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 bject: As per action of meeting: complete Pb procedure layout.
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1.

Heavy Water Monitoring Technique for the 232-Th Chain Contaminant: 212-Pb Precipitation and Alpha Counting

SNO-STR-93-033

1993-07-12

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Michal Shatkay
Cathy Shewchuk

1) Preconcentration of contaminants

1.1 Add EDTA at 1ppb in the water to complex the lead.

The effect of the EDTA on the precipitation procedure is still to be investigated by G. Laberge, although from the literature it is expected that there will be considerable interference during precipitation due to the persistence of the Pb-EDTA complex. There is also the possibility that the concentration of EDTA would be 0.1ppb instead of 1ppb: the exact concentration is not fixed as of yet.

1.2 Add, at the 1ppt level, some stable lead to act as carrier.

The actual amount of carrier added depends on the concentration factor of the R/O. In all instances, the amount added cannot yield more than 0.1mg of Pb carrier in the final concentrate volume and the amount added should be known very accurately. By comparing the amount of added carrier to the amount of lead recovered by precipitation, it is possible to determine what the systematic error is for the entire procedure. For the cases where 0.1mg of carrier is used, the recovery efficiency cannot be determined gravimetrically. The recovery can however be measured by Flame Atomic Absorption (FAA) which uires that the precipitate be redissolved and diluted. There has been no rk done on this issue and the method of dissolution of the precipitate has not been determined either.

1.3 Concentrate the Pb-EDTA complex using reverse osmosis (R/O).

This work is already well underway. The R/O membrane has been chosen and will operate at about 6 litres/minute on the test bed. The design criteria for the R/O is for a flow rate of 100 litres/minute with the possibility of going to 200 litres per minute. The preliminary results for the R/O membrane were of 98% water recovery efficiency for a single stage and 98.8% Pb-EDTA recovery efficiency (for a Nitto 759 membrane). The planned running time on the R/O fo a single measurement is 20 hours: this would not change for the 200 litre/minute R/O flow rate, thus giving a factor of two gain in the signal activity. At the 100 l/min flow rate, the total volume of water sampled would be 120 tons, and at 200 l/min it would be twice that amount.

The following scenarios are proposed for the 100 l/min flow rate.

a) Two Stage R/O

```
100 l/min -- R/O -- 98 l/min
              |
          2 l/min
              |
             R/O -- 1.6 l/min
              |
         40 cc/min with 40cc online Cation exchange column
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b) Tree Stage R/O

```
100 l/min -- R/O -- 98 l/min
              |
          2 l/min
              |
             R/O -- 1.6 l/min
              |
         40 cc/min
              |
             R/O -- 39.2 cc/min
              |
        0.8 cc/min with 0.8cc online Cation exchange column
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2) Extraction of Lead from Pb-EDTA

Pass the R/O concentrate through a Dowex 50 cation exchange column to separate the lead from the EDTA and retain the lead on the column followed by elution of the lead from the column into a volume of hopefully no more than 500cc.

This work has to be continued since only one measurement has been done by Cathy Shewchuk yielding a combined retention and elution efficiency of 95%. The elution was done with 4M nitric acid on a 2cc column with a flow of 1BVM giving a total eluate volume of 30BV.

The two stage scenario implies that the eluate volume will be 30 times 40cc, or 1.2 litres. It is not possible to work with such a volume to precipitate the lead. The volume would be reduced to 500cc by the use of a Dura Dry MP cryo-vacuum drier which can operate at 20 litres per 24 hours. One hour would be the time required to reduce the 1.2 litres to one half litre. The molarity at the solution would then be very high and it would be necessary to adjust it to 0.2M. On the other hand, the three stage scenario would be greatly prefered. The eluate volume would only be 24cc (30BVs times 0.8cc) at 4M nitric acid which, when diluted by a factor of 20, would yield a final working volume of 480cc at 0.2M nitric acid - which is exactly what is required.

Generally, the time required for retention of the lead on the column and for elution of the lead from the column is essentially equal. The size of the cation exchange column to be used has not yet been determined. More studies under different conditions are required and the background for this part of the procedure has not been measured as well.

3) Precipitation of 212-Pb as PbCrO4

As of 1993-07-16, the recovery efficiency for the lead carrier is (for nine measurements made under almost identical conditions):

(98.4+-4.5)%

The uncertainty shown above is one sigma calculated from the standard deviation of the nine trials. An careful analysis of the instrumental uncertainties gave a one sigma interval of +-4.5% as well.

When low level activity or actual in situ work is done, only Ultrapure reagents are used in the precipitation procedure. The background measurements that were made established the background level at 5.0+-2.2 for a full procedural blank with the straight background at 3.91+-1.97. The full procedural blank includes the straight background contribution. This can only get worst when the effect of the R/O, cation exchange and elution are investigated in terms of their contributions. Four trials have been completed with the use of HNO3 (Nitric acid) instead of HCl (which normally is added to the solution at step 3.2 along with the lead carrier when an eluate is not used). The results show that there is no difference in recovery efficiency between the two different acids. The procedural background must therefore be measured for ultrapure nitric acid as was done for the ultrapure hydrochloric acid.

3.1)

Empty Nalgene teflon heatable beaker (HB) of the 10% reagent grade nitric acid solution (back into its stock bottle) and of all filter holder (FH) assembly components. Rinse HB and FH components in CRPP ultraclean water thoroughly and set FH components down in fumehood to dry on a clean surface.

3.2)

Pour into the HB the 500cc eluate. Cover the HB with its polypropylene lid. Carefully immerse a teflon coated magnetic stirring bar (SB) into the solution and set the stirring speed for a gentle stir.

3.3)

Cover the HB with a sheet of aluminum foil that is crimped by hand onto the extruding lip of the beaker and poke holes into the foil as required to insert the following equipment. Suspend a 25ml plastic burette filled with a diluted solution of Ultrapure water (CRPP) and concentrated (28-30%) reagent grade NH4OH (3:1) over the HB and also place a pH probe into the solution (make sure that the pH meter is calibrated according to note d below). Also place a glass thermometer suspended in the solution to monitor the temperature during titration. This will permit the pH measurement to be temperature compensated. Let the NH4OH drip slowly into the solution and carefully watch the pH. When the pH starts to rise in large increments with the addition of single drops, stop adding the 3:1 NH4OH. This will occur near the pH of 3. Now continue titrating with a 50:1 solution until the pH reaches about 5.6 to 5.7. Take a single drop of the 50:1 solution and dilute it in several cc's of CRPP water... Continue titrating dropwise with the new dilute base until the pH of 5.90 is obtained. The total volume of reagent required for the titration should not exceed more than about 30cc. With the dropwise addition of more and more dilute NH_4OH, it is fairly straight forward to always obtain a pH of 5.90 for the solution. Remove the pH probe and thermometer while rinsing them thoroughly with Ultrapure water (CRPP). Also remove the burette before going on to the next step.

3.4)

Cover the HB again with the polypropylene lid. While continuing to stir gently, heat the solution on the hot plate (see note e) for no more than 10 minutes. This will bring the solution temperature to about 30 degrees celsius. After a few minutes have elapsed since the heating began, slowly add dropwise 2ml of Analar grade K_2CrO_4 solution using a dedicated 10cc polypropylene pipette. The K_2CrO_4 solution is 1.5M in a 100ml polypropylene volumetric flask. After the 10 minute heating period has elapsed, remove the HB from the HP and let it sit in the fumehood for 15 minutes to let it cool down somewhat. Do not attempt to remove the SB from the solution at this point since it will most likely be covered with some of the precipitate.

3.5)

Tare a thick (serial# VVLP02500) 0.1 micron pore size millipore hydrophilic membrane (i.e., filter) and install it in the FH. Pour 50cc of the solution into the FH assembly and turn on the water aspirator vacuum suction. Add more of the solution as soon as the level in the FH drops below the 25cc mark, but do not exceed the 50cc level. Once all the solution has been poured into the FH, add 25cc of Ultrapure water (CRPP) to the HB and rinse it well before emptying it into the FH. Let the solution pass completely through the filter before removing the vacuum.

3.6)

Remove the filter from the FH and place it under an IR lamp for a half hour period before weighing it on an analytical balance (+-0.1mg resolution at least).

3.7)

Completely rinse all equipment in ultrapure water (CRPP) before immersing in 10% nitric acid as found in step 3.1. Dispose of the filtrate in the appropriate way depending on if it is radioactive or stable lead that was precipitated. The flask which supports the FH and holds the filtrate is also thoroughly cleaned with a 10% nitric acid rinse followed by a wash with Radiacwash.

4) Alpha Counting of Precipitated Source

At this point in time, it is not clear whether one counter will be abandoned for the other: it may well be that they are to complement each other.

4.1) Ortec 576A Dual Alpha Spectrometer

The efficiency of this counter is presently at 27.5% and the efficiency will b increased to 32% by simply reversing the order in which the planchette components are inserted into the chamber. The source will therefore sit closer to the SSB detector. The effect on the spectrum for a closer source will be to reduce the energy resolution although there will be a gain in counting efficiency. Two sources can be counted simultaneously with the spectrometer.

4.2) Alpha-Beta Counter

The alpha-beta counter will hopefully have a much better efficiency of about 90% although this remains to be shown by Angela Plagemann and Cliff Hargrove. ntrary to the spectrometer, the alpha-beta counter will not measure the energy of he alpha particles but will use coincidences between alpha's and beta's to identify the decay and sort it out from the background.

NOTES:

a) The HB is always covered when outside work is not being done on the contained solution. The cover itself is a thick circular piece of polypropylene plastic.

b) The FH are always covered with a piece of Parafilm when not in use during execution of the procedure and in between refills.

c) All the Pb work takes place inside a plastic fumehood which uses heavily filtered air. This serves to reduce the dust intake in the solutions.

d) The pH meter is calibrated according to the procedure outlined in its manual. The buffers employed for calibration are at pH 4.00+-0.02 and 7.00+-0.02. The temperature of the buffers is determined with the help of a capped plastic bottle wherein a thermometer is held in water by a rubber stopper.

e) A calibrated hot plate is used. The setting is set such that the temperature on the hot plate surface is about 75+-5 degrees celsius for the gentle heating step of the procedure. The temperature on the hot plate surface was measured with a metal coil thermometer supplied with the Nalgene heatable aker.