How Rigorous is Rare Earth Fluoride Micro-Precipitation?

Barry Stewart and Carl Schloesslin

Carlsbad Environmental Monitoring and Research Center

New Mexico State University

Carlsbad, NM 88220

Introduction

We have investigated the reliability and durability of a method for preparing sources for alpha spectroscopy that has been known for many years, and has been widely utilized. Every lab seems to have its own version of how it should be done, and that in itself suggests that the technique is fairly rugged. But how rugged? To answer, or at least address the question, we have completed a number of tests, some of which have surprising results. The two most important parameters for us to monitor are recovery and spectral resolution, or peak width.

Tests and Results – Part I: Method Parameters

The "Sandard Method" - We use NdF_3 in our laboratory. Use of La[1], Ce[2], and Nd[3] have all been successfully used. For most routine applications, there is no clear advantage. However, Hindman[2] states that NdF_3 is a bit slower to form than LaF_3 or CeF_3. Extremely pure oxides of any of these can be obtained, and with the exception of Ce, which must be reduced to +3, the oxides are easily dissolved in dilute HCl, which means that the laborious preparations described[2,3] are unnecessary.

Lanthanum was chosen for our tests and evaluations. After appropriate separations, the dried actinide residue is taken up in 4 mL 2*M* HCl and transferred to a 50-mL polycarbonate centrifuge tube. 50 µg of La is added (100 µg is used for uranium samples), and then appropriate reagents are added for oxidation state adjustment ($TiCl_3$ for U and ascorbic acid for Pu/Np). One mL of HF is added to generate LaF_3, giving a final volume of ~12 mL. The precipitate is allowed to digest for 10-30 minutes and then filtered through a polypropylene filter with 0.1-µm pores[*]. With these filters, the use of a substrate suspension is entirely unnecessary, although we use a carbon suspension because it clearly identifies the active area of the deposit. The filter and residue is dried briefly under a heat lamp (~60° C) and then mounted on a SS planchet with double sided tape. All samples prepared for this presentation were counted long enough to accumulate 25,000 counts.

Test 1 – The Effect of Sample Volume. Using Pu-238, a series of samples were prepared, each in 2*M* HCl with 50 µg of La. 3-4 drops of 1*M* ascorbic acid were addd to ensure absence of Pu^{+6}. Then 1 mL of HF was added, and after 10 minutes, the samples were filtered. There was no attempt to maintain HF concentration throughout. Results (Fig. 1) indicate a clear trend toward worsening resolution (wider peaks) and loss of Pu. Because the effect of precipitate digestion time had not yet been investigated, we wanted to see if longer digestion time would improve the performance.

In the second experiment (Fig. 2), the only change was to increase the length of digestion to 20-30 minutes. Recoveries improved, but overall, spectrum resolution deteriorated slightly.

---

[*] A note on filters. Gelman Metricel polypropylene, 0.1-µm pore size, and Environmental Express polypropylene, 0.1-µm pore size, are identical. Other types of filters and pore sizes should be tested for yield and resolution. Some can be made to work (Tuffryn HT-200, DM-450, etc.) by use of substrate suspension as described[2,3].

In a third experiment (Fig. 3), digestion time was carefully monitored at 30 minutes. Clearly, resolution deteriorates as sample volume increases, but like the first experiment, the 30-mL sample has low Pu recovery.

Test 2 – The Effect of Acid Concentration. Conditions were the same as previous experiment, except from here on digestion time is held at 30 minutes. The sample volume is ~12 mL. In this experiment, there is a clear trend of deteriorating resolution as acidity increases (Fig. 4). Surprisingly, however, recovery did not decrease. At 10*M* HCl, recovery remains >95%. A follow-up experiment (Fig. 5) confirms the decreasing resolution and constant recovery. However, the resolution is poorer for every sample in the set.

Test 3 – The Effect of Digestion Temperature. Maintaining the conditions from previous tests, we then looked at digestion at elevated temperature. To do this, samples were brought to test temperature in a water bath. HF was added and the digestion was continued for 10 minutes. Samples were filtered as soon as possible after removal from the water bath. Results indicate (Fig. 6, 7) that resolution gets worse when samples are precipitated from warm or hot solutions. Recovery may decrease at higher temperature, possibly due to higher solubility of the precipitate. However, cooling the sample prior to filtration, while it might improve recovery, may not improve resolution. This is because resolution is set by the particle size of the precipitate when it forms.

Test 4 – The Effect of Digestion Time. Maintaining the same protocol, we varied digestion time from 2 to 1000 minutes. Recoveries varied considerably within the test, and the results did not repeat very well (Fig. 8, 9). In the first experiment, resolution began to deteriorate after 8 hours digestion, but that could not be verified by the second experiment.

Test 5 – The Effect of Analyte Mass. Because of the mechanism by which actinides are incorporated into the LaF_3 lattice, only limited amounts of long-lived nuclides can be accommodated. Increasing amounts of U-238 were added to 50-µg samples of La carrier and precipitation carried out in the normal manner. After filtration, instead of mounting for counting, the samples were stripped and submitted for analysis by ICP-MS. From the ICP results uranium recovery and mole ratio of La/U were calculated. Results (Fig. 10) show that the La/U mole ratio at first begins to decrease as the amount of U present increases. It then levels off and remains constant, regardless of how much U was in the sample. While La/U ratio remains constant, U recovery continues to decrease until such time as sufficient U is present that it will precipitate on its own. At this point, however, the mass would be far too great for alpha spectroscopy.

Test 6 – The Effect of Non-homogenous precipitation. In this experiment, we investigated the effect of generating the LaF_3 precipitate before the analyte was present. This would address a situation such as oxidation state not being properly adjusted before precipitation was initiated. Plutonium and Am were quantitatively precipitated even though the LaF_3 precipitate was already fully formed (Fig. 11). For U, precipitation was not complete. The amount of U used (22.85 dpm) is more than can be precipitated by 50 µg of La, so a second sample was prepared using 100 µg. In the first case, only 36% of U was precipitated. With an additional 50 µg of La, recovery improved to 58%.

Tests and Results – Part II: Durability

Storage of samples after counting has always been a cause for concern especially if there might be a need to re-count a sample at a later date. How should the samples be protected against deterioration which might be caused by rough handling? We utilize thin films in our laboratory to prevent recoil contamination of our detectors. The film is applied directly to the sample after the filter and precipitate has been mounted on a stainless steel planchet. So a second question that we asked was how could the film be removed in the event a sample needed additional separations or cleanup? Our first durability test was to simply strip the film from a number of samples and then recount the samples to see if any of the sample was lost. Since the film touches the active area of the mounted sample, it should provide a sensitive indication of durability.

Durability Test 1 – Removal of thin film. Twenty-two samples were tested by stripping their films. To minimize systematic errors, the same detector used for counting the filmed sample was used to count the

sample after the film was removed. The % difference was calculated for each sample. The average % diff was -0.31% ± 1.6%. The largest difference was –6.5%.

Durability Test 2 – "File drawer test." In our laboratory, an entire batch of samples is put into a plastic bag and then stored in ordinary file cabinets. In this experiment, a sample was sealed in a disposable petri dish, and the dish was inserted into a rotary tumbler device. The motion produced was a simple rotary motion that caused the sample planchet to be inverted and then slide across the petri dish, returning to the upright position as the rotator moved through its cycle. The rotation speed was set at 20 rpm, which produced 20 cycles of turning the planchet upside down. This action somewhat approaches the random motions to which a sample might be subjected through opening and closing a file drawer or sorting through them to find a specific sample. After 6 minutes of rotation (corresponding to 120 inversion cycles), no statistical change in count rate was observed.

Durability Test 3 – Coin envelope. Another type of file drawer test was to put a sample into a plastic coin envelope and shake it around to see if any activity could be dislodged. We thought the plastic envelope might cause deterioration more quickly because of greater likelihood of the bag touching the source than with the petri dish. The sample was removed periodically and recounted. After 4.5 minutes, no statistical difference in count rate was observed.

Durability Test 4 – Abrasion test. This test is a more aggressive version of the "file drawer" test. A sample was placed upside down in a disposable petri dish. The dish was moved back and forth with sufficient force to slam the planchet against the side of the dish. The frequency of the oscillations was 3 per second which gave six sliding movements per second. Only the weight of the planchet was used to hold the sample in contact with the bottom of the dish. The results are shown in the following table.

Time, sec.	# of movements	DPM
0	0	955.5 ± 9.8
30	180	945.8 ± 9.7
60	360	914.8 ± 9.4
90	480	905.5 ± 9.3

Summary

Based on our observations, the rare earth fluoride micro-coprecipitation technique is tolerant to a fairly wide range of acid concentration, solution volume, digestion time, and precipitation temperature while still providing nearly quantitative results. For optimum spectral resolution, however, we recommend small sample volume and low acid concentration with precipitation occurring at room temperature. Digestion times of as much as 4 hours should not affect resolution. Digestion times as short as 2 minutes will still provide nearly quantitative recovery and excellent resolution.

The durability of the mounted sample is greater than we anticipated. Although storage of samples for relatively long periods does not require precautions to be taken against inversion or movement of the sample, we believe the petri dish provides greater security than the plastic coin envelope.

---

[1] S. R. Joshi, *J. Radioanal. Nucl. Chem. 90,* No. 2, 409-414 (1985).
[2] C. W. Sill, *Nuclear and Chem. Waste Mgmt. 7,* 201-215 (1987).
[3] D. F. Hindman, *Anal. Chem. 58,* No. 6, 1238-1241 (1986).

NOTE: In Figures 1-9 and 11, the bars in the graphs indicate recovery and the error bars are ± 2-σ. The lines show FWHM. In Figure 10, the error bars are ± 5%.

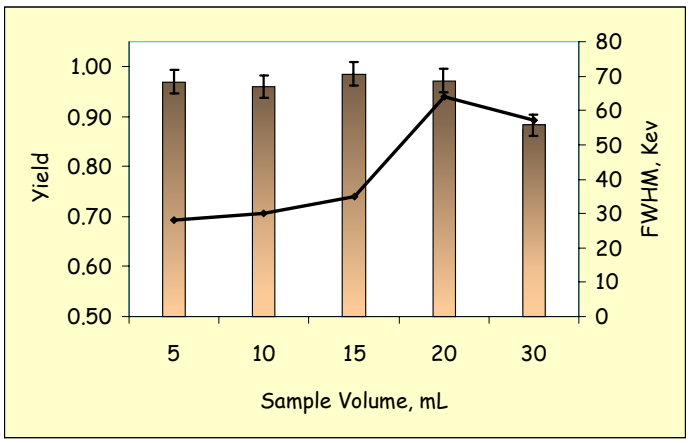

Figure 1

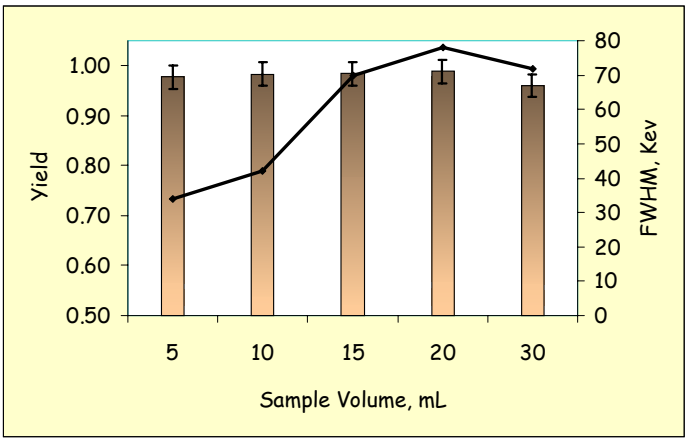

Figure 2

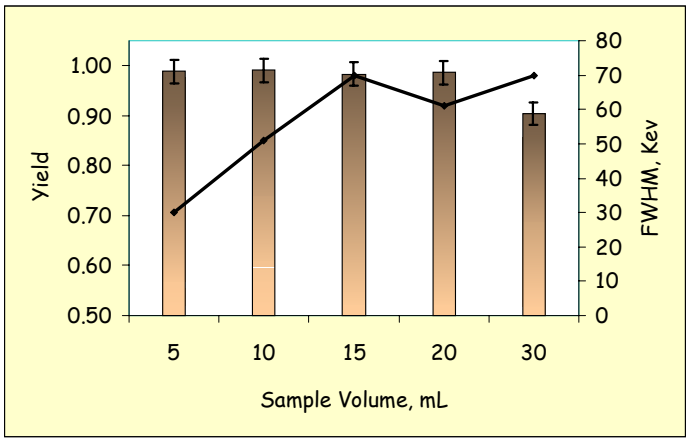

Figure 3

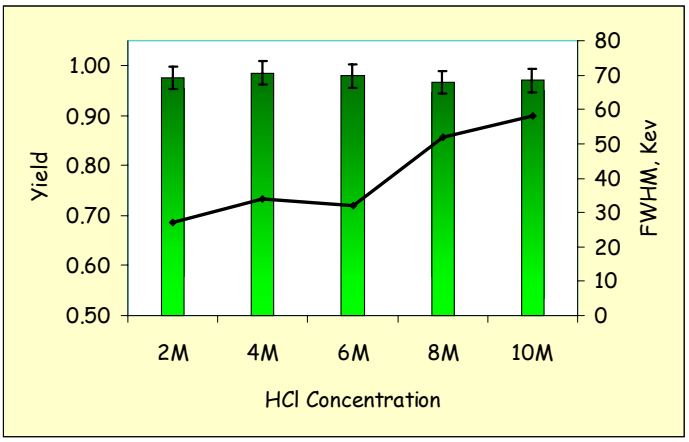

Figure 4

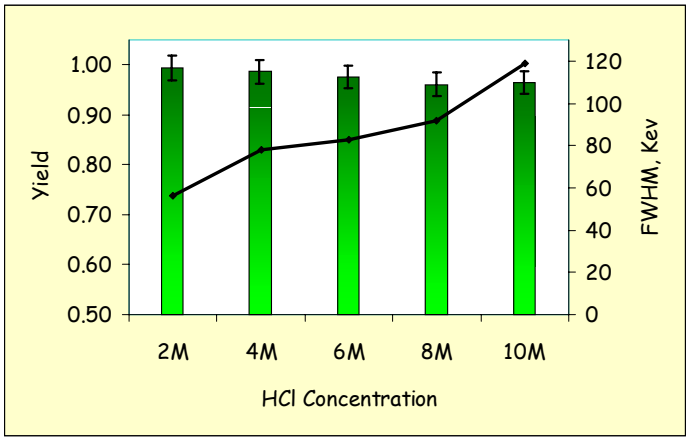

Figure 5

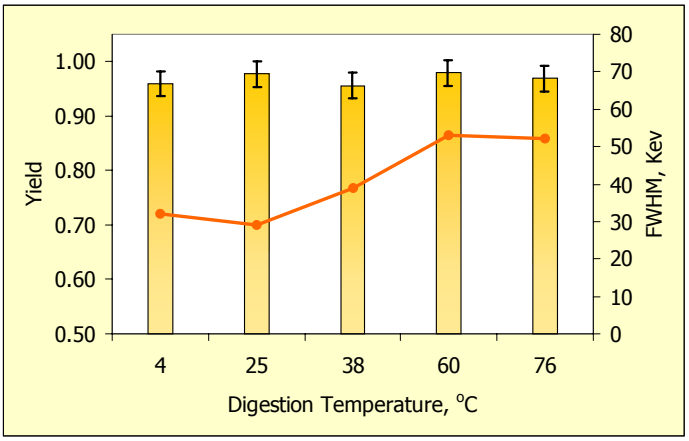

Figure 6

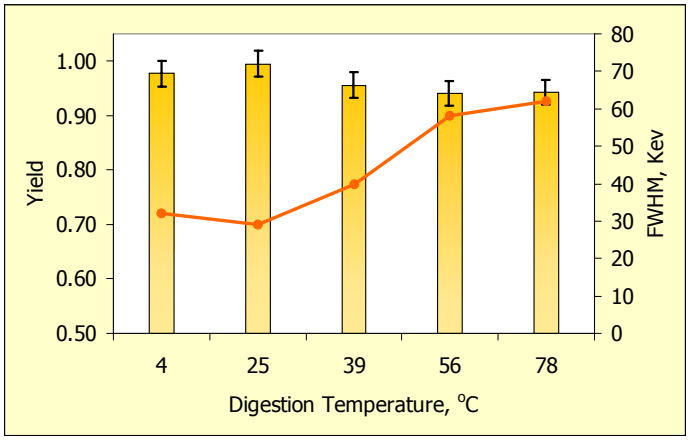

Figure 7

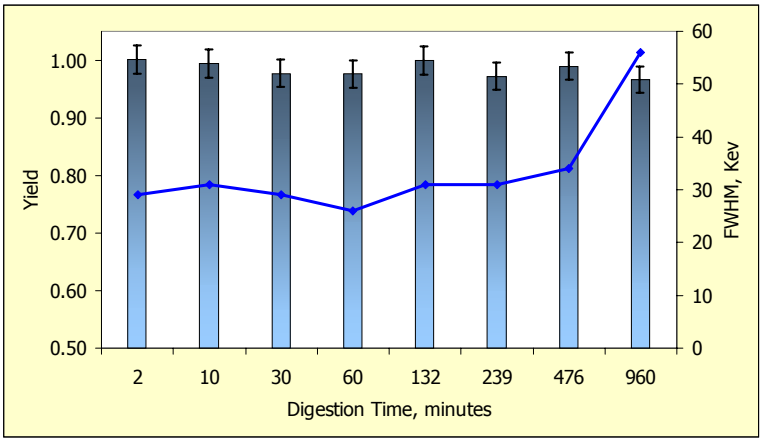

Figure 8

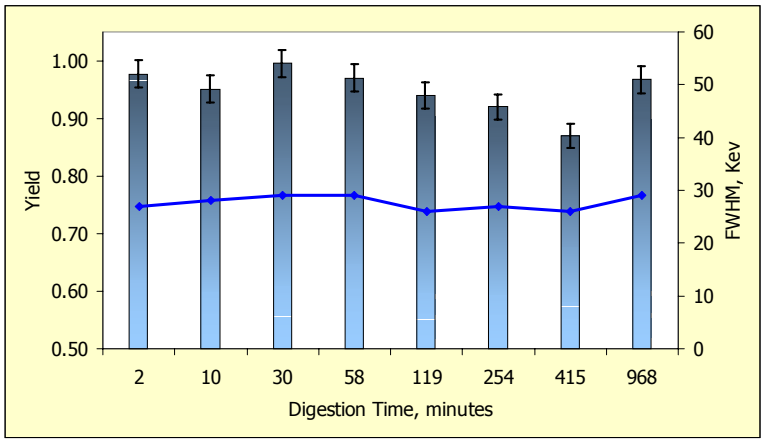

Figure 9

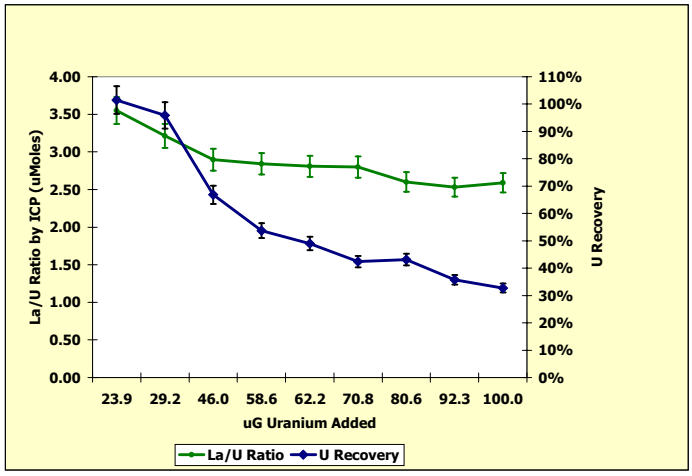

Figure 10

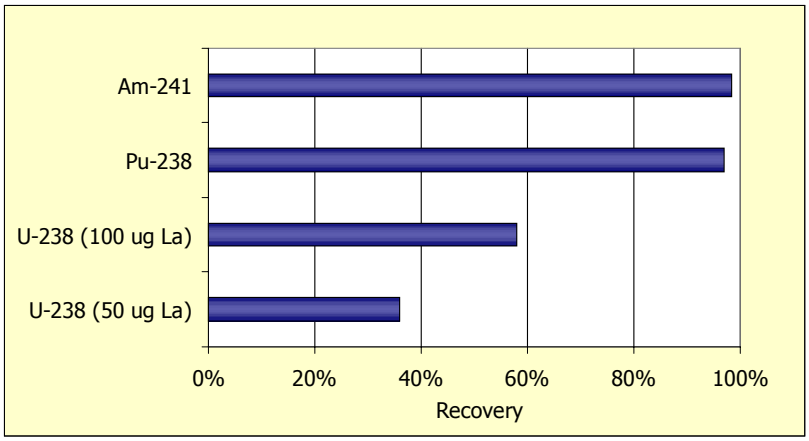

Figure 11