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THE DETERMINATION OF UO_2 AND UF_4 IN FUSED FLUORIDE SALTS

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ABSTRACT

The determination of uranium oxide solubilities in fused fluoride salts is important in the electrolytic preparation of uranium metal. This project was initiated to develop a method for the determination of UO_2 separately from UF_4 in UF_4-CaF_2-LiF fused salts. Previous methods used for the determination of UO_2 in fused fluoride salts involved inert gas fusions where oxygen was liberated as CO_2, and hydrofluorination where oxygen was released as H_2O; but the special equipment used for these procedures was no longer available. These methods assumed that all of the oxygen liberated was due to UO_2 and does not consider impurities from reagents and other oxygen sources that amount to a bias of approximately 0.3 wt. %. This titrimetric method eliminates the bias by selectively extracting the UF_4 with a Na_2EDTA-H_3BO_3 solution. The remaining uranium oxide residue is treated and titrated gravimetrically to a potentiometric endpoint with NBS standard $K_2Cr_2O_7$. An aliquot of the Na_2EDTA-H_3BO_3 extract is also titrated gravimetrically to a potentiometric endpoint, this uranium component is determined and calculated as UF_4.

INTRODUCTION

Based on previous work[1] ammonium oxalate has been used to dissolve uranium tetrafluoride. When used with fused salt samples for this project, the ammonium oxalate dissolved the UF_4, the LiF, and reacted with an appreciable amount of CaF_2 to produce insoluble calcium oxalate hydrate (Figure 1). These reactions all contribute to an excess of fluoride ions in the extract. The UO_2 is insoluble in the ammonium oxalate and remains as a residue with the calcium oxalate hydrate ($CaC_2O_4 \cdot H_2O$) and unreacted CaF_2. These excess fluoride ions in the ammonium oxalate extract would interfere with the determination of UF_4. Attempts to remove the fluoride by fuming with H_2SO_4 and $HClO_4$ were unsuccessful due to precipitation of the uranium (IV) oxalate complex in an acidic medium[2]. Earlier unpublished work at ORNL indicated that the di-sodium salt of EDTA (di-sodium ethylenediamine tetraacetic acid) would dissolve UF_4, but would not dissolve uranium oxides. Previous studies at the New Brunswick Laboratory[3] (NBL) showed that the fluoride interference observed during the titration of U^{IV} could be eliminated with the addition of boric acid, which complexed the fluoride ion prior to the titration, and eliminated the need for a fuming step in the determination of UF_4. These two reagents are also compatible for the subsequent determination of UO_2 and UF_4.

EXPERIMENTAL

APPARATUS

The analytical balance used is a Mettler AK160 which has a capacity of 160 g and a sensitivity of 0.1 mg. The millivolt meter was a Radiometer model PHM 84 research digital pH meter with a mV scale sensitivity of 1 mv. The electrode pair consisted of a standard calomel reference electrode and a platinum electrode made from coiled 16-gauge wire. A Whatman data plate 440 programmable hot plate/stirrer was used. The data plate was programmed to give an audible signal at the end of the various time intervals and to change stirrer speed automatically. The titrant delivery system employed was a 125 ml squeeze bottle with a removable polyethylene tip. The tip was drawn out to deliver single 4-5 mg drops.

REAGENTS

The chemicals used were reagent grade and were not purified further.

1. 5% Na_2EDTA-2.5% Boric Acid Solution: Dissolve 50 g of Na_2EDTA and 25 g of boric acid and dilute to one liter.
2. Sulfamic Acid Solution 1.5 M: Dissolve 73 g of H_2NSO_2OH in water and dilute to 500 ml.
3. Nitric Acid, Concentrated ACS-Grade
4. Perchloric Acid, ACS-Grade, 70%.
5. Orthophosphoric Acid, ACS Grade 85%: Condition each 2 1/2 liter bottle by the addition of the 1 ml of 6% potassium dichromate solution.

Prepare the 6% $K_2Cr_2O_7$ solution by dissolving 6 g of $K_2Cr_2O_7$ in water and diluting to 100 ml.

6. Ferrous Sulfate, 1 M: Add 50 ml of concentrated H_2SO_4 to 300 ml of H_2O. Add 140 g of $FeSO_4 \cdot 7H_2O$ and stir until dissolved. Cool and dilute to 500 ml with H_2O.

7. Nitric Acid-Sulfamic Acid-Ammonium Molybdate Solution: Dissolve 4.0 g of ammonium molybdate in 400 ml of H_2O. Add 500 ml of concentrated HNO_3 and mix. Add 100 ml of 1.5 M sulfamic acid solution and mix.

8. Potassium Dichromate Solution, 0.050 N: Dissolve 4.9032 g of dry primary standard $K_2Cr_2O_7$ in H_2O, dilute to 2 liter and weigh. Standardize with NBS SRM 950 b or an equivalent U_3O_8.

9. Sulfuric Acid Solution, 1 M: Add 55 ml of concentrated H_2SO_4 to 500 ml of H_2O and dilute to one liter.

10. Vanadyl Sulfate Solution: Prepare a solution using 15 g vanadyl sulfate diluted to 500 ml with 1 M H_2SO_4.

SEPARATION OF UO_2 AND UF_4

Process samples are received as fused pellets which are ground to fine powders using a mortar and pestle. The powdered samples are transferred to 25 x 50 mm polyethylene vials and capped. Weigh 0.5 to 1.0 g aliquots of each sample into 150 ml beakers and add 150 ml of 5% Na_2EDTA-2.5% H_3BO_3 solution. The solutions are then placed on hot plates and are boiled for 30 minutes with mechanical stirring. The samples are then allowed to settle and cool. When cool, the supernatant is filtered through an 8 μm Millipore filter membrane into a tared 500 ml vacuum flask, using a Gelman magnetic filtering apparaus. Then add 100 ml of the 5% Na_2EDTA-2.5% H_3BO_3 solution to the residue left in the beakers and boil the solutions for an additional 15 minutes with mechanical stirring. This is continued until all of the UF_4 (green salt) is dissolved (usually 2-3 times). When the UF_4 has dissolved, the entire sample is filtered and washed several times with water. The insoluble uranium oxide remains as a combined residue on the filter disc with the CaF_2 (Figure 2). The dissolved UF_4 and LiF remain in the Na_2EDTA-H_3BO_3 extract. The filter disc with the residue is transferred to a 150 ml beaker and 20 ml of concentrated nitric acid is added. This decomposes the membrane filter and dissolves the UO_2 and CaF_2. The HNO_3 solution is evaporated to wet crystals. Ten ml of concentrated $HClO_4$ is added and the solution is fumed down to 2-3 ml to remove the excess fluoride, and allowed to cool. When cool, the $HClO_4$ solution is transferred to a tared polyethylene bottle with a minimum of water. The polyethylene bottle is reweighed to obtain a solution weight. This solution contains the uranium originally present in the fused salt as UO_2. The 500 ml vacuum flask is reweighed to obtain a solution weight for the Na_2EDTA-H_3BO_3 extract. The solution contains uranium originally present as UF_4 in the fused salt.

Determination of UO_2 and UF_4

The titrimetric method described is adapted from the original Davies and Gray procedure[4] and is virtually free of interferences. Most interferences are removed by fuming, the addition of reagents, or by extraction prior to the titration. The method involves the reduction of uranium (VI) to the (IV) state with an excess of Fe(II) in a concentrated phosphoric acid medium containing sulfamic acid. The excess Fe(II) is then oxidized by nitric acid with Mo(VI) as a catalyst. The sample is diluted with a sulfuric acid-vanadyl sulfate solution and titrated to its U(VI) endpoint with standard potassium dichromate using a combination platinum wire-calomel electrode configuration.

A 4.0 to 6.0 g aliquot of each sample solution is weighed and transferred to a 400 ml beaker. Five ml of sulfamic acid is added; followed by the addition of 40 ml of concentrated phosphoric acid which has been treated with $K_2Cr_2O_7$ to reduce any oxidizing impurities. The sample is placed on a stirrer and the speed set for 150 RPM's. A 5 ml volume of ferrous sulfate solution is added and a 30 second waiting period is observed to assure the complete reduction of U^{VI} to U^{IV}. A 10 ml volume of nitric acid-sulfamic acid-ammonium molybdate solution is added to oxidize the excess Fe(II). A dark brown color which appears at this point will clear in 20-30 seconds. The sample is allowed to stir for four minutes. After four minutes the stirrer speed is increased to 400 RPM's and the sample is diluted with a solution containing 100 ml of 1$\underline{M}$ H_2SO_4, 50 ml warm H_2O(approx. 75°C) and 5 ml of the vanadyl sulfate solution. The platinum wire-calomel electrode is immersed into the solution and the sample is titrated gravimetrically with standard $K_2Cr_2O_7$ to a reading of 590 mV. Near the end point, time is allowed for the solution to equilibrate, but the time elapsed from the addition of the vanadyl sulfate to the end of the titration must not exceed 5 minutes.

RESULTS AND DISCUSSION

Synthetic mixtures containing varying amounts of U_3O_8, UF_4, CaF_2 and LiF were prepared and analyzed. Results (Table 1) showed an average recovery of 97.6% for U_3O_8 and 101.6% for UF_4. Since actual samples contain UO_2., UF_4, CaF_2, and LiF and may perform differently from synthetic mixtures containing U_3O_8, we prepared a set of process samples and demonstrated that the results obtained were in agreement with the predicted values. Triplicate analysis of a single sample (Table 2) containing approximately 9 mg UO_2 and 91 mg UF_4 showed a relative standard deviation of 0.345% for UO_2 and 0.092% for UF_4.

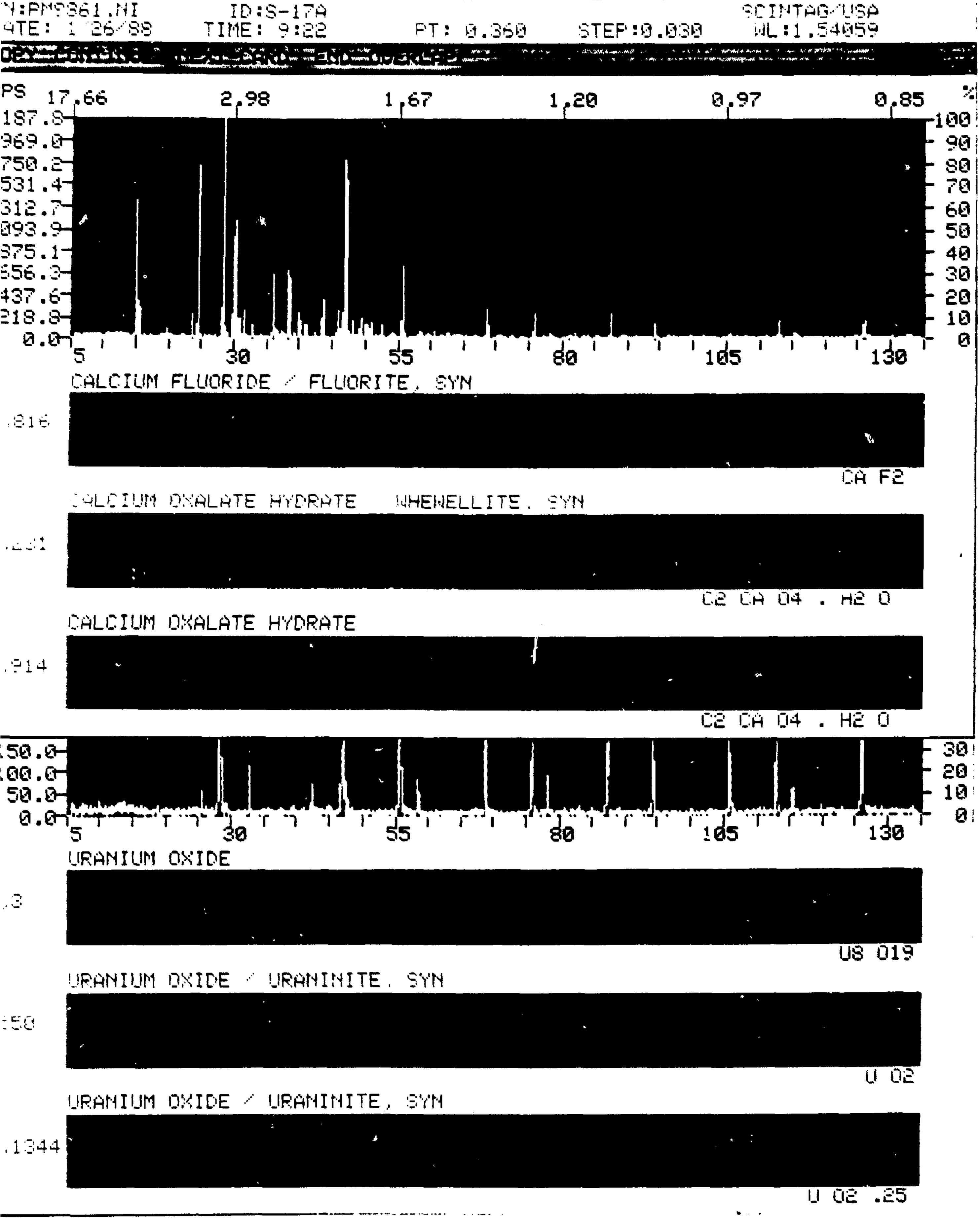

FIGURE 1. X-ray diffraction pattern of the residue from the ammonium oxalate extraction

Figure 2

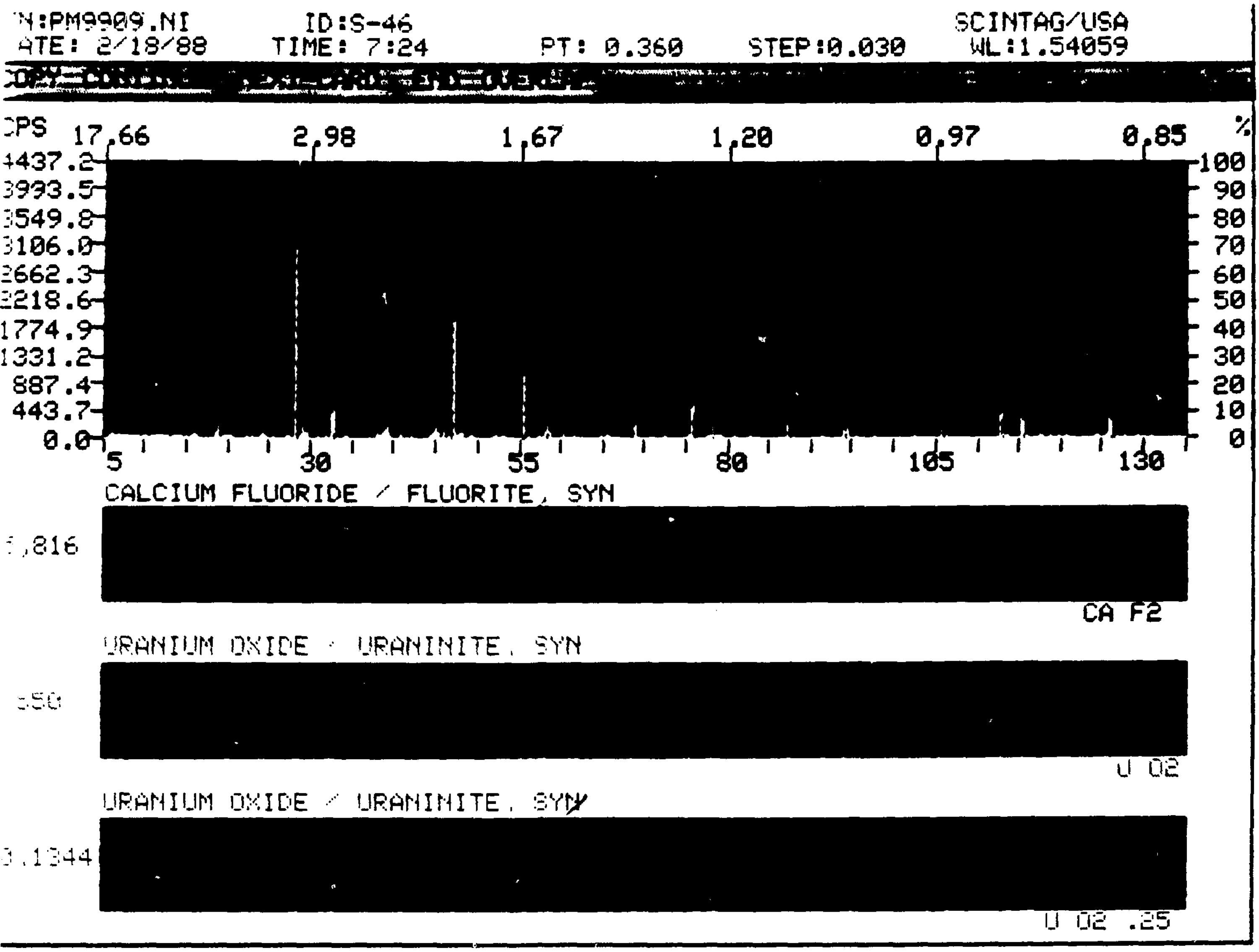

FIGURE 2. X-ray diffraction pattern of the residue from the $Na_2EDTA-H_3BO_3$ extraction

Table 1. Results from the Analysis of Synthetic Mixtures

Synthetic Mixtures (mg)				mgU/g measured as		Total U found	Actual U added	
CaF_2	LiF	U as UF_4	U as U_3O_8	U_3O_8	UF_4	mgU/g	mgU	% Total U Recovered
STD-1								
600.6	199.4	151.2	0	.1	-	.1	0	-
600.6	199.4	151.2	0	-	152.5	152.4	151.2	100.8
STD-2								
500.2	286.0	151.7	16.6	16.0	-	16.1	16.6	97.0
500.2	286.0	151.7	16.6	-	152.7	153.6	151.7	101.2
STD-3								
642.5	100.9	191.4	8.56	8.10	-	8.15	8.56	95.2
642.5	100.9	191.4	8.56	-	192.6	193.7	191.4	101.2
STD-4								
516.8	396.7	58.5	4.24	4.15	-	4.13	4.24	97.4
516.8	396.7	58.5	4.24	-	59.0	58.7	58.5	100.3
STD-5								
240.8	601.2	117.9	4.2	4.4	-	4.4	4.2	104.8
240.8	601.2	117.9	4.2	-	122.8	123.1	117.9	104.4
STD-6								
808.7	328.3	303.3	12.7	7.7	-	11.9	12.7	93.7
808.7	328.3	303.3	12.7	-	198.2	307.6	303.3	101.4

Table 2. Results from the Triplicate Analysis of a Single Process Sample

		Mg U/g			
	Sample Wt.	Extract	Residue	Mg UF_4/g	Mg UO_2/g
S-67-A	.5024 g	138.30	15.30	182.46	18.04
S-67-B	.5065	138.29	15.32	182.44	18.07
S-67C	.5443	138.07	15.40	182.16	18.16

The values of this method are that it is simple, time efficient, makes use of existing procedures, the measurements of UO_2 and UF_4 are made on the same aliquot, the UO_2 is determined as a measure of uranium virtually free of interferences, and the method has high precision at low concentrations (10 mg or less).

CALCULATIONS

$$\text{MgU/g} = \frac{1/W_1 * W_2}{W_3} * W_4 * F$$

where: W_1 = original sample weight
W_2 = solution weight
W_3 = aliquot weight
W_4 = grams of $K_2Cr_2O_7$ used
F = $K_2Cr_2O_7$ Factor (mgU/g)

Note: The $K_2Cr_2O_7$ factor is the ratio of mg uranium to g of $K_2Cr_2O_7$ and is determined by titrating a standard uranium solution with the $K_2Cr_2O_7$ to be used.

Mg-UF_4/g = MgU/g * 1.3193

Mg-UO_2/g = Mg U/g * 1.1344

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