Progress Report on the Joint α-Spectroscopy Project of the Wisconsin Department of Natural Resources and the State Laboratory of Hygiene – Radiochemistry Unit.

(July 5, 2000)

Introduction

In this report, a description of the problems encountered with the methods for the analysis of polonium, uranium, and thorium is discussed, and a description of the way that these problems have been solved is presented. Quality control experiments are presented for each method. At this point, we are ready to begin analyzing groundwater samples.

Development of the Method for the Analysis of Polonium 210.

As mentioned in the previous quarterly report (March 17, 2000), Dr. Isabel Fisenne, at the Environmental Measurements Laboratory, recommended the use of procedure Po-02-RC from the HASL-300 manual, 28th Ed. for the analysis of polonium 210. Some severe problems developed when this procedure was implemented, and, consequently, the procedure had to be altered. In addition, the procedure does not include some important laboratory hygienic practices and does not include the underlying chemical and physical principles of the method.

When procedure Po-02-RC was used to analyze a 10-L sample of Madison tap water, a gelatinous precipitate formed. Literature research and some simple chemical tests performed in the Radiochemistry Unit suggested that the precipitate was silica gel. A sample of the precipitate was submitted to the Wisconsin Occupational Health Laboratory Inorganics Unit for elemental analysis using a x-ray fluorescence measurements. The results, which were performed on April 10, showed that the precipitate contained high levels of calcium, magnesium, and silicon.

I contacted Dr. Fisenne about this problem. In a conversation that took place on March 16, she was aware that the formation of a silicate precipitate was likely when 10 L of sample was used, although procedure Po-02-RC made no mention of such a precipitate. Dr. Fisenne recommended trying to dissolve the precipitate by boiling the sample in a Teflon beaker with 10 mL of concentrated nitric acid and 5 mL of 40% hydrofluoric acid. On March 17 this procedure was tried four times in succession on the gelatinous precipitate derived from a sample of Madison tap water, but there was no perceptible reduction in the volume of the precipitate.

The first steps in procedure Po-02-RC are to acidify the water sample with nitric acid and to concentrate the polonium in the sample by boiling a total of 10-L of the sample down to a volume of about 5 milliliters. Natural waters routinely contain as much as 15 ppm of silicic acid $Si(OH)_4$. Moreover, the phase diagram of nitric acid shows that the vapor pressure of HNO_3 is relatively low when the concentration of HNO_3 is less than that of the azeotropic HNO_3 concentration of 69.2 wt%. Consequently, as the volume of the acidified water sample decreases by evaporation, the concentration of HNO_3 increases, tending towards the azeotropic concentration. (This behavior was confirmed in an experiment performed on April 7 and 8 in which a 3-L, acidified sample of Madison tap water which had been reduced to a volume of 140 milliliters was titrated with sodium hydroxide. More than 98% of the nitric acid that was present initially still remained in the solution.) Thus, both the silicic acid and HNO_3 concentration increase as the sample is evaporated. Since the polymerization of silicic acid to silica gel is catalyzed by strongly acidic solutions (polymerization is slow in moderately acidic conditions, i.e., in the pH range of about 1 to 5), the conditions for the formation of silica gel become more favorable as the volume of the sample is reduced.

The formation of silica gel is clearly unacceptable. Silica gel retains a significant volume of the solution and can act as a cation exchange resin, both of which will lower the recovery of polonium. There seemed to be at least three options for the treatment of the sample: (1) chemically alter the silicic acid so that it cannot polymerize to form silica gel (2) alter the conditions of the experiment so that the formation of silica gel is not kinetically favorable, or (3) allow the silica gel to form and digest the gel chemically, causing it to depolymerize and form soluble compounds. The recommended treatment of the silica gel with nitric and hydrofluoric acids by Dr. Fisenne is a method belonging option (3). As will be discussed below, this method is inadequate for two reasons: (1) the concentration of hydrofluoric acid is too low and (2) insoluble fluoride precipitates form.

In addition to the prevention of silica gel formation, the volume of the sample must be reduced to the point that the sample can be fit into the deposition cell. The main part of the deposition cell is a polypropylene bottle which has a nominal volume of 60 milliliters (actually the volume is somewhat greater if the volume of the neck of the bottle is taken into account). Thus, a final sample volume of about 50 milliliters would be acceptable. It is possible that a larger bottle could have been employed, although increasing the volume would be expected to decrease the fraction of polonium deposited for a given period of time and would require some experimental investigation to ensure that an acceptable polonium yield was achieved.

Although the chemistry of polonium is somewhat complex and not completely understood, it is clear that polonium tends to adsorb on the surfaces of particulate matter, such as colloids and precipitates, and that significant amounts of polonium can adsorb on the walls of glass containers if the pH of the solution is more basic than about 2. Thus, during the course of the procedure the solution must be kept acidic and any particulate matter formed must be completely dissolved.

If the formation of silica gel is inevitable, it would seem that either option (1) or (2) would be advisable, since the prevention of the gel may result in a less time consuming procedure than a procedure in which the gel is allowed to form and then digested. Initially, two methods belonging to option (2) were tried. Silicic acid reacts with hydrofluoric acid to form fluosilicic acid, H_2SiF_6. Fluosilicic acid is miscible with water in all proportions. Consequently, an experiment, initiated on April 13, was tried in which 30 mL of HF was added to the sample before the silica gel formed. The experiment was a partial success in that a gel did not form, although a faintly green, translucent precipitate formed. The precipitate probably consisted of various metal fluorides, such as MgF_2, CaF_2, and PbF_2. Magnesium fluoride and calcium fluoride are somewhat soluble in hydrochloric acid.[1] However, the use of solutions much in excess of 0.5 M HCl is unacceptable since under such conditions either the coprecipitation of polonium with PbS will not occur because of the solubility of PbS in acidic solutions or, if one forgoes the coprecipitation step, the high acidity of the solution will cause excessive corrosion of the Ni disc that is used for the deposition of the polonium, leading to a decrease in the amount of polonium deposited. An attempt made to dissolve this precipitate with various concentrations of hydrochloric acid failed to bring about complete dissolution. Even concentrated HCl failed to bring about complete dissolution.

In the second method belonging to option (1), initiated on April 25, excess molybdic acid, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, was added to a Madison tap water sample. Molybdic acid reacts with $Si(OH)_4$ to form silicomolybdic acid, $H_4(SiM_{12}O_{40})$, a compound which is highly soluble in water and which gives water a characteristic yellow color.[2] In an experiment started on April 25, 7.98 grams of molybdic acid was added to a total of 8.0 L of acidified Madison tap water. When the volume of the water was reduced to less than 1 liter, a non-gelatinous precipitate formed. Solid silicomolybdic acid decomposes at about 100 C, so the precipitate may have been an insoluble decomposition product of silicomolybdic acid. Because of the presence of the precipitate this method was abandoned.

Three methods belonging to option (2) were tried. Since option (2) involves kinetically inhibiting the formation of silica gel, the resulting solution may be supersaturated in silicic acid and, therefore, from a thermodynamic point of view, unstable. Consequently, it is clear that the conditions of the experiment must be carefully controlled in order not to bring about the sudden formation of silica gel. The rate of polymerization of silicic acid below 80 C is relatively slow. Consequently, an acidified sample of Madison tap water was reduced by boiling to a volume of about 200 milliliters, and, then, the sample was held at about 70 C, a temperature which would not induce polymerization but would hopefully bring about evaporation of the sample in a reasonable length of time. However, the evaporation process proved to be exceedingly slow, and the experiment was aborted after about one week.

As mentioned previously, the polymerization of silicic acid is catalyzed by strongly acidic solutions. Thus, in two methods belonging to option (2) the pH of the solution was adjusted as the volume of the solution was decreased, in order to avoid the increase in the acidity of the solution. In an experiment initiated on April 5, a 2.5-L sample of acidified Madison tap water was reduced to a volume of about 200 milliliters. A few drops of metacresol purple indicator and 3.6 grams of maleic acid were added to the solution. The pH of the solution was adjusted to the salmon pink endpoint of metacresol purple ($pH \approx 2$) with concentrated ammonium hydroxide. The purpose of the maleic acid was to act as a buffer to hold the pH of the solution approximately constant as the volume of the solution was reduced (the pK_a of maleic acid is 1.83). Upon evaporating the solution to less about 100 milliliters, some foaming began to occur, and at about 25 milliliters the foam began to harden. Apparently the foaming is caused by maleic acid, a moderately surface-active compound. When enough polished water was added to the solution to bring the volume up to 100 milliliters, the maleic acid dissolved and there was no evidence of a gelatinous precipitate. This approach may have worked but it was felt that the excessive foaming could interfere with the deposition of the polonium, i.e., some of the polonium could be captured in the foam and would not be available for deposition on the Ni disc or the solution may have foamed to the point where some of the solution was lost from the deposition cell. In addition, it was not clear that larger samples could be consistently reduced to 50 mL, so it was decided to forego this approach.

The acidity of the solution could also be reduced by allowing formaldehyde to react with the nitric acid as in the following redox reaction:

$$4NO_3^-(aq) + 4H^+(aq) + HCHO \rightarrow 4NO_2(g) + CO_2(g) + 3H_2O(l).$$

Such an experiment was tried on April 21. The formaldehyde reacted vigorously with the solution, evolving the brown gas NO_2. Ten liters of Madison tap water was reduced to 50 mL without the gelatinous precipitate forming, although there seemed to be some barely perceptible, needle-shaped crystals floating in the solution. Apparently, the formaldehyde did not react quantitatively with the nitric acid, because the pH of the solution could not be carefully controlled using this method. In fact, upon adding base to the solution, the pH of the solution seemed to go through a buffer region characterized by formic acid (pKa = 3.75). In retrospect, although reaction (1) should have went to completion from a thermodynamic perspective, the rate of reaction (1) probably decreased as a result of kinetics, when the NO_3^- and $4H^+$ concentrations dropped below certain levels. The solution was clearly supersaturated in silicic acid since whenever a drop of base was added to the solution, a gel would immediately form about the drop. (Silica gel formation is also catalyzed by moderately strong bases.). Because the pH could not be adequately controlled, this approach was abandoned.

It is well known that geologists use hydrofluoric acid to dissolve silicate-based rock; thus, it seemed that a literature search for methods used to dissolve silicate rock would be beneficial. Several references were found in which rock was dissolved in either concentrated hydrofluoric acid or a 1:1 mixture of hydrofluoric acid and nitric acid.[345] The precipitates that formed were subsequently dissolved using a Lewis base, either boric acid, $B(OH)_3$ or aluminum chloride $AlCl_3$. Consequently, option (2) was retried, in which the water sample was predigested with hydrofluoric acid silicic acid. In an experiment started on May 5, 10 liters of Madison tape water was boiled down to about 300 milliliters. The solution was transferred to a 400-mL Teflon beaker, and 30 mL of 40% HF was added to the solution. The solution was reduced to about 5 mL on a hotplate. There was no gelatinous precipitate, but, as before, there was a faintly green, transparent precipitate. Upon adding a total of 80 mL of boric acid solution (50 g/L) and allowing the solution to warm for about an hour on a hotplate, the precipitate dissolved and the solution was clear.

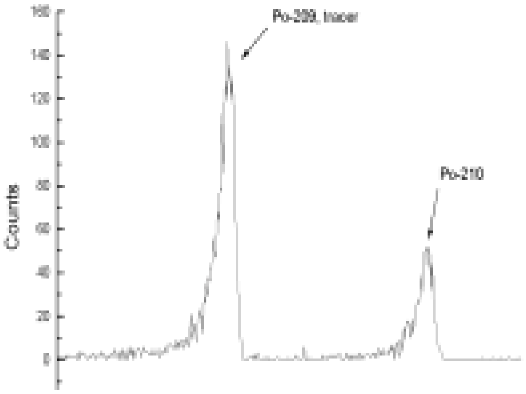

Figure 1. Plot of Polonium Spectrum for a 10-L sample of Madison tap water.

Subsequently, the polonium was coprecipitated with lead sulfide, the precipitate was dissolved in HCL, transferred to the deposition cell, and the polonium was allowed to deposit on the Ni disc for 4 hours. Figure 1 shows the alpha spectrum of the Ni disc. The peak at 4.866 MeV is due to Po-209, the tracer, and the peak at 5.304 MeV is due to Po-210. Most of the Po-210 is from the sample of Madison tap water, but, as is discussed below, a portion of the peak is due to the reagents used in the procedure.

Once the basic procedure for the analysis of polonium had been established, some time was spent testing the new procedure in order that numerous small but important details could be determined. A copy of this procedure, *SOP ESS RAD Method 008 Polonium 210*, is included in this report (see Appendix B). (For comparison, a copy of Procedure Po-02-RC can be found at web site http://www.eml.doe.gov/publications/procman/ Vol. 1, Sec. 4.54, Procedure Po-RC-02.) Although Procedure *SOP ESS RAD Method 008 Polonium 210* works quite well, it should still be possible to refine the procedure further, when, of course, time allows.

The next step would be to run quality control experiments. This involves determining the overall recovery of the tracer in the method, the degree to which reagents used in the procedure contaminate the sample, and the percent recovery of a Po-210 spike added to the sample. On May 17 an analysis of a series of ten samples of spiked Madison tap water samples was started in which 67 mBq of the Po-209 tracer and about 24 mBq Po-210 spike were added to the samples, and from May 19 to June 5 a series of seven reagent blanks were started in which the procedure was carried out using polished water instead of a sample of Madison tap water and in which no Po-210 spike was added. The results of the reagent blank experiments are given in Table 1.

Table 1. Reagent Blanks.

Sample no.	Overall efficiency	Reagent activity (mBq)
1	0.224	2.584
2	0.204	3.753
3	0.224	2.672
4	0.102	3.411
5	0.079	4.199
6	0.207	2.570
7	0.207	2.570

The overall efficiency of the method was calculated using the following equation:

$$\text{overall efficiency} = \frac{(\text{Total Po 209 counts})/(\text{count time})}{\text{activity of Po 209 tracer added to sample}}.$$

The poor efficiencies of samples 4 and 5 were due to leakage of the deposition cell. This problem has since been remedied and included in Procedure *SOP ESS RAD Method 008 Polonium*. Once the overall efficiency of the method was calculated, the activity due to Po-210 could be calculated from the corresponding number of counts. The average of the values in Table 1 is 3.26 mBq with a standard deviation of 0.76 Bq. Using 3.26 mBq for the reagent activity, the activity of Po-210 in the 10-L sample of Madison tap water (see Figure 1) was found to be 2.0965 mBq/L.

It should be mentioned that the overall efficiency is the product of the chemical recovery and the detector efficiency:

$$\text{overall efficieny} = \text{chemical recovery} \times \text{detector efficiency}.$$

Since the detector efficiency is about 40%, a value of 0.22 for the overall efficiency gives a value of 55% for the chemical recovery.

Next, the spiked samples were analyzed. The % recovery of the spike was calculated using the data from the 10-L sample of Madison tap water sample analyzed previously (see Figure 1), the reagent blank data, and the following formula:

$$\%\ \text{recovery spike} = \frac{(\text{Total Po}^{210}\ \text{counts - Po}^{210}\ \text{sample and reagent activity} \times \text{overall efficiency})}{\text{activity of Po}^{210}\ \text{spike added to sample} \times \text{overall efficiency}} \times 100\%.$$

The data are summarized in Table 2.

Table 2. % recovery of spikes for ten samples.

Sample no.	Overall efficiency	% recovery spike
1	0.238	129.4
2	0.223	117.7
3	0.242	688.9
4	0.233	112.5
5	0.144	121.8
6	Aborted	Aborted
7	0.211	108.0
8	0.229	97.7
9	0.206	105.3
10	0.207	112.2

It is clear that the % recovery of spike data in Table 2 is biased towards higher values than normal. (Ideally, the % recovery of spike should be 100%.) The value of 688.9% is too large to be due to statistical error. Sample no. 6 would have given a result similar to that of sample no. 3, but the run was aborted in order to count another sample.

It was concluded that results like those of sample nos. 3 and 6 could only be due to Po-210 contamination. Po-210 is near the end of the U-238 decay series. Consequently, glassware employed in other procedures that use some of the isotopes of the U-238 decay series as spikes—e.g., U-238, U-234, Th-230, and Ra-226—can be contaminated with Po-210. Under a variety of conditions, polonium strongly adheres to the surface of glass containers, and, as a consequence, a simple washing of the glassware may not be sufficient to remove all of the Po-210 contamination. A wash under highly acidic conditions may be needed to remove the polonium contamination. Thus, it is important to use proper cleaning procedures to remove all of the Po-210 contamination, or, better yet, to isolate the glassware intended for Po-210 analysis from glassware used in other analyses. The latter option is the one that will be used for the analysis of Po-210. From the above results it was clear that another quality control study would be necessary.

While the quality control experiments were being performed, some work was done to determine to what degree certain reagents were responsible for the Po-210 reagent activity. On May 26 two solutions were made by adding about 68 mBq of Po-209 and 1 mL of Pb carrier [the lead carrier is made from $Pb(NO_3)_2$ such that the concentration of Pb is 1 mg/mL] to 40 mL of 0.5 $\underline{M}$ HCl. The solution was placed directly in the deposition cell, and the polonium was allowed to deposit for 4 hours. The results of this experiment are given in Table 3.

Table 3. Reagent activity due to lead.

Sample no.	Overall efficiency	Reagent activity (mBq)
1	0.209	2.023
2	0.170	2.154

The average of the above values is Pb 2.08 mBq. Thus, since the reagent activity was determined to be 3.26 mBq, the lead carrier accounts for about two-thirds of the reagent contamination. In fact, because of contamination of the beakers used in the reagent blank analysis, the lead carrier solution may account for more than two-thirds of the contamination.

From Table 3 it is clear that the overall efficiency of the lead carrier experiments, in which the Po-209 is added directly to the deposition cell, is about the same as the overall efficiency of the other experiments (Tables 2 and 3). Thus, it is clear that almost all of the Po-209 that is added the samples reaches the deposition cell, and, therefore, that the loss of polonium in the sample occurs during the deposition procedure and during the oxidation of the Ni disc. It should be mentioned that polonium is a very volatile metal (55% of polonium is volatilized in air in 45 hr. at 55 C[6]). Consequently, polonium from a sample can readily contaminate the detectors. One way to minimize this is to heat the Ni disc to 300 C for about 5 minutes in order to oxidize the polonium on the Ni disc.[7] The vapor pressure of the oxidized polonium is much lower than that of the non-oxidized polonium, and, as a consequence, the contamination of the detector is minimal. Although polonium is undoubtedly lost during the oxidation process, the oxidation step is necessary to keep detector contamination to a minimum.

Table 4. Reagent Blanks.

Sample no.	Overall efficiency	Reagent activity (mBq)	Error (mBq)
1	0.187	2.718	0.444
2	0.152	3.883	0.599

A new batch of Madison tap water was tested for Po-210. First, two reagent blanks were prepared. The results are summarized in Table 4. The weighted average of the two values is 3.131 mBq with an uncertainty of 0.357 mBq. (The weighted average takes into account the uncertainty in each value in order to arrive at an average with the least uncertainty.[8])

Table 5. Madison Tap Water Samples.

Sample no.	Overall efficiency	Total Po-210 activity (mBq)	Sample activity (mBq/L)	Error (mBq/L)
1	0.178	3.572	0.441	0.330
2	0.168	2.773	-0.358	0.291

Next, two 2-L samples of Madison tap water were prepared for analysis. Table 5 summarizes the results. The activities of the sample and reagents were calculated from the spectra. The activity of the 2-L Madison tap water sample was calculated by subtracting the weighted average of the reagent blank experiments, i.e., 3.131 mBq, from the total Po-210 activity. The weighted average for the Po-210 activity of the Madison tap water is –0.009 mBq/L with an uncertainty of 0.218. Thus, to within the statistical accuracy of this experiment, the sample of Madison tap water contained no detectable quantities of Po-210.

The method was checked by spiking a 1-L sample of Madison tap water with about 24 mBq of Po-210. The results are summarized in Table 6. First, the total activity of Po-210 was determined for each sample and then the Po-210 contribution of the reagents, 3.131 Bq, was subtracted from the total Po-210 activity to give the amount of the Po-210 spike recovered. The amount recovered was expressed as a percentage of the amount of Po-210 added to the sample. The weighted average of the % Po-210 recovered is 98.136% with an uncertainty of 2.859%. Thus, within statistical error, the method recovers 100% of the spike. This result along with the chemical recovery of 55%, which compares favorably with the methods used for the analysis of uranium and thorium, shows that the method is acceptable for the analysis of Po-210.

From the alpha spectra of various polonium samples it has been noticed that the Po-210 peak has a rather long tail on the low-energy side which often extends to the Po-209 peak. A method has been devised to account for this, and it is included in the Appendix A. Because of time constraints, the corrections were not employed in the above results, but if they were, it is likely that the percent recovery of the Po-210 spike would have been even closer to 100%. Such a calculation was tried and the calculated uncertainty in the parameter α was found to be about 100%. Even so, because of the nature of the calculation, such a large uncertainty in α probably would not effect the uncertainty in the value of Po-210 very much, so that the correction will probably be applied in future calculations.

Table 6. Spiked samples.

Sample no.	Overall Efficiency	Total Po-210 activity (mBq)	Error (mBq)	% Po-210 recovered	Error
1	0.229	25.404	1.332	92.571	8.701
2	0.238	26.424	0.782	97.335	5.084
3	0.221	27.639	0.840	102.414	5.842
4	0.241	26.494	0.768	97.630	4.931

Method for the Analysis of Uranium.

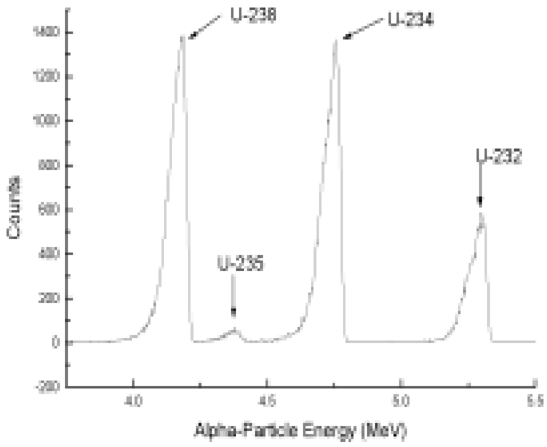

Figure 2. Spectrum of Uranium Proficiency Standard.

As mentioned in the previous progress report, it was decided not to use U-236 as a tracer, because it obscured the peak due to U-235. Instead, it was decided that U-232 would be used as a tracer. The only drawback in using U-232 as a tracer is that it decays into Th-228, so that in the measurement of naturally occurring Th-228, the contribution due to the tracer would have to be taken into account. Consequently, it was decided to use separate water samples for the analysis of uranium and thorium. This, of course, requires more sample, but the amount of the reagents used, including columns, is about the same.

Figure 2 shows the spectrum resulting from a natural uranium proficiency standard (from Environmental Resource Associates) which was processed using Eichrom's Procedure ACWO1 Rev. 1.0 and using the U-232 tracer. It is clear that the U-232 peak is well-separated from the other uranium peaks, which are well-separated from one another.

A short quality control study was performed using a batch of Madison tap water as the matrix. It was found that the contribution of the reagents to the U-234, U235, and U-238 peaks was practically zero. A 1-L sample of Madison tap was then analyzed for uranium using 10.07 pCi of the U-232 tracer. The results are summarized in Table 7. It is seem that there is a "disequilibrium" between the activities of U-234 and U-238; that is, if U-234 is in secular equilibrium with U-238, one would expect them to have the same activity. However, disequilibrium is common in ground water, and is primarily due to the recoil of Th-234 into the water when U-238 decays. The Th-234 or one of its progeny adsorb onto the surface of the rock in the aquifer and when U-234 is formed by the beta decay of Pa-234; it readily dissolves in the water.

$$U^{238} \xrightarrow{\alpha} Th^{234} \xrightarrow{\beta,\, 24.1\,\text{days}} Pa^{234} \xrightarrow{\beta,\ 6.75\,\text{hrs.}} U^{234}.$$

To three 1-L samples of Madison tap water were added 2.47 pCi of natural uranium spike and 10.07 pCi of the U-232 tracer. The percentages of the spike recovered, taking into account the 0.897 pCi of uranium already in the Madison tap water samples, are given in Table 8. It is seen that two of the percent recoveries are somewhat high (ideally they should be 100%). The percent recoveries would average to 100% if the amount of uranium in a liter of Madison tap water was about 1 pCi (instead of 0.897 pCi).

Table 7. Uranium in Madison Tap Water.

Uranium activity (pCi/L)			
U-234	U-235	U-238	Total U
0.737	0.013	0.157	0.897

Table 8. % Recovery of Natural Uranium Spike.

Sample	Overall efficiency	% Recovery spike	Error
1	0.246	106.552	0.023
2	0.267	107.072	0.023
3	0.197	100.632	0.035

A uranium proficiency standard was analyzed three times. The results are given in Table 9. The weighted mean is 49.282 pCi/L with an uncertainty of 0.218 pCi/L. The known total uranium concentration of the proficiency standard is 53.0 pCi/L, which does not fall within the experimental uncertainty; however, the experimental value does fall within the control limits for the proficiency standard, i.e., between 44.0 and 62.0 pCi/L. The discrepancy between the experimental value and the actual value (–7.0%) shows that a systematic error may exist in the method; however, an earlier analysis of the same proficiency standard by the Radiochemistry Unit using an alternative procedure (one that determines total uranium activity) yielded a result of 50.4 pCi/L. In the next few days some effort will be made to determine if systematic error exists in the method.

Table 9. Uranium Proficiency Standards.

Sample	Overall Efficiency	Uranium activity (pCi/L)				Total Uranium Error (pCi)
		U-234	U-235	U-238	Total U	
1	0.181	23.602	0.986	24.440	49.028	0.405
2	0.217	24.224	0.986	24.506	49.716	0.373
3	0.232	23.750	0.963	24.367	49.080	0.358

Method for the Analysis of Thorium.

A short quality control study was performed using a batch of Madison tap water as the matrix. A single reagent blank was analyzed for Th-230 using 1.866 pCi of Th-229 tracer. The reagents were found to contribute an activity of 0.033 pCi ± 0.007 pCi to the Th-230 peak. A 0.5-L sample of Madison tap was then analyzed for Th-230 uranium also using 1.866 pCi of Th-229 tracer. Taking into account the activity due to the reagents, the Th-230 activity of the Madison tap water sample was found to be 0.135 pCi/L ± 0.029 pCi/L.

Table 10. % Recovery of Th-230 Spike.

Sample	Overall efficiency	% Recovery of Th-230	Error
1	0.222	99.00	3.56
2	0.215	100.53	3.64
3	0.241	99.88	2.16

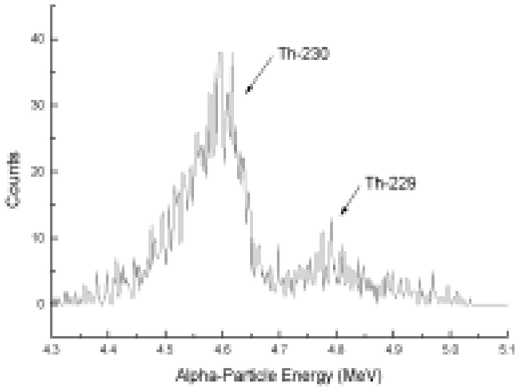

Figure 3. Thorium Proficiency Standard.

To three 0.5-L samples of Madison tap water were added 3.118 of Th-230 spike and 1.866 pCi of Th-229 tracer. The percentages of the spike recovered, taking into account the contribution from the reagents and the 0.5 L of Madison tap water, are given in Table 10. The weighted average of the percent recoveries of the Th-230 spike is 99.83% ± 1.65%.

Some problems were encountered when Eichrom Procedure ACW10 for the analysis of thorium was implemented. In general, the thorium peaks were very broad, sometimes to the point of being nearly flat. Figure 3 shows the spectrum of 0.1-L, Th-230 proficiency sample to which 0.75 pCi of Th-229 tracer was added. The Th-229 and Th-230 peaks somewhat overlap. Nonetheless, a simple region-of-interest analysis was used to estimate the Th-230 concentration in the proficiency standard, in which the boundary between the Th-229 and Th-230 intervals was taken as the point of minimum counts between the two peaks. A value of 27.3 pCi/L ± 1.4 pCi/L was calculated. This compares with an actual value of 25.4 pCi/L. Since a portion of the peak due to Th-229 overlaps with the Th-230 peak, the region of interest analysis would tend to underestimate the Th-229 activity and overestimate the Th-230 activity; thus, it is not surprising that the calculated value is too large.

In Eichrom Procedure ACW10 the thorium is separated from the other actinides on a column. When the thorium is eluted from the column, the eluted solution is subjected to a cerium fluoride microprecipitation. The thorium coprecipitates with the CeF_3. When the microprecipitation was tried on solutions of hydrochloric acid to which Th-230 and Th-229 had been added, the two peaks were well-separated; thus, the problem of peak broadening was due to a part of the procedure preceding the microprecipitation.

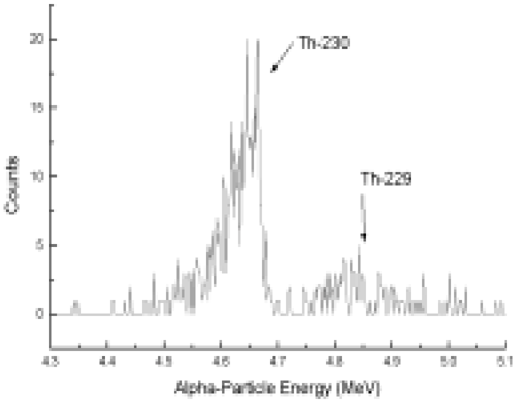

Figure 4. Alpha-particle spectrum of proficiency standard after column funnel had been cleaned.

During the microprecipitation step, 7.24×10^{-7} mole of Ce(III) is used as a carrier. A large excess of hydrofluoric acid is used to bring about the precipitation of the cerium. Of course, other common metals precipitate as fluorides, such as calcium and magnesium, both of which are present in great abundance in many natural waters. Moreover, before the microprecipitation step, 6.25×10^{-4} mole of calcium is added to the sample in the form of $Ca(NO_3)_2$, in addition to the calcium already present. Then, $(NH_4)_2HPO_4$ is added in order to coprecipitate the thorium with $Ca_3(PO_4)_2$. Thus, the number of moles of calcium in the sample exceeds the number of moles of cerium by a factor of at least 863. If some of this calcium or magnesium is eluted with the thorium, CaF_2 or MgF_2 would be produced during the microprecipitation. Even if these fluoride precipitates did not act as carriers for thorium, they would still tend to obscure the alpha-spectrum peaks by adding mass to the precipitate through which some of the alpha particles would have to travel, causing a loss of alpha-particle energy and a concomitant broadening of the peak. It seemed that some of the calcium or magnesium in the sample may have been eluted with the thorium. When solutions are added to the columns that are used to separate the actinides there are recesses in the funnels on top of the columns where the solution tends to accumulate and not be rinsed into the column. Thus, another experiment was performed in which the funnel on the top of the column was taken apart and cleaned after the sample had been introduced to the column. The spectrum that resulted from this procedure is shown in Figure 4. This time there is good separation between the Th-230 peak and the Th-229 peak. It is seen that the Th-230 peak has a sharp rising edge on the high-energy side. The Th-229 peak does not appear to have a sharp rising edge because the Th-229 peak is actually made up of 5 separate peaks which are similar in magnitude. A new calculation using this data gave a value of 25.2 pCi/L ± 3.2 pCi/L, a value well in agreement with that of the proficiency standard. The only problem with this measurement was the overall efficiency was 0.029, a very low value. The low overall efficiency was probably due to the fact that all of the column operations could not be completed on July 3, and, because of the July 4 holiday, the thorium was not eluted from the column until the morning of July 5. During this time the column may have dried and developed channels, so that only a small portion of the thorium was eluted. This experiment will be retried in such a way that all of the column procedures a completed in one day.

EG&G Ortec Software

Results obtained using the EG&G analysis software to analyze the spectra have been inconsistent. For example, the software has a difficult time discerning between two peaks that have considerable overlap. Another problem is that if the tracer has more than one peak, the activity that is input into the software for the tracer is the activity of the peak with the largest branching ratio. For example, Th-229 has five peaks of similar magnitude with the largest peak having a branching ration of 0.582; thus, 41.8% of the Th-229 signal is not used in the analysis, a situation in which a significant amount of the signal is being thrown away. Moreover, although the software subtracts background counts, it does not subtract the counts due to the reagents. Thus, the activities of the various nuclides have been calculated with the aid of Microsoft Excel.

Conclusions.

The quality control experiments indicate that the methods for the analysis of polonium, uranium, and thorium are working quite well and that groundwater samples can now be analyzed.

Appendix A

Correction of Po-209 activity.

At times the peaks due to Po-209 and Po-210 overlap slightly in the alpha spectrum—the low energy tail of the Po-210 peak overlaps the high-energy part of the Po-209 peak. Since the chemistry of Po-209 and 210 is nearly identical, the two isotopes should deposit on the Ni disc in such a way that the functional forms of the two peaks have the same shape. More specifically, the function for the Po-209 peak, F_{209}, and the function for the Po-210 peak, F_{210}, should be related by

$$F_{209}(E_i - \Delta E), \; = \; \alpha \, F_{210}(E_i) \quad \text{(for all } i\text{)}, \tag{1}$$

where E_i is alpha-particle energy of the ith channel, α is a proportionality constant, and ΔE is the energy difference between corresponding points on the two peaks, i.e., ΔE is the energy by which the two peaks are offset from one another. For example, if $E_{209,\text{ peak}}$ and $E_{209,\text{ peak}}$ are the energies of the maxima of F_{209} and F_{210}, respectively, then $\Delta E \; = E_{210,\text{ peak}} - E_{209,\text{peak}}$. Summing equation (1) over all channels yields

$$\Sigma_{\text{all } i} \, F_{209}(E_i) \; = \; \alpha \Sigma_{\text{all } i} \, F_{210}(E_i),$$

or

$$N_{209,\text{T}} \; = \; \alpha N_{210,\text{T}},$$

where $N_{209,\text{T}}$ and $N_{210,\text{T}}$ are the total counts of Po-209 and Po-210, respectively. It is clear that α is just the ratio of the total amount of Po-209 to the total amount of Po-210 in the sample.

Ordinarily, if the two peaks do not overlap, one can just define two non-overlapping regions of interest (ROI), or energy intervals, each of which encompasses one of the two peaks, and integrate the counts due to Po-209 and Po-210 over their respective ROIs to get the relative amounts of Po-209 and Po-210 in the sample. However, if the peaks overlap, as in Figure 1, such a procedure will not yield accurate results. As seen in Figure 1, above the maximum energy for Po-209, $E_{209,\text{max}}$,, all of the counts are due to Po-210. Thus, it is useful to define an ROI, named ROI_3, which ranges from a value slightly greater than $E_{209,\text{max}}$, call it $E_{209,\text{max}} + \delta$, to a value slightly greater than $E_{210,\text{max}}$, call it $E_{209,\text{max}} + \delta$, where δ is the same in both cases.; thus, ROI_3 is given by

$$(E_{209,\text{max}} + \delta, \, E_{210,\text{max}} + \delta).$$

Notice that the length of this interval is just ΔE, the offset energy between the two peaks. The number of counts in this interval, denoted $N_{\text{T},3}$, is just

$$N_{\text{T},3} \; = \; \Sigma_{\text{ROI}_3} F_{210}(E_i) \; = \; N_{210,3} \tag{2}$$

where Σ_{ROI_3} represents a summation over all of the channels in interval ROI_3, and since all of the counts are due to Po-210, $N_{210,3}$ is just the number of Po-210 counts in interval ROI_3.

It is convenient to define second interval, interval ROI_2, which is given by

$$(E_{209,\text{max}} + \delta - \Delta E, \, E_{210,\text{max}} + \delta - \Delta E).$$

Intervals ROI_2 and ROI_3 are adjacent to one another, and it is clear from equation (1) that ROI_2 has the same relationship to F_{209} that ROI_3 has to F_{210}. Thus, it is clear that

$$\Sigma_{\text{ROI}_2} F_{209}(E_i) \; = \; \alpha \Sigma_{\text{ROI}_3} F_{210}(E_i),$$

which simplifies to

$$N_{209,2} \; = \; \alpha N_{210,3}\,, \qquad (3),$$

where $N_{209,2}$ is the number of Po-209 counts in interval ROI$_2$. Likewise, $N_{209,1}$, the number of Po-209 counts in the interval ROI$_1$, defined as

$$(E_{209,\max} + \delta - 2\Delta E,\ E_{210,\max} + \delta - 2\Delta E),$$

is proportional, $N_{210,2}$, to the number of Po-210 counts in interval ROI$_2$

$$N_{209,1} \; = \; \alpha N_{210,2} \qquad (4),$$

The total number of counts in interval ROI$_2$, $N_{T,2}$, is given by

$$N_{T,2} \; = \; N_{209,2} + N_{210,2}. \qquad (5)$$

Likewise, the total number of counts in interval ROI$_3$, is given

$$N_{T,1} \; = \; N_{209,1} + N_{210,1},$$

where $N_{210,1}$ is the number of Po-210 counts in interval ROI$_3$. Often it is the case that $N_{210,2} = 0$, i.e., for all practical purposes, there are no counts due to Po-210 in interval ROI$_1$, so that the above equation becomes

$$N_{T,1} \; = \; N_{209,1}. \qquad (6)$$

Combining equations (2), (3), (4), (5), and (6) yields

$$N_{T,3}\alpha^2 - N_{T,2}\alpha + N_{T,1} = 0.$$

Solving this equation for α gives

$$\alpha = \frac{N_{T,2} \pm \sqrt{N_{T,2}^2 - 4N_{T,1}N_{T,3}}}{2N_{T,3}}.$$

It is clear that the "+" sign must used since if $N_{T,1} = 0$, $\alpha = N_{T,2}/N_{T,3}$, as would be expected. Thus, α can be determined from the total number of counts in each of the intervals ROI$_1$, ROI$_2$, and ROI$_3$, and since $N_{209,1}$ is just $N_{T,1}$, equation (4) allows for the calculation of $N_{210,2}$, which by equation (5) is the number of counts that must be subtracted from $N_{T,2}$ to give $N_{209,2}$.

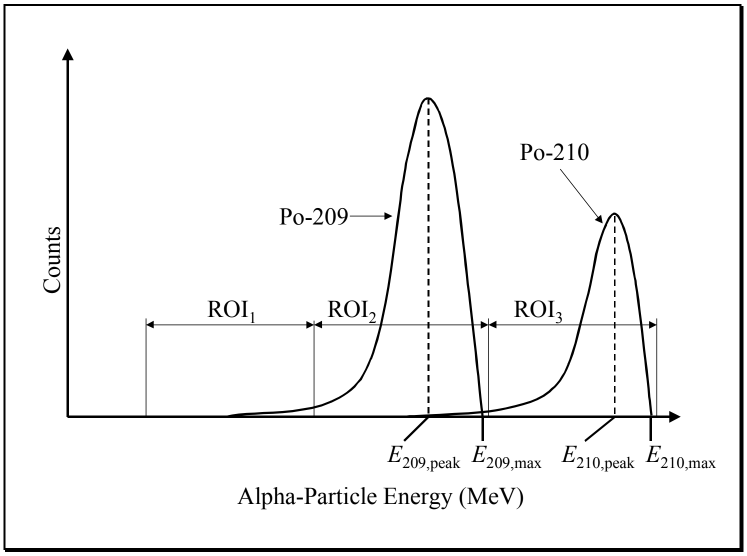

Figure 1. Polonium Alpha Spectrum.

Appendix B.

SOP ESS RAD Method 008 Polonium 210.

Preparation of Water Samples for the Analysis of Po-210.

1.0 Purpose and Applicability.

1.1 The purpose of this standard operating procedure is to give a method of preparing water samples for analysis of Po-210 by alpha spectroscopy. This method includes all steps up to but not including the collection of the alpha spectrum. This method is applicable to freshwater samples, including tap water, groundwater, and surface waters, which do not contain large amounts of suspended materials. The method may very well be applicable to water samples containing suspended materials and to waters with higher solute concentrations than fresh water, although the method has not as yet been tried with such samples.

2.0 Summary.

Initially, procedure Po-02-RC of the Environmental Measurements Laboratory, United States Department of Energy (Reference 7.1), was used to analyze for Po-210 in tap water samples of the City of Madison. It was found that a gelatinous precipitate formed upon evaporating several liters of the acidified water sample down to a volume of about 100 milliliters (procedure Po-02-RC requires that the volume be reduced to 5 milliliters). Based on the chemical properties of the gel and an analysis of the dried gel by the Inorganics Unit at the Wisconsin State Laboratory of Hygiene, it was determined that the precipitate was silica gel, which probably had various metal cations bound to it.

Ground water samples can contain up to 15 ppm SiO_2 (Reference 7.4), which ordinarily reacts with water to form silicic acid, $Si(OH)_4$, i.e.,

$$SiO_2(s) + 2H_2O(l) \leftrightarrow Si(OH)_4(aq).$$

Strong acids catalyze the polymerization of silicic acid to silica gel (Reference 7.11). Silica gel acts as a cation exchange medium; thus, its presence is unacceptable in any procedure for the analysis of polonium. Once formed, the dissolution of silica gel requires rather extreme conditions—silica gel can be dissolved with hot concentrated hydrofluoric acid (References 7.7, 7.8, and 7.9). However, in this procedure, in order to save time, it seemed prudent to add hydrofluoric acid to the solution prior to the formation of silica gel. The hydrofluoric acid reacts with silicic acid, $Si(OH)_4$, to form fluosilicic acid, H_2SiF_6, a compound that is soluble in water and that does not polymerize, at least not under the conditions used in this method. Thus, in this procedure hydrofluoric acid is added to the acidified sample once the volume of the sample is reduced to 300 milliliters.

After the addition of hydrofluoric acid the volume of the sample is further reduce to about 5 to 10 milliliters. Then, boric acid is added to the sample, and the sample is heated for a period of time in order to dissolve insoluble fluoride precipitates.

Once a clear solution is obtained, polonium is coprecipitated out of solution using a Pb carrier. The precipitate is dissolved in hydrochloric acid, and the polonium is spontaneously deposited from solution onto a Ni disc. Using Po-209 as a tracer, the Po-210 activity can be determined using alpha spectroscopy.

It should be mentioned that the solution chemistry of polonium is not well understood, especially at the tracer level (Reference 7.13). Thus, although an effort is made to outline the relevant chemistry in this procedure, it is not possible to do so unambiguously at every step.

3.0 Interferences.

3.1 **Effect of pH.** During most of the procedure it is important to keep the pH of the solution below a value of about 1. At values of pH above 1 polonium can adsorb onto the walls of the container, causing substantial loss in the amount of polonium. An exception to this is when the pH of the solution is adjusted to about 3.5 to 4 in the centrifuge tubes (step 8.16). In a succeeding step the contents of the centrifuge tubes are acidified, which should cause any adsorbed polonium to redissolve. Also, in step 8.8 it is important not to reduce the volume of the solution below five milliliters so that when the solution is subsequently diluted, the pH will remain below 1. (If the level of the solution drops below 5 milliliters, concentrated nitric acid can be added in order to reduce the pH.)

3.2 **Effect of Particulates.** Much experimental evidence suggests that polonium adsorbs on the surface of particulate matter, such as dust, precipitates, and colloids, especially at values of pH exceeding 1. Furthermore, polonium can occur as inclusions in precipitates. Thus, in addition to keeping the pH less that 1, it is important, as much as possible, to exclude dust from the water samples and to ensure that any precipitates that form be completely redissolved. Fluoride precipitates form when the sample is digested with hydrofluoric acid (steps 8.7 and 8.8). [The solubilities of CaF_2 and MgF_2 in cold water are 16 ppm and 76 ppm, respectively (Reference 7.12).] These precipitates are effectively redissolved with boric acid (steps 8.9 to 8.14), although, as is discussed in the next section, care must be taken to ensure that the precipitate is dissolved from the wall of the Teflon beaker. In addition, when the solution to which the boric acid was added cools (step 8.15), boric acid may precipitate owing to the high concentration of solutes and the further concentration of solutes by evaporation. This precipitate is readily dissolved by adding water to the solution.

Another possible interference due to particulates arises during the spontaneous deposition of polonium onto the Ni disc. Any particulates that are present in the solution can settle on the Ni disc causing a reduction in the number of alpha particles reaching the detector and a broadening of the alpha spectrum peaks. Particulates are removed by filtering the solution in step 8.26. In addition, the filter step is necessary because particulates present during the spontaneous deposition of polonium may act as nucleation centers promoting the deposition of polonium on the nuclei rather than the surface of the Ni disc.

.

3.3 **Adherence of Fluoride Precipitates to Teflon.** Some of the fluoride precipitate which forms during the digestion of the sample with hydrofluoric acid (steps 8.7 and 8.8) strongly adhere to the bottom and walls of the Teflon beaker. When the precipitate is redissolved with boric acid, care must be taken to ensure that any precipitate above the level of the solution is redissolved. This can be done by raising the level of the solution in the Teflon beaker to the level of the precipitate with additions of polished water and by scraping the precipitate into solution with a rubber policeman.

3.4 **Polonium Volatilization.** Metallic polonium is quite volatile. At 55 C, 50% of polonium metal is vaporized into the air after a period of 45 hours (Reference 7.12). Although polonium is usually found in solution in the +2 and +4 oxidation states, it is often advised that any kind of sample being analyzed for polonium not be heated while dry. Thus, in step 8.8, in addition to not evaporating all of the acid for the reason discussed in section 3.1, the sample should not be heated to dryness because of possible loss of polonium due to vaporization. An exception to this rule is when the Ni disc, containing the spontaneously deposited polonium, is heated in air (see step 8.35). This is done to oxidize the deposited metallic polonium in order to lessen its vapor pressure so that the degree to which the polonium contaminates a detector during the collection of an alpha spectrum is diminished (Reference 7.10). Although it may seem that much of the polonium would be lost when the Ni disc is heated, probably less than 10% of the polonium is lost because submonolayer amounts of polonium seem to adhere to the most metal surfaces more strongly than polonium atoms adhere to the surface of polonium metal.

Effect of Oxidizing Species. Because of the half-cell reaction

$$\mathrm{Ni}^{2+}(\mathrm{aq}) + 2\mathrm{e} \rightarrow \mathrm{Ni(s)} \quad E^{\circ} = -0.23 \text{ V},$$

a Ni disc residing in pure water will tend to have an electrochemical potential of less than –0.23 V versus the standard hydrogen electrode. These conditions would be ideal for the spontaneous deposition of polonium, which has a critical deposition potential of about 0.81 V. (Any potential less than 0.81 V would favor the deposition of polonium.) However, the solution contains oxidizing species, such as O_2, NO_3^-, and Fe^{3+}, which can raise the electrochemical potential of the Ni disc and prevent polonium from depositing or cause the re-oxidation of any polonium which has already deposited on the Ni disc. Adding excess ascorbic acid, a reducing agent, will electrochemically reduce these oxidizing species, thus diminishing their concentrations to acceptable levels, and will lower the electrochemical potential of the Ni disc so that the deposition of polonium is thermodynamically favorable.

Effect of Glassware used for Other Procedures. Po-210 is near the end of the U-238 decay series. Consequently, glassware employed in other procedures that use some of the isotopes of the U-238 decay chain as spikes—e.g., U-238, U-234, Th-230, and Ra-226—can be contaminated with Po-210. Since, under a variety of conditions, polonium strongly adheres to the surfaces of a glass containers, a simple washing will usually not remove all of the Po-210 contamination. Thus, it is important to use proper cleaning procedures to remove all of the Po-210 contamination, or, better still, to isolate glassware intended for Po-210 analysis from other analyses.

4.0 Definitions.

4.1 Polished water–

5.0 Equipment.

5.1 Calcium gluconate gel (Pharmascience).

5.2 Long rubber gloves (about 13½ inches).

5.3 3-L glass beaker.

5.4 150-mL glass beaker.

5.5 250-mL glass beaker.

5.6 400-mL Teflon beaker.

5.7 1-L graduated cylinder.

5.8 10-mL polymethylpentene graduated cylinder.

5.9 Three 50-mL centrifuge tubes.

5.10 Large Teflon stir bar.

5.11 60-mL polypropylene bottle.

5.12 Glass stir rod.

5.13 Small Teflon stir bar—for use in the deposition cell. Since the Ni disc of the deposition cell is magnetic, stir bars tends to stick to the disc. In order to prevent this a short, stout stir bar is needed. A Fisherbrand 5/16 x 5/8″ octagonal magnetic stir bar works.

5.14 Silicone rubber septum (≥ 0.125 inch thick and ≤ 18 mm in diameter.)

5.15 Rubber policeman.

5.16 Large hotplate.

5.17 Combination hotplate and stirrer.

5.18 Vortex mixer.

5.19 Polypropylene forceps.

5.20 Funnel.

5.21 Whatman No. 41 filter paper.

5.22 100 °C thermometer.

5.23 360 °C thermometer.

5.24 1 inch diameter nickel disc.

5.25 Small ointment tin.

6.0 Reagents.

6.1 Polished water.

6.2 Concentrated nitric acid (Fisher Scientific, 68–71%, trace metal grade).

6.3 Concentrated hydrofluoric acid (Fisher Scientific, 47–51%, trace metal grade).

6.4 Concentrated hydrochloric acid (Fisher Scientific, 35–38%, trace metal grade).

6.5 0.5 $\underline{M}$ HCl.

6.6 Boric acid solution (Mallincroft, granular, analytical reagent): 25 g in 500 mL of polished water.

6.7 Concentrated ammonium hydroxide (Fisher Scientific, 20–22%, trace metal grade).

6.8 Standardized Po-209 solution.

6.9 Standardized Po-210 solution.

6.10 Bromophenol Blue Indicator (Fisher Scientific, 0.04%, Certified).

6.11 Lead carrier (10 mg Pb per liter): 15.98 g lead nitrate (Fisher Scientific, Certified A.C.S.) diluted to 1 liter with concentrated HNO_3.

6.12 Saturated thioacetamide (Fisher Scientific, Certified A.C.S.) solution. Thioacetamide often contains some elemental sulfur so that the solution will have to be filtered before use.

6.13 L-Ascorbic acid (Fisher Scientific, Certified A.C.S.).

7.0 Related Documents.

7.1 Procedure Po-02-RC, Polonium in water, vegetation, soil, and air filters, HASL-200, 28th Edition, Environmental Measurements Laboratory, United States Department of Energy.

7.2 Specification 7.16, *ibid*.

7.3 Fainberg, A. A. and Haring M. M., *Record Chem. Progr.* **14**, 157-74 (1953).

7.4 Govet, G. J. S., *Anal. Chim. Acta* **25**, 69-80 (1961).

7.5 Haïssinsky, M., *J. Chim. Phys*. **34**, 94-95 (1937).

7.6 Haïssinsky, M., *J. Chim. Phys*. **30**, 27-46 (1933).

7.7 Langmyhr, F. J. and Graff, P. R., Studies in the Spectrophotometric Determination of Silicon in Materials Decomposed by Hydrofluoric Acid I. Loss of Silicon by Decomposition with Hydrofluoric acid, *Anal. Chim. Acta* **21**, 334-339 (1959).

7.8 Langmyhr, F. J. and Sveen, S., Decomposability in Hydrofluoric Acid of the Main and Some Minor and Trace Minerals of Silicate Rocks, *Anal. Chim. Acta* **32**, 1-7 (1965).

7.9 Langmyhr, F. J. and Paus, P. E., The Analysis of Inorganic Siliceous Materials by Atomic Absorption Spectrophotometry and the Hydrofluoric Acid Decomposition Technique, *Anal. Chim. Acta* **43**, 397-408 (1968).

7.10 Sill, C. W. and Olsen, D. G., Sources and Prevention of Recoil Contamination of Solid-State Detectors, *Anal. Chem*. **42**, 1596-1607 (1970).

7.11 Tarutani, T, Polymerization of Silicic Acid: A Review, *Analytical Sciences* 5, 245-252 (1989)

7.12 Weast, R. C., *CRC Handbook of Chemistry and Physics*, 57th Edition, CRC Press, Boca Raton, Florida (1976).

7.13 Buschbeck, E. C., *Gmelin Handbook of Inorganic and Organometallic Chemistry*, Polonium Supplement Volume 1, 8th Edition, Springer-Verlag, Berlin (1990).

8.0 Procedure.

Reduction of Sample Volume.

8.1 Transfer a 2.5 L aliquot of a 10 L pre-acidified (pH ≈ 2) water sample to a 3-L beaker.

8.2 Add 50 mL of concentrated HNO_3, 30 to 80 mBq of Po-209 tracer, 30 to 80 mBq of Po-210 spike, if need be, and 1 mL of Pb carrier solution to the beaker.

8.3 Evaporate the solution in the beaker on a hotplate, adding aliquots of the original 10-L sample until the whole sample had been added to the 3-L beaker.

> It should be mentioned that the water sample should be placed in a single beaker rather than be distributed among several beakers in an attempt to accelerate the evaporation process. The reason for this is that the polonium with adsorb onto the surface of the beakers when the value of the pH is above about 1. Distributing the solution among several beakers may dilute the acid to the point where adsorption occurs. It may be argued that one could just add more nitric acid to the other beakers, but, as is discussed in step 8.7, acid catalyzes the formation of silica gel from solutions which contain silicic acid, such as groundwater. Thus, in such cases it is best to use the least possible amount of nitric acid.

8.4 Evaporate the solution down to a volume of 300 mL.

Digestion of Silicic Acid with Hydrofluoric Acid.

8.5 Place a Teflon stir bar in a 400-mL Teflon beaker.

8.6 Transfer the solution from the 3-L beaker to the Teflon beaker. Rinse the 3-L beaker three times with 10 mL portions of polished water, and transfer the rinses to the Teflon beaker.

8.7 Add 30 mL of 40% hydrofluoric acid to the Teflon beaker using a 10-mL polymethylpentene graduated cylinder.

> The use of long rubber gloves is mandatory when handling HF or any solution containing HF. HF can move through the skin rapidly and can cause the precipitation Ca, in the form of CaF_2, in the body tissues. This can lead to necrosis of the affected tissues, even bones. If tissues come in contact with HF, it is important to wash the affected area with copious amounts of water, and to apply calcium gluconate gel to the affected area. A tube calcium gluconate gel is stored next to the hydrofluoric acid. The procedure to be employed if one is exposed to hydrofluoric acid is given in SOP ESS RAD GENOP 023.
>
> If the hydrofluoric acid is not added to the solution, silicic acid, $Si(OH)_4$, will polymerize by a condensation reaction forming siloxane bonds between adjacent Si atoms; e.g., two silicic acid molecules will undergo the reaction:
>
> $$2Si(OH)_4(aq) \rightarrow (OH)_3Si–O–Si(OH)_3(aq) + H_2O(l).$$
>
> The condensation reaction is catalyzed by strong acids. Eventually the silicic acid will polymerize to form colloids, and, then, a gel. The formation of a silica gel will interfere with the analysis of polonium. First, the silica gel acts as a cation exchange medium, capable of binding polonium ions. Second, the water retained by the silica gel undoubtedly contains polonium ions which, during the procedure for the spontaneous deposition of polonium on the Ni disc, will only be transferred to the surface of the Ni disc very slowly, thus decreasing the yield of polonium in the procedure.
>
> The hydrofluoric acid reacts with silicic acid to form fluosilicic acid:
>
> $$Si(OH)_4(aq) + 6HF(aq) \rightarrow H_2SiF_6(aq) + 4H_2O(l).$$
>
> The fluosilicic acid thus formed is highly soluble in water and will not polymerize.

8.8 Evaporate the solution in the Teflon beaker on a hotplate while slowly stirring until the the solution has been reduced to a volume of between 5 and 10 mL. (At the lower volumes white fumes should be observed. Avoid any contact with the white fumes since they contain HF.). If the level of the solution should drop below 5 mL, add enough concentrated HNO_3 to bring the solution level to about 5 mL.

> During this step of the procedure it may be noticed that the solution turns an orange-brown color. As the solution is evaporated, both the acidity and the concentration of nitrate in solution increase. As is discussed in step 8.28, nitrate, NO_3^-, functions as an oxidizing agent in acidic media forming nitric oxide, NO. Nitric oxide further reacts with oxygen to form nitrogen dioxide, NO_2, an orange-brown gas which responsible for the color of the solution. As an example, iron in solution in the form Fe^{2+} is readily oxidized to Fe^{3+}, especially under the conditions of high acidity and nitrate concentration which prevail in this solution.

Dissolution of Fluoride Precipitates with Boric Acid.

8.9 Add 75 mL of boric acid solution to the solution in the Teflon beaker.

8.10 If precipitates can be seen on the side of the Teflon beaker, fill the beaker with polished water to a level above that of the precipitates, and use a rubber policeman to scrape the precipitate off the walls of the beaker and into solution. (Since both the Teflon beaker and the precipitate are white, it is often difficult to discern whether there is a precipitate on the walls of the beaker, especially when the beaker contains a solution. Shining a flashlight on the side of the beaker helps to illuminate the areas where precipitate is adhering.) When adding the polished water, it is a good idea to use a wash bottle to rinse the drops of acid that collect on the sides of beaker back down into solution. Some of these droplets may form on the rim of the beaker and may not be accessible to the stream of water from the wash bottle. Since these droplets contain concentrated HF, it is a good idea to wipe the droplets off of the rim with a paper towel (while using rubber glove, of course), and to allow the towel dry in the hood before discarding it.

> During the hydrofluoric acid digestion steps, a precipitate usually forms on the bottom and sides of the Teflon beaker. Some of these precipitates adhere to the Teflon so tenaciously that it is difficult, in not impossible, to scrape them off the sides of the beaker and into the solution with a rubber policeman. In the event that this happens it is best to fill the beaker with polished water to the level of the precipitates and to allow the solution to dissolve the precipitate.
>
> The fluoride ions combine with various metal ions in solution to form precipitates, e.g., calcium fluoride, CaF_2, magnesium fluoride, MgF_2, lead fluoride, PbF_2, ferric fluoride, FeF_3, and ferrous fluoride, FeF_2. The last two precipitates are green and may impart a green tint to the mixture of fluoride precipitates. Boric acid, $B(OH)_3$, acts as a Lewis acid by complexing fluoride ions which leads to the dissolution of the precipitates; e.g.,
>
> $$CaF_2(s) + 2B(OH)_3(aq) \rightarrow Ca^{2+}(aq) + 2[BF(OH)_3]^-(aq).$$
>
> In addition, boric acid reacts with excess fluoride ions in solution, greatly reducing the danger posed by hydrofluoric acid.
>
> The solubility of tracer level polonium is not affected when hydrofluoric acid is added to solutions containing hydrochloric acid or sulfuric acid (Reference 7.5). Little or no work seems to have been done on the effect of hydrofluoric acid on nitric acid solutions containing tracer level polonium.
>
> It should be mentioned that aluminum chloride could be used, instead of boric acid, to dissolve the fluoride precipitate. However, in step 8.16 the pH of the solution is adjusted to a value of about 3.5 to 4, and under these conditions excess aluminum can form the insoluble hydroxide $Al(OH)_3$.

8.11 Turn the heat on the hotplate fairly low so that evaporation is minimal. Allow the solution to heat on the hotplate and to stir for at least 1 hour (this will give the solution time to dissolve the precipitate from the beaker walls). Increase the heat setting on the hotplate, and allow the solution to evaporate down to about 80 mL. (Once the solution has been reduced, the walls of the beaker should be rinsed with polished water once more to wash any residual HF into solution.)

> Although the solution can remove the bulk of the precipitate from the bottom and walls of the Teflon beaker in a relatively short time, much of the precipitate remains suspended in solution in particulate form for some time. Warming the solution accelerates the dissolution process, but complete dissolution may take more than one hour and may require additional aliquots of boric acid solution. A solution which contains particulate matter will appear cloudy.

8.12 Pour a few milliliters of the solution from the Teflon beaker into a 150-mL glass beaker. Note whether the solution is clear or turbid, and transfer the contents of the 150-mL glass beaker back into the Teflon beaker. Rinse the glass beaker twice with a few milliliters of polished water and transfer the rinses to the Teflon beaker.

8.13 If the solution was clear, proceed to step 8.15; if the solution was cloudy, proceed to the next step.

8.14 Add 5 mL of boric acid solution to the Teflon beaker and some polished water if the volume of the beaker is below about 80 mL; then, allow the beaker to warm on a hotplate for at least 30 minutes. Repeat step 8.12.

8.15 Hold the stir bar in the Teflon beaker in place with a second stir bar placed on the underside of the beaker. Distribute the solution in the Teflon beaker equally among three 50-mL centrifuge tubes. Rinse the Teflon beaker twice with approximately 10-mL portions of polished water, and distribute the rinses equally among the three centrifuge tubes. As the solution cools, a precipitate may form in the Teflon beakers and/or in the centrifuge tubes This precipitate is boric acid and can be dissolved by adding 5 mL aliquots of polished water to the beakers or tubes until the precipitate has dissolved.

8.16 Add 6 drops of bromophenol blue indicator (0.04%) to each of the centrifuge tubes. Then, to each centrifuge tube, add concentrated ammonium hydroxide until the blue-green endpoint is reached (bromophenol blue indicator goes from yellow to purple in the pH range 3.0 to 4.6). The solutions should be mixed by shaking the covered tubes or by agitating the contents of the covered centrifuge tubes with a vortex mixer. If a precipitate appears before the endpoint is reached, add hydrochloric acid drop-wise, mixing after each added drop, until the precipitate has completely dissolved. If the endpoint of the solution in one tube has been surpassed, then mixing the contents of that tube back and forth among the other two tubes may result in the pH of all of the solutions being less than 3.5.

With the addition of ammonium hydroxide a gelatinous precipitate may appear. Much of this precipitate is probably $Mg(OH)_2$, which forms by the following reaction:

$$Mg^{2+}(aq) + 2OH^{-}(aq) \leftrightarrow Mg(OH)_2(s) \quad K_{sp} = 1.2 \times 10^{-11} \text{ (18 C)}.$$

Some of the precipitate may be due to $Al(OH)_3$, for which $K_{sp} = 1.1 \times 10^{-15}$ (15 C), and some may be due to $Ca(OH)_2$ which has a solubility of 1.85 gram per liter. At this point in the procedure, when a sample of Madison tap water was made basic, the precipitate had a reddish-brown tint indicating the probable presence of some ferric hydroxide, $Fe(OH)_3$, for which $K_{sp} = 1.1 \times 10^{-36}$ (18 C). (The values of K_{sp} and solubility were taken from Reference 7.12.)

It should be mentioned that the pH of the solution must be adjusted in the centrifuge tubes rather than in the beaker. At the higher pH values the polonium can adsorb to the walls of a beaker. There is no problem if the pH is adjusted in the centrifuge tubes, since in a subsequent step the solutions in the centrifuge tubes are re-acidified which causes the desorption of polonium from the walls of the centrifuge tubes.

Coprecipitation of Polonium with Lead Sulfide.

8.17 Add 2 mL of thioacetamide solution to each of the centrifuge tubes, and mix the solutions by shaking or agitating on a vortex mixer.

8.18 Put the centrifuge tubes in a hot water bath and allow the contents of the tubes to digest for about one hour. (A black precipitate, PbS, will form which acts as a carrier for polonium.)

In hot solution, thioacetamide, CH_3CSNH_2, undergoes the following hydrolysis reaction:

$$CH_3CSNH_2(aq) + H_2O(l) \rightarrow CH_3CONH_2(aq) + H_2S(aq).$$

The hydrogen sulfide generated dissociates according to the reaction

$$H_2S(aq) + H_2O(l) \rightarrow HS^{-}(aq) + H_3O^{+}(aq),$$

and the $HS^{-}(aq)$ reacts with lead to give lead sulfide:

$$Pb^{2+}(aq) + HS^{-}(aq\ ) + H_2O(l) \rightarrow PbS(s) + H_3O^{+}(aq).$$

Much of the polonium is present in solution in the +4 oxidation state. Polonium has a strong tendency to form complexes and at the pH and nitrate concentration used in this step, polonium may be present as a series of basic nitrato complexes, i.e., as complexes with the general formula $[Po(OH)_x(NO3)_n]^{(4-x-n)+}$. However, for the sake of simplicity, polonium in the +4 oxidation state will be designated as Po^{4+}. The Po^{4+} is first reduced according to the reaction

$$Po^{4+}(aq) + HS^{-}(aq\ ) + H_2O(l) \rightarrow Po^{2+}(aq) + S(s) + H_3O^{+}(aq),$$

and the Po^{2+} coprecipitates with the lead:

$$Po^{2+}(aq) + HS^{-}(aq\ ) + H_2O(l) \rightarrow PoS(s) + H_3O^{+}(aq).$$

It should be mentioned that any iron present will precipitate as the sulfide and be carried on to the next step of the procedure. Since

$$Fe^{3+}(aq) + 3e \rightarrow Fe^{2+}(aq) \quad E^{\circ} = 0.770\ V$$

and

$$S(s) + 2H_3O^{+}(aq) + 2e \rightarrow H_2S(aq) + 2H_2O(l) \quad E^{\circ} = 0.141\ V,$$

it is clear that most of the Fe^{3+} will be converted to Fe^{2+} by the reaction:

$$Fe^{3+}(aq) + H_2S(aq) + 2H_3O^{+}(aq) \rightarrow Fe^{2+}(aq) + S(s) + 2H_2O(l\ ).$$

The Fe^{2+} so produced will precipitate as FeS.

8.19 Allow the contents of the centrifuge tubes to cool to room temperature. A gelatinous precipitate may have formed during the thioacetamide digestion. This is not problem because the precipitate can be dissolved in the next step, along with PbS.

The formation of the precipitate probably occurs, at least in part, because the dissolution of many hydroxides, like $Mg(OH)_2$, is an exothermic process, and, consequently, the solubility of such hydroxides decreases with temperature.

8.20 Centrifuge the tubes at 1600 rpm for a period of ten minutes. Decant the supernatants and discard the supernatants in a bottle specifically set aside for thioacetamide waste.

If there is no gelatinous precipitate, it may be difficult to decant all of the supernatant without losing some of the precipitate. Some of PbS may not adhere to the centrifuge tube very well and may be lost when the last few milliliters of the supernatant is decanted. If this is the case, it is advisable to decant as much of the supernatant as possible, and, then, to produce some hydroxide precipitate by adding a drop of concentrated NH_4OH. Centrifuge the tube once more. The gelatinous precipitate should settle to the bottom of the tube carrying the PbS with it.

Dissolution of the Lead Sulfide Carrier.

8.21 Dissolve the precipitate in one centrifuge tube by adding 1 mL of concentrated hydrochloric acid and warming the tube on a hot water bath. If a gelatinous precipitate is present, the precipitate may dissolve very slowly unless additional HCl is added. If the dissolution process is not complete within 15 minutes, add an additional 0.5 mL of concentrated HCl to the tube while warming it in a hot water bath. Repeat as many times as is necessary. Once all of the PbS has dissolved, the solution should be a bright yellow, and none of the black PbS should be visibly apparent. (It is important that the PbS be dissolved with concentrated HCl. Once the HCl is diluted, as in the next step 8.23, the rate at which PbS dissolves is exceedingly slow.) Some non-gelatinous white precipitate may persist but this is alright. These are just fluoride precipitates, which will eventually be dissolved in step 8.24.

> When the PbS is dissolved in concentrated hydrochloric acid, Pb forms a bright yellow chloro complex:
>
> $$PbS(s) + 4Cl(aq) \rightarrow [PbCl_4]^{2-}(aq) + S^{2-}(aq).$$
>
> When the solution is diluted with water, as in the next step, the $[PbCl_4]^{2-}$ dissociates, and the solution turns clear.

8.22 Transfer the contents of the first centrifuge tube to a second centrifuge tube two. Warm the centrifuge tube in a hot water bath to dissolve the precipitate. If the precipitate does not dissolve within 15 minutes, add additional 0.5 mL aliquots of concentrated HCl every 15 minutes until the precipitate dissolves. Transfer the content of the second tube to the third tube and repeat this step with the third tube.

8.23 Add 10 mL of 0.5 M HCl to the first two tubes and warm the tubes in a hot water bath. Pour the hot solution from the first two tubes into the third tube. Rinse the first two tubes with 10 mL of polished water, and transfer the rinses to the third tube. During this step make sure that any precipitate that is present in the first and second tubes is quantitatively transferred to the third tube. Keep one of the empty tubes for step 8.26; discard the other empty tube.

8.24 If there is a white precipitate in the centrifuge tube, add 1.0 mL of boric acid solution to the centrifuge tube, and warm the tube on a hot water bath. Allow at least 15 minute to pass. If the solution has not cleared, repeat this step until a clear solution has been obtained.

Preparation of the Nickel Disc for Spontaneous Deposition of Polonium.

8.25 Using a polypropylene forceps to hold the Ni disc, rinse the nickel disc with ethanol, followed by a rinse with polished water. Then, dip the disc in concentrated HCl for about 2 minutes, again followed by a rinse with polished water.

Preparation of Deposition Cell and Spontaneous Deposition of Polonium.

8.26 Add 10 mL of 0.5 M HCl to the empty centrifuge tube from step 8.23. Place the tube in a hot water bath, and allow the solution in the tube to become hot.

8.27 Using a funnel and Whatman No. 41 filter paper, filter the solution from the centrifuge tube into a 60-mL polypropylene bottle (see Figure 1). Wash the filter with the 10 mL of hot 0.5 M HCl prepared in the previous step . Discard the filter.

> The filter step is important in order that any particulate matter that may be present be removed. The particulate matter could act as nucleation centers for the deposition of polonium. Moreover, the particulate matter could settle on the nickel disc, causing a reduction in the alpha-particle signal and a broadening in the peaks of the alpha-particle spectrum.

8.28 Add 100 mg of ascorbic acid and a small stir bar to the 60-mL polypropylene bottle. (A stir bar that is almost round should be used. If a long, narrow stir bar is used, then, because nickel is magnetic, the stir bar will stick to the Ni disc and will not rotate.)

> From experiments performed in the Radiochemistry Unit it is clear that uranium, thorium, and actinium do not spontaneously deposit along with polonium on a Ni disc; thus, the common actinides will not give rise to interfering peaks in an alpha spectrum.
>
> The critical deposition potential for the electrodeposition of polonium on a Ni disc is about 0.81 V (Reference 7.6), so that polonium will spontaneously deposit on the electrode when the potential of the electrode is less than 0.81 V (versus the standard hydrogen electrode). There are a number of oxidizing species present in the solution which may elevate the potential of the Ni disc to the point that polonium deposition is prevented or that some of the deposited polonium may be re-oxidized. One such species is nitrate, NO_3^-, which has the corresponding half-cell reaction
>
> $$NO_3^-(aq) + 4H_3O^+(aq) + 3e \rightarrow NO(aq) + 6H_2O(l) \quad E^\circ = 0.96\ V.$$
>
> It is seen that nitrate is a reasonably strong oxidizing agent in acidic solutions; however, the coprecipitation step gets rid of most of the nitrate, so that re-oxidation of polonium due to nitrate should not be a problem.
>
> Another potential oxidizing agent is Fe^{3+} which has the correspond half-cell reaction:
>
> $$Fe^{3+}(aq) + 3e \rightarrow Fe^{2+}(aq) \quad E^\circ = 0.770\ V.$$
>
> However, it was shown in step 8.18 that after the coprecipitation the bulk of the iron should in +2 oxidation state, and, therefore, should not be a problem.
>
> The redox behavior of oxygen is complex, but two reactions of oxygen that can occur in acidic solution are
>
> $$O_2(aq) + 2H_3O^+(aq) + 2e \rightarrow H_2O_2(aq) + 2H_2O(l) \quad E^\circ = 0.682\ V,$$
>
> $$O_2(aq) + 4H_3O^+(aq) + 4e \rightarrow 6H_2O(l) \quad E^\circ = 1.229\ V.$$
>
> Thus, oxygen is capable of raising the potential of the Ni disc, and, therefore may inhibit the deposition of polonium or cause the re-oxidation of any polonium deposited on the Ni disc. Because of the coprecipitation step, the polonium should be in the +2 oxidation state, and during the spontaneous deposition step polonium is in a 0.5 M HCl solution. Under these conditions most of the polonium is thought to exist as anionic chloropolonium complexes like in $[PoCl_3]^-$ and $[PoCl_4]^{2-}$ (References 7.3 and 7.13, pg. 343). In the presence of oxygen, the potential of the Ni disc may exceed 0.81, leading to the oxidation and loss of polonium on the Ni disc:
>
> $$Po(Ni) + \tfrac{1}{2}O_2(aq) + 4Cl^-(aq) + 2H_3O^+(aq) \rightarrow [PoCl_4]^{2-}(aq) + 4H_2O(l).$$
>
> Ascorbic acid participates in the following half-cell reaction:
>
> $$\underset{\text{(dehydroascorbic acid)}}{C_6H_6O_6(aq)} + 2\,H_3O^+(aq) + 2e \rightarrow \underset{\text{(ascorbic acid)}}{C_6H_8O_6(aq)} + 2H_2O(l) \quad E^\circ = 0.080\ V.$$
>
> When an excessive amount of ascorbic acid is added to the solution, it can reduce O_2, and any Fe^{3+} or NO_3^- left in solution, and will establish the potential of the Ni disc at

about 0.080 V or below, far below 0.81 V, the critical deposition potential of polonium. Consequently, polonium spontaneously deposits on the Ni disc.

It should be noted that, thermodynamically, it is possible for the ascorbic acid to react directly with polonium in solution. However, the rate of this reaction is apparently very slow, possibly because the formation of any polonium apart from the Ni surface would require that the polonium go through a nucleation stage. Typically, there is a high free-energy barrier to the formation of a bulk material formed by nucleation processes because of the high surface area to volume ratio of the nucleation centers. The Ni disc acts somewhat like a catalyst, by transferring electrons from ascorbic acid to Po^{2+}, and Ni acts as a relatively low-energy surface for the deposition of polonium.

8.29 Place a silicone rubber septum and the clean nickel disc in the cap of the 60-mL bottle, and screw the cap onto the bottle (see Figure 2). (The septum assures that the Ni disc is firmly and squarely seated on the lip of the bottle, thus helping to prevent leakage.)

8.30 Invert the bottle, use a felt tip pen to mark the level of the solution in the bottle, and pierce a small hole in the center of the bottom of the bottle with a hot glass stir rod (so that when the bottle is heated, as in the next step, the increase in gas pressure above the solution will not force the solution out of the bottle).

8.31 Prepare a hot water bath by placing a 400-mL beaker on a combination hotplate and magnetic stirrer and partially filling the beaker with about 200 mL of water. Place a thermometer in the beaker, and adjust the hotplate so that the temperature of the water is maintained at about 80 C.

8.32 Place the inverted bottle in the hot water bath (see Figure 3). Turn the magnetic stirrer on, and make sure that the stir bar is spinning. During the first 5 minutes that the bottle is in the hot water bath, remove the bottle several times and tighten its cap to prevent leakage which commonly occurs as a result of the thermal expansion of the polypropylene bottle. Maintain the temperature of the bath at 80 C while stirring for 4 hours. If the level of the solution in the bottle drops significantly during the four hours, the liquid is probably leaking from the bottle. Evaporation should not cause the level of the solution to drop significantly.

8.33 Pour the solution from the deposition cell into a bottle specifically set aside for deposition cell waste.

Holding a piece of Parafilm over the hole in the bottom of the bottle with a finger prevents leakage of solution from the hole when the cell is turned upright and the bottle cap is removed.

8.34 Remove the Ni disc, rinse it with polished water and, then, ethanol.

Some corrosion of the Ni disc by the hot acid is normal, and is of no concern.

8.35 Place the Ni disc on a hotplate at 300 C, cover the disc with a 400-mL glass beaker, and leave the Ni disc on the hotplate for 5 minutes.

The purpose of this step is not so much to dry the disc as it is to oxidize the polonium on the surface of the Ni disc. Elemental polonium is quite volatile. The oxidation of polonium lowers the volatility of polonium which significantly reduces the contamination of the detector by polonium. The hotplate to be used for oxidizing the polonium should be prepared before the Ni disc is placed on it. This is done by placing a 400-mL beaker upside down on the hotplate and sliding the end of a thermometer underneath the beaker so that the bulb of the thermometer is in the center of the hotplate. The other end of the thermometer can be supported with another beaker (see Figure 4). Once the temperature has stabilized at about 300 C, the thermometer can be removed, and the Ni disc can be placed under the beaker for a period of five minutes. A Corning hotplate set at about 6¾ gives a stable temperature of about 300 C. When oxidation has occurred, there should be a noticeable color change in the portion of the Ni disc exposed to the solution during deposition. For example, after oxidation, a Ni disc from a regent blank often has a golden patina; whereas, a Ni disc from a sample often turns black. If there is not a dramatic color change, increase the temperature of the hotplate and leave the Ni disc on the plate until such a color change is observed.

8.36 Place the Ni disc in a labeled ointment tin until it is time to collect the alpha spectrum.

9.0 Figures.

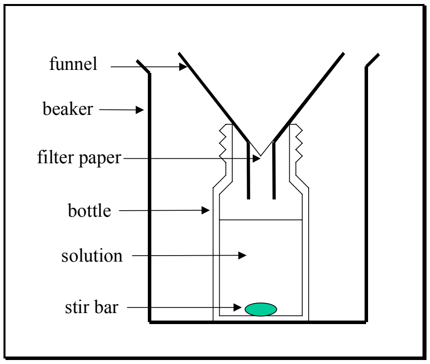

Figure 1. Filter Setup.

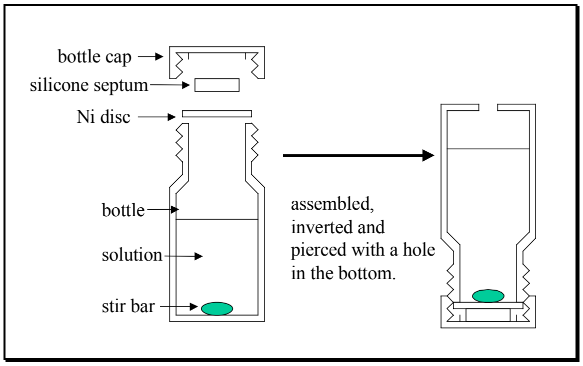

Figure 2. Schematic of Deposition Cell.

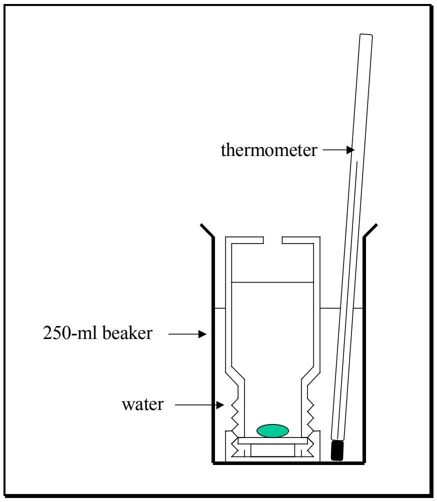

Figure 3. Schematic of Hot Water Bath.

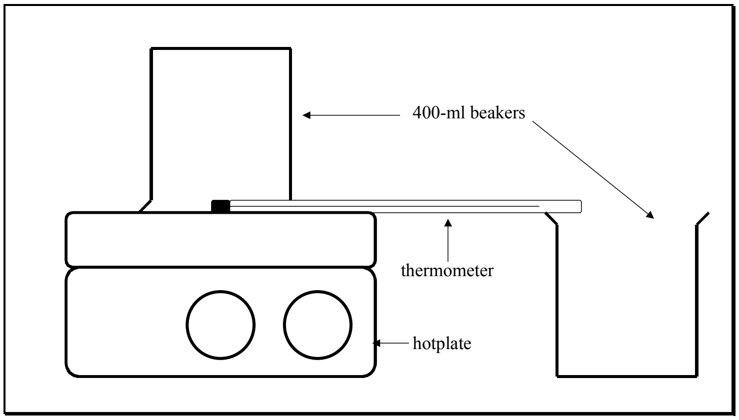

Figure 4. Heating Apparatus for Oxidizing Polonium on Ni disc.

Written by: ________________________________ Date: ______________________

Title: ____

Unit: ____

Reviewed by: ________________________________ Date: ______________________

Title: ____

Unit: ____

Approved by: ________________________________ Date: ______________________

Title: ____

Unit: ____

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[1] *Handbook of Chemistry and Physics*, 57th Ed.,CRC Press, Inc., Cleveland (1976-1977). p. B-99 and B-128.

[2] See, e.g., Govett, *Anal. Chim. Acta* **25**, 69-80 (1961).

[3] Langmyhr, F.J. and Graff, P.R., *Anal. Chim. Acta* **21**, 334-339 (1959).

[4] Langmyhr, F.J. and Graff, P.R., *Anal. Chim. Acta* **32**, 1-7 (1965).

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