SNO-STR-97-005

The production of ^{228}Th–less ^{224}Ra solutions using HTiO

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February 4, 1997

Introduction

The use of ^{224}Ra sources has obvious advantages for the calibration of the water systems proposed in SNO. The half-life of 3.66 days is of the right order so that counting does not require especially quick processing; after a few weeks, however, any trace of a spike has decayed away. Also, radium is not thought to plate out on surfaces in the same way as and so any spike added to a circulation system can be assured to follow the flow of the water in a system. The motivation for calibration is that the extraction and counting of ^{224}Ra is the main method for the monitoring of levels in the detector itself. The amount of present in such a spike is a vital factor as the chemistry of means that it can plate-out on surfaces and lead to a slow, contaminatory release of ^{224}Ra over a two year time period.

The separation of ^{224}Ra thus seems to be a useful technique to develop, and the experiments detailed below have been used to obtain sources of known concentration of all the relevant species in the chain so as to calibrate the seeded ultrafiltration (SUF) rigs being developed at Oxford. The method uses hydrated titanium oxide (HTiO), the seed in SUF, at a set pH to remove both and ^{212}Pb from a solution which contains ^{228}Th, ^{224}Ra and ^{212}Pb in equilibrium (see figure 1). The chemical processing itself is fairly simple in method and execution, and reproducibility seems to be good. At the moment levels of less than 0.5% ^{228}Th/^{224}Ra, in activity terms, have been obtained.

Method

As has been detailed in many studies of ion-exchangers, the variation of pH can be used to select for various elements. The separation of one element from another is therefore fairly easy as long as they differ by a sufficiently large extent in chemical

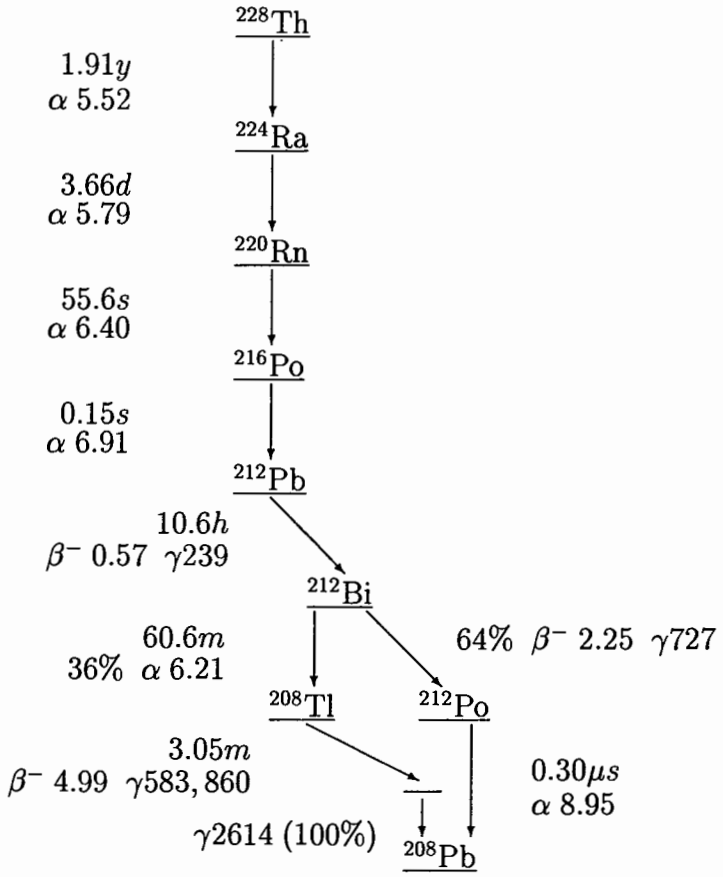

Figure 1: The Thorium-228 Decay Chain. The Q values of β and α decays are in MeV, while γ transitions are in keV. All times are half lives. The ^{208}Tl 583 keV line is used for γ counting, while the ^{212}Bi–^{212}Po–^{208}Pb transitions form the β–α counting sequence.

properties. The way in which ion-exchangers work means that it is both the valence and the size of the ions which determine this separability, and hence the removal of ^{224}Ra (valence II) from (valence IV) should be possible.

The requirements of a ^{224}Ra spike solution are not precisely determined for the detector itself (if indeed one is to be used), but as high a disequilibrium of and ^{224}Ra as possible in the sample is the most important factor. In the 5 tonne system at Oxford, a separation of around 100 (i.e. 1% ^{228}Th) is necessary.

The first tests of the method involved the determination of the pH which would lead to maximum separation of and ^{224}Ra activities. A few ml's of an aqueous solution, in equilibrium with its daughters, was added to 600ml of 1M HNO_3 and $TiCl_4$ was added so that Ti metal was present at the level of 50 ppm[1]. Also, a few ml's of a ^{226}Ra aqueous solution were added to the beaker to provide a direct measurement of the

[1]All ppm numbers referred to in this report are grammes per gramme.

Figure 2: The first pH variation experiment.

extraction of radium[2]. This solution was stirred constantly and gradually neutralized to pH 10. Samples of the solution were withdrawn at each integer pH and pushed through a 0.2μm pore size filter. The permeates were then γ counted using a standard GeLi detector. The ^{226}Ra was measured using the direct γ line at 185 keV.

The various activities for different members of the chain are obtained by counting the ^{208}Tl γ line activity at different times. The ^{212}Pb activity is obtained by measuring the line approximately two hours after the sources were filtered. This delay is introduced so as to obviate any effects due to the 1 hour ^{212}Bi intermediate daughter. The ^{208}Tl concentration will grow in with the ^{212}Pb half-life (10.6 hours) if there is excess ^{224}Ra, and so counting within around 3 hours was necessary. The activities are obtained by counting the samples after around three weeks: this is equivalent to around 6 ^{224}Ra half-lives, so that any remaining ^{224}Ra is reduced to around 1.5% of its initial level.

The results of the experiment are shown in figure 2. The y-scale of this graph is a fractional activity scale, and each species has been normalised to its initial value. As can be seen, the and ^{212}Pb are removed at low pH's, whereas ^{224}Ra is not removed until around pH 6. Obviously, the elements are being selectively taken up as the pH changes, and such an effect can be used to introduce disequilibria when filtering the source.

It is interesting to note that this effect is only seen as the pH is varied upwards. If the pH starts at 10 and acid is added, with previously prepared HTiO, the ^{224}Ra is removed in a curve that follows the curve. This hysteresis in ^{224}Ra take-up is important in the SUF rigs for SNO, as the membranes are coated with previously prepared HTiO solutions and used at pH 7.

The exact reason for this separation is not very well known, and could be due to an increase in surface area as colloidal HTiO is formed. Analysis of the Ti metal in the permeate showed that the amount of precipitated HTiO follows the and ^{212}Pb curves very closely. As this surface area increases, the and ^{212}Pb plate out on the HTiO at these low pH values. It is known that both and ^{212}Pb plate out preferentially with respect to ^{224}Ra at these low pH's, so that ^{224}Ra is only extracted at pH 7, where the HTiO actually starts acting as an absorber. This is very tentative, and without very detailed study, the actual cause could be difficult to pin down.

The measurements themselves show that if the pH is taken up to 4, the ^{224}Ra comes through at around 90%, but the is reduced to around 1%. The systematic errors and

[2]The chemical properties of ^{226}Ra and ^{224}Ra are indistinguishable.

the counter background do not allow a better estimate to be made, although this initial experiment was very encouraging.

The next stage was to look at the reproducibility of this experiment, and to consider any improvements that could be made. Also, the above tests were conducted at the hundreds of Becquerels per ml level, which is obviously far too high for the spikes required in the 5 tonne system or indeed for the detector. In order to work at more relevant levels, the β–α counters are needed.

Disequilibria and β–α counting

The liquid scintillator β–α counter has been detailed previously, but a quick recap is in order. The counters can take 12ml of an aqueous sample and count with 50% efficiency for chain decays, and 80% for ^{226}Ra chain decays. The background is of the order of 1 count per day in the chain, and around 20 counts per day for ^{226}Ra. As the counters are 'real time', the samples can be counted for any length of time, and the time spectrum of the events can be fitted to three competing exponentials so as to study the relative amounts of the long lived members of the chain. The time spectrum is divided into one hour intervals so as to easily resolve any ^{212}Pb disequilibria, and to limit the significance of any 60 minute bismuth decays.

In the 5 tonne system at Oxford, the specification for a ^{224}Ra source is fairly well established. In order to achieve good statistics around 2000 ^{224}Ra decays per day are required. This equates to extracting 100% of the ^{224}Ra from a 20 mBq source. The target for the activity is set by the background in the tanks before the spike is added. At present, this background is at the level of around 10 a day, so a ^{224}Ra spike should not add more than 10 counts per day. This is important as any added to the tanks will most likely stick to the walls of the tanks and produce a gradual contaminatory release of ^{224}Ra. This means that at least 99% of the activity should be removed.

Obviously, the scaling of the chemistry over the 5 orders of magnitude between this experiment and the γ experiment above could not be lightly assumed, and sources were produced to make sure the extraction still worked at this level, as well as looking at the reproducibility of the extraction and the effect of contact time. This latter variable is the amount of time the solution is allowed to stir before the requisite spike is withdrawn and pushed through the filter.

For these experiments 100ml of 1M HNO_3 were used, and 50 ppm of titanium metal was added in the form of $Ti(SO_4)_2$. Again the pH was brought up to 4 by the addition of NaOH[3], and 11 ml aliquots were taken. These were pushed through the

[3]10M and 1M solutions of NaOH were used so as not to change the overall volume, and hence

Name	Production Time and Date	Contact Time (in min)	Comments
Feed	15:00 - 4/5/94	–	Sample of feed
1-5	15:15 - 4/5/94	5	First sample
1-15	15:30 - 4/5/94	15	pH=5.6
2-10	16:10 - 4/5/94	10	New preparation
3-0	16:40 - 4/5/94	≈ 1	Sample taken as fast as possible
3-20	17:00 - 4/5/94	20	Longest contact time

Table 1: Summary of the sources prepared in experiment RE5. The names of the sources are split into two parts: the first is the preparation number, while the second is the contact time. All sources were extracted at pH 4 unless otherwise stated.

0.2μm filter straight into the scintillator jars. The permeate was made up to 12ml with 1ml of 1M HNO_3 so as to make sure the final sample was at 0.1M HNO_3, as in the standard aqueous sources used at Oxford. This was to ensure that the calibration of the counters did not change, although previous experiments had shown that such variations in salt concentration did not effect the response of the scintillator too much.

This process was repeated three times, with the same beaker being used for each preparation. The beaker was thoroughly cleaned with 1M HNO_3 between each 'run' so as to remove any traces of the radionuclides. The contact times were varied in a fairly random fashion, although a good spread was achieved over the three runs. The preparation of the sources is summarized in table 1.

As stated above the samples represent a fair range of different contact times, although 1-15 was something of a mistake in that the pH drifted during the 10 minutes between extractions. This was found to be due to the mixing speed of the stirrer being too slow. This speed was increased, and the pH of the third preparation was seen to change by only 0.1 pH units in the 20 minutes between samples. The source 1-15 was counted anyway, so as to give an indication of the difference such an error makes.

The samples were placed on the six β–α counters and counted immediately for 113 hours in the first run. This gives enough information for a fairly good fit of the ^{212}Pb and ^{224}Ra activities, but further data was needed at much later times in order to fix the thorium levels. This gap in the data is handled by ignoring those channels when fitting. A further two runs were taken: one started 343 hours after production, and the other 1128 hours after production. The second run was useful in the sense

the ppm Ti, by too great an extent.

that it showed the technique to be working qualitatively, while the third run pinned down the activity quantitatively.

In order to obtain any information from the counters, it was necessary to fit the differential time spectra so as to extract the varying activities of the three long lived[4] radionuclides (^{228}Th, ^{224}Ra and ^{212}Pb). Poisson distributed bin heights are needed due to the low statistics data. After some manipulation, the parameters of the three exponentials that make up the fit function can be used to give the initial (t=0) activities of ^{228}Th, ^{224}Ra and ^{212}Pb. The derivation of the chain equations and these coefficients is shown below:

Calculation of Activities from Fitting Time Curves

If we start with the three linked radioactive decays:

$$\frac{dN_{Th}}{dt} = -\lambda_{Th} N_{Th}$$

$$\frac{dN_{Ra}}{dt} = \lambda_{Th} N_{Th} - \lambda_{Ra} N_{Ra}$$

$$\frac{dN_{Pb}}{dt} = \lambda_{Ra} N_{Ra} - \lambda_{Pb} N_{Pb}$$

then we can say immediately:

$$\lambda_{Th} N_{Th}(t) = P_1 e^{-\lambda_{Th} t}$$

where the constant P_1 is the activity at t=0. Introducing this formula into the Ra equation:

$$\frac{dN_{Ra}}{dt} = P_1 e^{-\lambda_{Th} t} - \lambda_{Ra} N_{Ra}$$

$$\Rightarrow \lambda_{Ra} N_{Ra}(t) = P_2 e^{-\lambda_{Ra} t} + \frac{\lambda_{Ra} P_1}{\lambda_{Ra} - \lambda_{Th}} e^{-\lambda_{Th} t}$$

where P_2 is a constant. For the Pb equation, the introduction of the above formulae gives:

$$\frac{dN_{Pb}}{dt} = P_2 e^{-\lambda_{Ra} t} + \frac{\lambda_{Ra} P_1}{(\lambda_{Ra} - \lambda_{Th})} e^{-\lambda_{Th} t} - \lambda_{Pb} N_{Pb}$$

leading to:

[4] With respect to the 1 hour bin width

$$\lambda_{Pb}N_{Pb}(t) = P_3 e^{-\lambda_{Pb}t} + \frac{\lambda_{Pb}P_2}{\lambda_{Pb}-\lambda_{Ra}} e^{-\lambda_{Ra}t} + \frac{\lambda_{Ra}\lambda_{Pb}P_1}{(\lambda_{Pb}-\lambda_{Th})(\lambda_{Ra}-\lambda_{Th})} e^{-\lambda_{Th}t}$$

Now, the counter actually measures $\varepsilon\lambda_{Pb}N_{Pb}$, as opposed to $\frac{dN_{Pb}}{dt}$, where ε is an efficiency constant. If we make the approximations:

$$\lambda_{Pb}, \lambda_{Ra} \gg \lambda_{Th}$$

$$e^{-\lambda_{Th}t} \approx 1$$

then the rate is:

$$Rate = \varepsilon(P_3 e^{-\lambda_{Pb}t} + \frac{\lambda_{Pb}P_2}{\lambda_{Pb}-\lambda_{Ra}} e^{-\lambda_{Ra}t} + P_1)$$

As can be seen, if the source is in equilibrium P_3=P_2=0, and a flat spectrum with respect to time is seen. So the fit has the form of three competing exponentials, and at t=0:

$$\lambda_{Th}N_{Th}(0) = P_1$$

$$\lambda_{Ra}N_{Ra}(0) = P_2 + P_1$$

$$\lambda_{Pb}N_{Pb}(0) = P_3 + \frac{\lambda_{Pb}P_2}{\lambda_{Pb}-\lambda_{Ra}} + P_1$$

Also, the constraints

$$P_1 \geq 0$$

$$P_1 + P_2 \geq 0$$

$$P_1 + \frac{\lambda_{Pb}P_2}{\lambda_{Pb}-\lambda_{Ra}} + P_3 \geq 0$$

can be applied in the fitting process, as negative activities are unphysical. In order to ease the calculation of the activities at t=0, we can transform the coefficients as below:

$$Rate \propto P_3 e^{-\lambda_{Pb}t} + \frac{\lambda_{Pb}P_2}{\lambda_{Pb}-\lambda_{Ra}} e^{-\lambda_{Ra}t} + P_1$$

Now:

$$\lambda_{Th}N_{Th}(0) = A_{Th}$$

$$\lambda_{Ra}N_{Ra}(0) = A_{Ra}$$

Figure 3: The differential time spectra of source 2-10.

Name	activity at t=0	^{224}Ra activity at t=0	^{212}Pb activity at t=0	Ratio ^{224}Ra /	Events in last run
Feed	32.40	33.79	34.41	1.04	–
1-5	0.0327	31.30	0.58	960	4
1-15	0.0450	16.65	0.001	370	5
2-10	0.116	38.15	0.40	320	13
3-0	0.0157	36.12	0.001	2200	2
3-20	0.0659	37.37	0.001	570	8

Table 2: Parameters of best fit for the six sources. The ratio above is the fraction of at t=0 with respect to ^{224}Ra at t=0.

$$\lambda_{Pb} N_{Pb}(0) = A_{Pb}$$

$$\frac{\lambda_{Pb}}{\lambda_{Pb} - \lambda_{Ra}} = \alpha$$

$$P_1 = A_{Th}$$

$$P_2 = A_{Ra} - P_1 = A_{Ra} - A_{Th}$$

$$P_3 = A_{Pb} - P_1 - \alpha P_2 = A_{Pb} - A_{Th} - \alpha A_{Ra} + \alpha A_{Th}$$

$$\Rightarrow Rate \propto \left[A_{Pb} e^{-\lambda_{Pb} t} + A_{Ra} \alpha (e^{-\lambda_{Ra} t} - e^{-\lambda_{Pb} t}) + A_{Th}(1 - \alpha e^{-\lambda_{Ra} t} + (\alpha - 1) e^{-\lambda_{Pb} t})\right]$$

In order to fit such sparse data, log likelihood has to be employed, although a straight chi-squared fit, with root N errors, could be used on the feed source due to its continually high count rate. A typical time spectrum, taken from source 2-10 is shown, with the first two runs shown in an expanded view, and the data from the third run also shown on the lower plot.

The fit parameters for all the samples are shown in table 2.

As a simple check of the fitting routine, we can compare the activity parameter, P1, with the measured number of counts in the final run. After the subtraction of the fraction of ^{224}Ra that still contributes, these correlate very well within the root N errors of the data. Given the small data sample, any errors assigned to the ^{224}Ra /ratio must have these large root N errors.

Looking at the data itself, it is fairly obvious that the different sources all have approximately zero ^{212}Pb, zero and around 100% ^{224}Ra. The only big difference is

with 1-15, the source that drifted to pH 5.6. As expected, more ^{224}Ra seems to have been removed, although there is still an absence of ^{228}Th. This does demonstrate the sensitivity of the experiment to differing pH values, and the importance of getting the pH right. There does not seem to be any strong correlation in the contact time differences; in fact the only slightly worrying point seems to be that the parameters indicate a slight excess of ^{224}Ra. This is difficult to explain, but a possible theory is simply that any contamination of the chemical apparatus would simply add to the spike used. This would seem to be rather high for such an explanation, although not impossibly so. A much more likely scenario is that the fitting routine still has a few problems that need ironing out, especially the dependance of the fit on the first 10 or 20 hours, where the value of the ^{212}Pb parameter is determined. The most probable problem is the contribution of the constraint applied to the sum of the fit parameters and the interference of the ^{212}Bi half-life.

This brings us to the thorny issue of background. As has been stated before, the background observed in the counters is around one count per day. This was observed on both a pure scintillator sample and on a standard scintillator/acid mix. Given that the last data run occurred over a period of 92 hours, this gives an approximate 'background' of 4 for the run. It must be made clear that this is a background which is present in all samples, regardless of their history. Thus, we could possibly subtract 4 counts from all the figures in table two, but to do so seems slightly cavalier. Given that the use of these ^{224}Ra sources would be in large volume (i.e. few tonne) calibrations, where the backgrounds are that much higher anyway, the only real conclusion that can be drawn is that were any of the above sources used to calibrate, they would not add significantly to the contamination background in the 5 Tonne system. In order to produce a definite number for the ^{228}Th/^{224}Ra disequilibrium it would be necessary to work at higher levels of activity. Having said this, the upper limit on the specific activity of the is at around 0.5% that of the ^{224}Ra, taking the worst case above and using the root N statistics.

Conclusions

The production of 'clean' ^{224}Ra sources is a very important subject in the calibration and study of the water systems in SNO. Obviously this is a workable method, and although in theory a fairly simple experiment, the evidence of the low-level source which drifted to pH 5.6 shows that care is needed in the preparation of the samples, unless samples of the spike are reserved for counting. The fitting of the time spectra shows the differential spectrum can be used at such high activity levels, but the technique will need much more work if it is to be applied at the activity levels envisaged

in the detector itself. Another point worthy of note is that the sources are also free of ^{212}Pb, which in itself is not of obvious importance, but may become a useful feature.

Other points of interest include the stability of the scintillator with respect to time, as demonstrated in the feed source, which was flat to within errors over 2-3 weeks. In fact, the feed source was counted separately in a run not shown here, and the count rate was well within errors even after a month and a half.

The fact that the chemistry does not seem to change over five orders of magnitude in activity is encouraging, although we are still a huge distance away from the detector situation, and no inference can be drawn that work at the mBq/ml will even approximate to the situation in the detector plant.

Looking on the bright side, we have demonstrated a number of the features of the scintillation counters: their stability, their low background, and their ability to differentiate unambiguously the members of the chain by the differential time spectrum. Certainly, the sources detailed above would be quite worthy of use in the 5 tonne system at Oxford, and work is continuing on calibrating the system in such a fashion.