	3.1±0.1
I	0	9	8.9±0.6	2.5±0.1
J	10	9	4.2±0.2	3.0±0.1

Table 6: Experiment D - ²²⁸Th

Conversely the ²²⁸Th DFs increase with decreasing pH (although above pH7 the variations are only slightly larger than the errors on the results.) with the decrease on addition of EDTA being smaller than for ²¹²Pb. The DFs of samples without EDTA tend to be smaller for ²²⁸Th than for ²¹²Pb.

D) 90ppm HTiO, EDTA at 0,10ppm, pHs 6,7,8,9

The results are shown in table 6. In this duplicate of experiment C the ²¹²Pb DFs with EDTA decrease with decreasing pH as before, however the DFs of samples without EDTA appear to be virtually pH independent (≈ 9 for pH 7,8,9). The ²²⁸Th DFs increase with decreasing pH as before, however at pH 7,8,9 the differences caused by addition of EDTA are negligible, being comparable to the errors on the results.

Conclusions

In most cases the results from the duplicate samples agreed within the margins of error which shows that the experimental techniques used are reasonably reliable. Also since the trends in the results from ²²⁸Th experiments C and D are the same we can be fairly confident that these effects are genuine.

- ²²⁶Ra

HTiO is very effective at absorbing ²²⁶Ra at pH 7 and 9, producing high DFs. EDTA impedes its operation although not substantially, and the addition of MgCl₂ appears to restore the action of the HTiO.

- ^{212}Pb

^{212}Pb is not absorbed as efficiently as ^{226}Ra by HTiO, with much lower DFs being achieved. The addition of EDTA substantially reduces the absorption of ^{212}Pb , an effect which escalates with increasing EDTA concentration and is only slightly reversed by the addition of MgCl_2 .

- ^{228}Th

The effectiveness of the absorption of ^{228}Th by HTiO is comparable to that of ^{212}Pb , however the effects of EDTA and varying pH are significantly different. The reduction in absorption on addition of EDTA is less dramatic, and does not worsen as greatly with increasing concentration as for ^{212}Pb , moreover the presence of MgCl_2 substantially improves the absorption of ^{228}Th .

The efficiency of the HTiO improves with decreasing pH, markedly on going from pH7 to pH6, both with and without the addition of MgCl_2 .

The addition of EDTA to the SNO detector would probably not affect the absorption of ^{226}Ra by HTiO, and is unlikely to significantly reduce the absorption of ^{228}Th . However more filtration experiments using EDTA concentrations of the proposed magnitude (ppb rather than ppm- see below and Appendix C) and with shorter contact times (the contact time of Batch Contact experiments is effectively infinite) are necessary to find out if the ^{212}Pb absorption efficiency of HTiO is significantly reduced.

Ultrafiltration Experiments

These experiments were carried out using a 0.03m^2 KALSEP hollow fibre filter. In each experiment the membrane was first washed with 0.1M NaOH and then rinsed four times with Millipore water until the permeate was reduced to $\approx\text{pH}8$.

The membrane was primed by placing the necessary amount of HTiO in 250ml of millipore water and circulating this solution for ≈ 45 minutes, by which time the solution had become clear indicating that the HTiO had been absorbed. One ml of ^{228}Th stock solution was diluted to 50ml, in order to avoid plating out, neutralised and gamma counted. This was then added to the feed containing appropriate amounts of MgCl_2 and EDTA stock solutions, with the total volume being made up to 5 litres with water, and thoroughly mixed before filtration. In experiments 9,10,11 and 12 feed and permeate samples were taken after $\approx 300\text{ml}$, 2.5l and 4.6l of solution had been filtered, to allow the calculation of DFs.

Expt	HTiO g/m ²	Water	MgCl ₂ (by mass)	EDTA	Recovery of activity
4	0.1	R.O.	0	0	62% immediately 75% after 1 week
5	0.2	R.O.	0	0	69% immediately 80% after days
6	0.2	R.O.	0.2%	0	60% immediately 61% after 2 days
7	0.2	R.O.	0.2%	10ppm	53% immediately 62% after 5 days
8	0.2	R.O.	0	10ppm	30% immediately 68% after 4 days
9	0.2	Millipore	0	0	58% after 2 hours 65% after 3 days
10	0.2	R.O.	0	0	75% after 2 hours 69% after 3 days
11	0.2	Millipore	0	10ppm	13% after 2 hours
12	0.2	Millipore	0	10ppb	60% after 2 hours

Table 7: Summary of ultrafiltration experiments

On completion of filtration the system was drained and then eluted three times; twice with 100ml of 1M HCl and once with 100ml of millipore water. 50ml of each wash solution was gamma counted and the radioactivity recovered in each case calculated.

A summary of the preparations are shown in table 7.

The results are shown in table 8. The DFs 1,2,3 are calculated from the permeate samples taken after 300ml, 2.5l and 4.6l respectively, except in the case of experiment 8 where DF3 is calculated from the entire permeate.

- Experiments 8 and 11

It can be seen from the low DFs obtained in both of these experiments that the addition of EDTA at 10ppm significantly reduces the absorption of ²¹²Pb by HTiO, regardless of whether RO or millipore water is used.

- Experiments 9 and 10

These experiments were identical except that Millipore water was used in 9, and

Expt.	^{212}Pb			^{224}Ra			^{228}Th		
	1	2	3	1	2	3	1	2	3
8	3.0	1.5	1.7	-	-	-	500	200	200
9	400	60	20	400	60	20	1,000	600	200
10	8.3	3.7	3.4	25	11	10	110	200	60
11	4.2	1.2	1.1	-	-	-	330	4.8	2.5
12	107	61	57	-	-	-	1,000	400	170

Table 8: DF's obtained from ultrafiltration experiments

RO water in 10. The DFs obtained when millipore water is used are significantly better than those produced using RO water, therefore in filtration experiments of this type the use of millipore water is desirable.

- Experiment 12

In this experiment, using millipore water in light of experiments 9 and 10, good DFs were produced in the presence of 10ppm EDTA.

Conclusions

A large amount of ^{212}Pb plating occurred in these experiments since the percentage recoveries were only $\approx 60\%$ even in the experiments where high DFs were obtained. In experiments 11 and 12 the feed buckets were rinsed with 3M HCl in an attempt to locate where the plating out was occurring. In this way, however, only a further 5% and 3% respectively of the initial activities used were recovered so the location of the missing ^{212}Pb remains a mystery. The percentage recovery in the first acid wash was found to increase to about 60% (from $\approx 45\%$ initially) after a period of approximately 7 days even in the case of experiment 8 in which the initial recovery was particularly low.

The addition of EDTA at 10ppb does not significantly affect the operation of the HTiO, however at 10ppm the absorption of ^{212}Pb by HTiO is impeded greatly. It is therefore important that further experiments are carried using a range of EDTA concentrations between these two values.

Appendix A: Comparison of HTiO stocks C1 and C2

Samples were prepared as for the previous batch contact experiments with 10ml

HTiO Stock	DF
C2	86±19
C2	72±16
C1	195±57
C1	124±37

900 ppm HTiO

800

Table 9: Comparison of HTiO stocks for ^{226}Ra

HTiO Stock	EDTA ppm	^{212}Pb DF	^{228}Th DF
C2	0	7.4±0.6	9.9±0.5
C2	0	5.7±0.4	8.7±0.6
C2	10	1.81±0.07	7.4±0.4
C2	50	1.24±0.05	5.0±0.2
C2	100	1.26±0.04	5.1±0.2
C1	0	13.0±1.3	23.9±1.3
C1	10	2.90±0.13	15.4±0.7

Table 10: Comparison of HTiO stocks for ^{228}Th

of C1 or C2, using both ^{226}Ra and ^{228}Th sources, and, in the case of ^{228}Th , with varying EDTA concentrations.

The ^{226}Ra results are shown in table 9.

Good DFs were produced by both stocks, however those for C1 were higher.

The ^{228}Th results are shown in table 10.

Both stocks were less efficient at absorbing ^{212}Pb and ^{228}Th , however the DFs produced by C1 were higher once more. The ^{212}Pb DFs in the presence of EDTA were particularly low for C2.

From these results we can conclude that the operation of C1 is more effective than that of C2.

Appendix B: Effect of varying HTiO concentration

A further pair of Batch contact experiments were carried out in order to investigate the efficiency of HTiO with varying concentration, both with and without MgCl_2 . A mixed source was used allowing the calculation of ^{226}Ra , ^{228}Th and ^{212}Pb DFs.

HTiO ppm	²²⁶ Ra DF	²¹² Pb DF	²²⁸ Th DF
30	23±9	1.9±0.2	2.9±0.1
10	8.5±9	1	1.8
3	5.5±9	1	1.4
1	2.3±9	1	1.3
0.3	1.3	1	1
0.1	1.3	1	1
0.03	1.4	1	1
0.01	2.7	1	1

Table 11: HTiO concentration v. DF. No MgCl₂.

HTiO ppm	²²⁶ Ra DF	²¹² Pb DF	²²⁸ Th DF
30	87±27	9.2±6.6	41±27
10	70±23	6.2±2.6	27±16
3	9.7±1.2	5.4±3.4	10.3±10.
1	4.3±0.3	3.1±0.8	4.3±1.6
0.3	1.4	1	1.9
0.1	1.4	1	1.7
0.03	1	1	1.3
0.01	1.6	1	1.9

Table 12: HTiO concentration v. DF. 0.2% MgCl₂.

HTiO ppm	²²⁶ Ra DF	²¹² Pb DF	²²⁸ Th DF
30	400±200	3.4±0.3	115±55
10	42±9	3.0±0.4	46±13
3	22±2	3.6±0.3	4.6±0.2
1	5.5±0.2	2.4±0.2	5.6±0.5

Table 13: 10 ppb EDTA, 0.2% MgCl₂.

The results are in tables 11 and 12 . In the case of both ²²⁶Ra and ²¹²Pb the DFs obtained are much better in the presence of MgCl₂, with those for ²¹²Pb without MgCl₂ being particularly low. In general good DFs are achieved for HTiO concentrations down to 10ppm, with the HTiO becoming virtually completely ineffective below 1ppm.

The errors on these results are large due to the high degree of plating out which occurred: ≈50% for ²²⁶Ra and ≈90% for ²¹²Pb. It was found that all the ²²⁶Ra plating occurred in the PMP conical shaking flasks, whereas for ²¹²Pb 50% plated out in the flasks with a further 40% of the activity remaining in the filters.

Appendix C: Varying HTiO concentration in the presence of MgCl₂ and EDTA

A further batch contact experiment carried out using HTiO concentrations down to 1ppm (the threshold for its operation), 0.2% MgCl₂, and 10ppb EDTA. The experiments are shown in table 13.

In this experiment plating out occurred to a slightly lesser degree: ≈25% for ²²⁶Ra and ≈85% for ²¹²Pb. EDTA at 10ppb does not seem to affect the absorption of ²²⁶Ra in the presence of MgCl₂, and the DFs for ²¹²Pb are greater than those obtained without EDTA or MgCl₂, but lower than those with MgCl₂ but no EDTA. However the presence of EDTA at this concentration does not significantly reduce the amount of ²¹²Pb plating which occurs.

It is likely that in order for EDTA to significantly reduce ²¹²Pb plating it will have to be present at concentrations sufficiently large to substantially impede the operation of the HTiO with respect to ²¹²Pb. More experiments need to be carried out in order to assess the effects of EDTA at concentrations between 10ppb and 10ppm.