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# Initial Development of a Method to Measure Carbon by Thermogravimetric Analysis-Mass Spectrometry

**M. L. Crowder**

October 2014

SRNL-STI-2013-00057, Revision 0



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M.L. Crowder

October 2014

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## EXECUTIVE SUMMARY

During HB-Line flowsheet development efforts at the Savannah River National Laboratory (SRNL), plutonium oxide ( $\text{PuO}_2$ ) samples were produced using different precipitation and calcination conditions. To evaluate a potential cost savings for future analyses, this study measured the carbon (C) content of ten SRNL  $\text{PuO}_2$  samples by two different methods: the accepted method of a carbon/sulfur (C/S) analyzer and a potential method of thermogravimetric analysis-mass spectrometry (TGA-MS). Though  $\text{PuO}_2$  produced by HB-Line was not used in this study, the AFS-2  $\text{PuO}_2$  campaign is currently using TGA-MS for moisture analysis. Thus, using the same TGA-MS analysis for C could potentially provide a cost savings.

During heating of  $\text{PuO}_2$  within the TGA, a sample's C is released and detected within the MS as carbon dioxide ( $\text{CO}_2$ ) at its molecular mass of 44. An important observation in this study was that heating samples in the TGA to approximately 1010 °C yielded MS peaks that indicated a small portion of the C may not have been volatilized from the sample. However, extending the TGA heating to 1040 °C appeared to complete the volatilization of C in the samples. Thus, future evaluations of the C by TGA-MS method must include heating samples to  $\geq 1040$  °C to ensure all C reaches the MS, where it is quantified.

For all samples tested, measurements by both methods showed C contents below 500  $\mu\text{g/g}$  Pu, which is below the standard AFS-2 purity specification<sup>1</sup> of 1000  $\mu\text{g/g}$ . Measurements of C by TGA-MS showed values within 20% of the C/S analyzer values for four of the ten samples tested, lower by 25-32% for an additional three samples, and lower by 60-70% for the remaining three samples. For samples where the methods differed by more than 20%, the TGA-MS values were lower than the C/S analyzer values. Prior to analysis, the TGA-MS samples were quickly sealed in vials, had minimal exposure to ambient air, and the samples were analyzed within two weeks of being produced by calcination. In contrast, the C/S analyzer samples were not sealed up as quickly, were stored 8-11 weeks before analysis, and were opened and closed for sub-sampling the day before analysis. Thus, the higher C contents observed by the C/S analyzer may have been due in part to additional adsorption of  $\text{CO}_2$  onto the surface of the  $\text{PuO}_2$  during handling, storage, and sub-sampling. Measurements of C by TGA-MS showed that exposures to ambient air of three hours or longer always yielded an increase in the C content of the  $\text{PuO}_2$  sample. This increase is attributed to adsorption of  $\text{CO}_2$  from ambient air.

SRNL recommends that HB-Line consider having the C methods compared again using sub-samples from a larger batch of  $\text{PuO}_2$  or possibly of  $\text{CeO}_2$ . Alternatively, samples from early AFS-2 production batches could be evaluated for C content by both TGA-MS and by the C/S analyzer. Whichever sample types are used to evaluate these methods, it is important that the samples for the different instruments be handled and stored in similar ways and that the samples be analyzed in the same time frame to keep the exposure to ambient air similar for the sample portions. The follow-up work to develop the C by TGA-MS method must also evaluate uncertainty and compare it to that of the C/S analyzer.

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## LIST OF ABBREVIATIONS

AFS-2	Alternate Feed Stock 2
CO	carbon monoxide
CO <sub>2</sub>	carbon dioxide
C/S	carbon/sulfur
IR	infrared
MFFF	MOX Fuel Fabrication Facility
MOX	Mixed Oxide
SO <sub>2</sub>	sulfur dioxide
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
TGA-MS	thermogravimetric analysis-mass spectrometry

## 1.0 Introduction

At the Savannah River Site (SRS), H Canyon and HB-Line expect to process plutonium into a purified plutonium dioxide ( $\text{PuO}_2$ ) feed for the MOX Fuel Fabrication Facility (MFFF). This production campaign, termed AFS-2 (Alternate Feed Stock 2), will yield  $\text{PuO}_2$  that must be thoroughly characterized for physical properties and chemical (impurity) contents. Characterization methods will include moisture determination by thermogravimetric analysis-mass spectrometry (TGA-MS), and carbon determination by combustion-infrared absorption spectrometry using a commercial carbon/sulfur (C/S) analyzer. Because TGA-MS results include moisture released during heating as well as carbon dioxide released during heating, this report documents the efforts to date to evaluate TGA-MS as a method to measure carbon in  $\text{PuO}_2$  samples while also making moisture determinations. A formal request for this evaluation was provided by HB-Line Engineering.<sup>2</sup>

The samples evaluated in this report were purified  $\text{PuO}_2$  samples produced from a variety of Pu(IV) oxalate precipitation and calcination conditions as part of AFS-2 development activities.<sup>3</sup> For perspective, the standard specification limit<sup>1</sup> for C content in AFS-2 oxide is 1000  $\mu\text{g/g}$  Pu, and the desired specification limit<sup>4</sup> for AFS-2 oxide is 500  $\mu\text{g C/g Pu}$ .

## 2.0 Experimental Procedure

### 2.1 Moisture Determination by TGA-MS

At the Savannah River National Laboratory (SRNL), moisture content in actinide oxides is typically measured by TGA-MS. Specifically, samples are heated to 1000 °C at 15 °C per minute in a contained Netzsch STA 409 PC Luxx thermogravimetric analyzer. The TGA is purged with argon and the TGA off-gas passes through a heated (180 °C) transfer tube, which contains a sample port where a portion of the gas stream is pulled continuously by high vacuum into the MS and analyzed.

For more than six years, SRNL has used calcium sulfate dihydrate ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), i.e., gypsum, as the standard material to calibrate the TGA-MS for moisture. In this study, SRNL employed calcium oxalate hydrate ( $\text{CaC}_2\text{O}_4 \cdot x\text{H}_2\text{O}$ ) to calibrate the TGA-MS for  $\text{CO}_2$ . A recent memorandum<sup>5</sup> describes this calibration approach and includes the  $\text{CO}_2$  calibration line used for TGA-MS results in this report.

### 2.2 Carbon Measurement by Carbon Analyzer

Since FY07, SRNL has measured the carbon and sulfur contents of actinide oxides by using a contained LECO CS-230 Carbon/Sulfur Determinator. Analysis is accomplished by combining a known sample mass combined with accelerator material (tungsten, tin, and iron chips) in a ceramic crucible and combusting the mixture in a stream of purified oxygen (99.5%) by means of an induction furnace contained within the instrument cabinet. The carbon in the sample is oxidized primarily to carbon dioxide ( $\text{CO}_2$ ) with some carbon monoxide (CO) possibly being produced. The sulfur is oxidized to sulfur dioxide ( $\text{SO}_2$ ) and sample gases are swept into the carrier stream. Sulfur is measured as  $\text{SO}_2$  in the first IR cell. Any CO produced is converted to  $\text{CO}_2$  in the catalytic heater assembly, while  $\text{SO}_2$  is converted to sulfur trioxide ( $\text{SO}_3$ ), which is removed from the system in a cellulose filter. Carbon is measured as  $\text{CO}_2$  in a second IR cell, and the  $\text{CO}_2$  and oxygen carrier gas are exhausted to the glovebox.

### 3.0 Results

During AFS-2 developmental studies,<sup>3,6</sup> TGA-MS results for various  $\text{PuO}_2$  samples showed a consistent pattern, with most of the  $\text{CO}_2$  volatilized at low temperature along with water, and a smaller portion of  $\text{CO}_2$  volatilized at temperatures near 800 °C. Examples are shown in Figures 3-1 and 3-2.

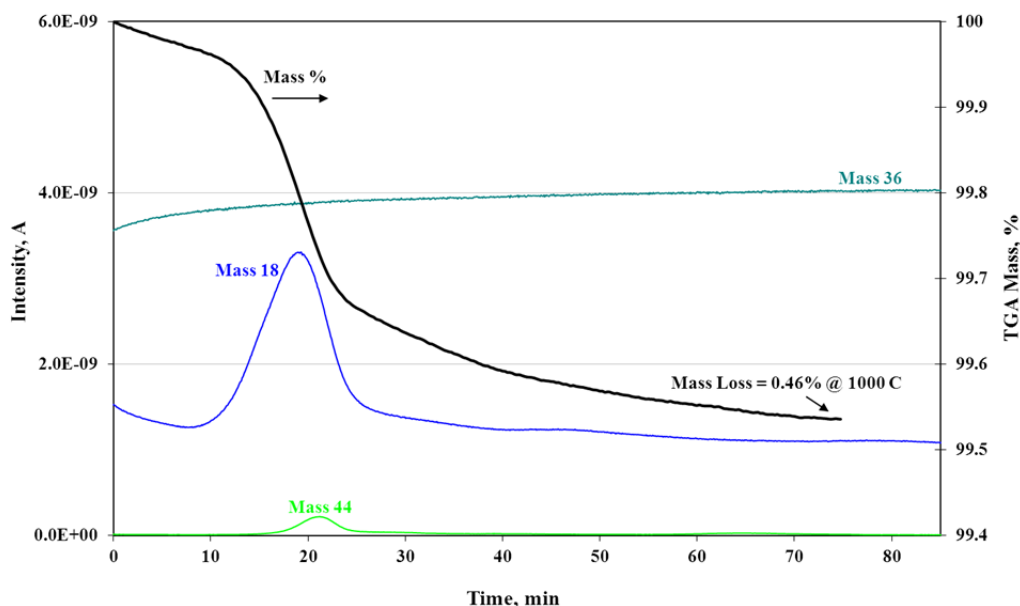


Figure 3-1. MS Signals (linear scale) from TGA-MS Analysis of Sample D30-Ba

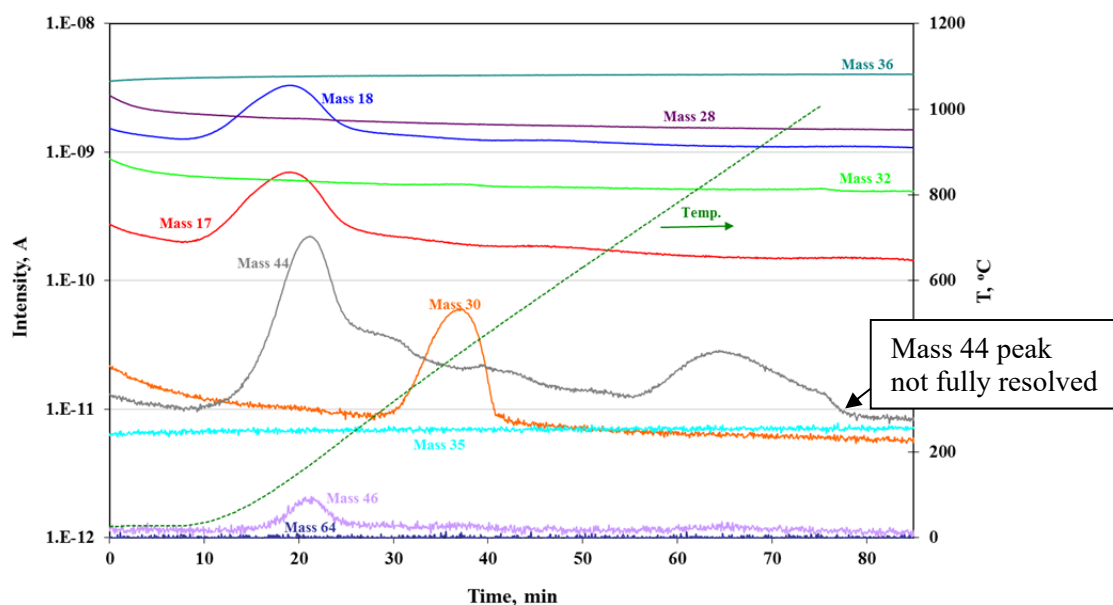
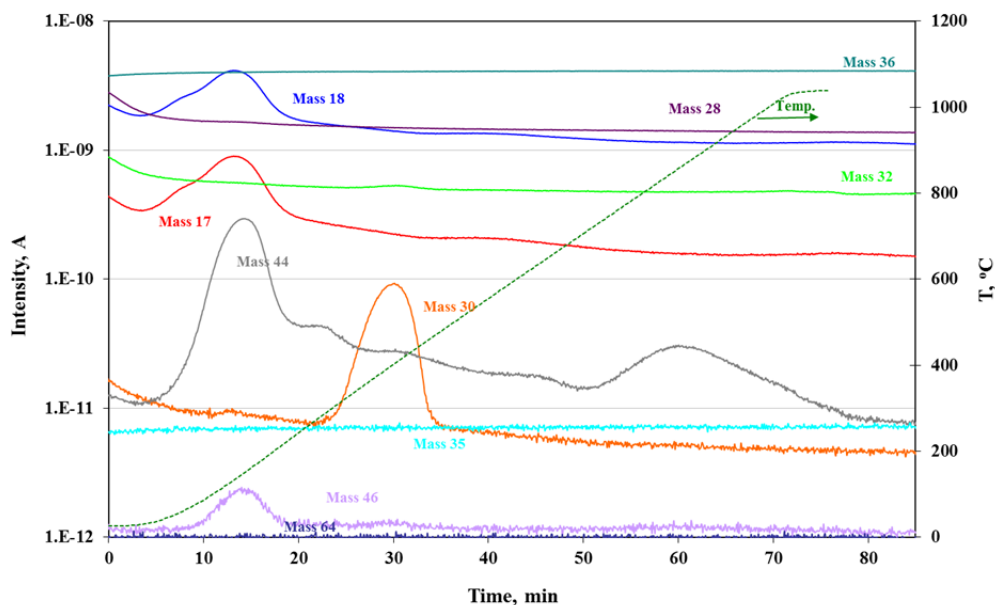


Figure 3-2. MS Signals (logarithmic scale) from TGA-MS Analysis of Sample D30-Ba

In this study, the first 15 TGA-MS samples were evaluated with the sample temperature profile, which involved an initial five-minute isothermal portion followed by a heating rate of 15 °C per minute up to 1000 °C. Since TGA operations involve programming the furnace temperature, not the sample temperature, the effective maximum temperature for these 15 samples was 1007-1010 °C. For all 15 of these samples, the shapes of the MS curves for water and CO<sub>2</sub> were similar. However, inspection of these MS signals showed that evolution of CO<sub>2</sub> was not complete at the end of the heating cycle, as shown in Figure 3-2. To test the hypothesis that not all C was being released from the sample, the TGA heating program was adjusted to involve an additional five minutes of heating that yielding maximum sample temperatures of ~1040 °C. A result using this heating program is shown in Figure 3-3.



**Figure 3-3. MS Signals (logarithmic scale) from TGA-MS Analysis of Sample D15-Aa**

The continuous shape of the Mass 44 signal in Figure 3-3 provided evidence that heating above 1010 °C was required to obtain complete evolution of CO<sub>2</sub> from the sample. Therefore, the last four samples in this study were heated to ~1040 °C to cause a more complete release of C above 1000 °C. Additional examples of MS results are provided in the Appendix, with three samples heated to ~1010 °C and three heated to ~1040 °C. In each case, for samples heated to ~1010 °C (Figures A-1 through A-3), the Mass 44 signal appears discontinuous. But for samples heated to ~1040 °C (Figures A-3 through A-6), the Mass 44 signal appears continuous and the evolution of CO<sub>2</sub> appears complete.

### 3.1 Carbon Content by TGA-MS

For the AFS-2 developmental study in which many batches of PuO<sub>2</sub> were produced at different processing conditions,<sup>3</sup> the carbon contents of these samples as measured by TGA-MS are shown in Table 3-1. In that study, the samples were sealed quickly after calcination and were analyzed by TGA-MS within two weeks of calcination. For simplicity, the exposure time to ambient air for initial TGA-MS samples is approximated as 0.5 h. For these TGA-MS analyses, many of the samples were split to allow an initial analysis of half the sample material and a subsequent analysis of the remaining sample portion after exposure to ambient air (with the vial lid off) for at

least 3 h. For sample B4-2, the TGA-MS sample was divided into three portions with different exposure times. As shown in Table 3-1, the C content of initial TGA-MS samples ranged from 140 to 260  $\mu\text{g/g}$  Pu. Notably, each time a sample portion was exposed to ambient air for at least 3 h, the C content increased.

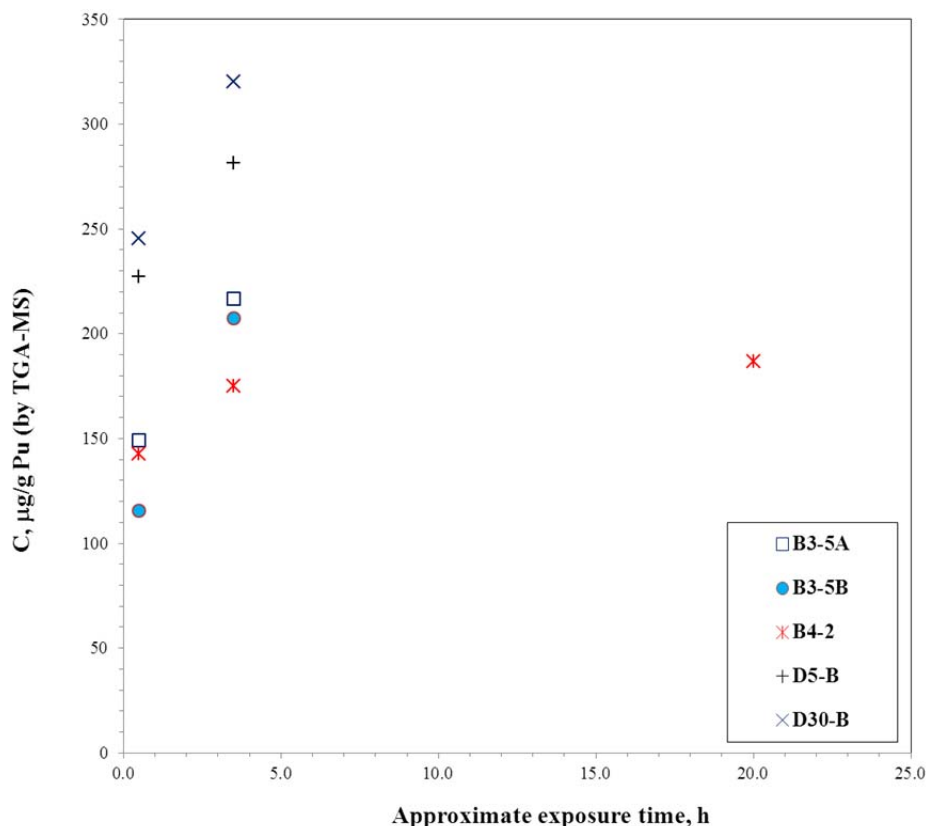
**Table 3-1. Carbon by TGA-MS.**

AFS-2 Sample	C by TGA-MS	Ambient Air Exposure Time	Average Rate of Increase in C (after initial analysis)
	$\mu\text{g/g}$ Pu*	h	$\mu\text{g/g}$ Pu/h
B3-5Aa	149	~0.5	22
B3-5Ab	217	3.5	
B3-5Ba	115	~0.5	31
B3-5Bb	207	3.5	
B4-1a	149	~0.5	12
B4-1b	199	4.5	
B4-2a	143	~0.5	11
B4-2b	175	3.5	
B4-2c	187	20	2
D5-A	307	~0.5	--
D5-Ba	227	~0.5	18
D5-Bb	282	3.5	
D30-A	179	~0.5	--
D30-Ba	245	~0.5	25
D30 Bb	320	3.5	
D15-Aa <sup>†</sup>	226	~0.5	2
D15-Ab <sup>†</sup>	357	66.5	
D15-Ba <sup>†</sup>	248	~0.5	7
D15-Bb <sup>†</sup>	368	16.5	

\*Based on estimated assay of 0.87 g Pu/g PuO<sub>2</sub>.

<sup>†</sup> Sample heated to ~1040 °C instead of ~1010 °C used for other samples.

The increase in C content due to ambient air exposure is illustrated in Figure 3-3. To make Figure 3-3 clearer by reducing the number of points at the same values, samples that did not have a three-hour exposure were not included. For each sample, a clear increase in C content is shown after a three-hour exposure. For sample B4-2, an additional exposure totaling 20 h showed a further increase in C. However, the rate of increase in C content slowed significantly after the first three-hour exposure.



**Figure 3-4. Carbon content by TGA-MS as a function of exposure time to ambient air.**

### 3.2 Carbon Content by C/S Analyzer

Results for the C content of the same samples, as measured by the C/S analyzer, are shown in Table 3-2. For this study, the small batch sizes led to limited sample mass for the C/S analyzer, so that only duplicate 0.25-g sample portions were analyzed, instead of the typical triplicate sample portions. In five of ten samples, the duplicate C contents were within 10% of one another and for two of the samples, the duplicates were within 20%. The C contents as measured by C/S analyzer ranged from 190 to 480 µg/g Pu.

**Table 3-2. Carbon by Carbon/Sulfur Analyzer**

AFS-2 Sample	C by C/S Analyzer μg/g sample	% difference	C by C/S Analyzer μg/g Pu* (Average)
B3-5A	350 320	9	385
B3-5B	260 270	4	305
B4-1	410 430	5	483
B4-2	160 170	6	190
D5-A	240 210	13	259
D5-B	160 200	22	207
D30-A	310 150	70	264
D30-B	190 200	5	224
D15-A	220 250	13	270
D15-B	240 340	34	333

\*Based on estimated assay of 0.87 g Pu/g PuO<sub>2</sub>.

### 3.3 Comparison of Analytical Methods for C

Results of C content as measured by both TGA-MS (initial, unexposed sample only) and by C/S analyzer are shown in Table 3-3. For the first three samples in the table, the C content measured by TGA-MS was 60-70% lower than that measured by C/S analyzer. For the remaining samples, four samples showed TGA-MS values within 20% of the C/S analyzer value, and the remaining three samples showed C contents in which the TGA-MS values were 25 to 32% lower than the C/S analyzer values.

**Table 3-3. Comparison of Carbon by TGA-MS and by C/S Analyzer**

AFS-2 Sample	Specific Surface Area m <sup>2</sup> /g	TGA-MS C μg/g Pu* (Initial Sample)	C/S Analyzer C μg/g Pu* (Average)	% change from C/S Analyzer value
B3-5A	6.8	149	385	-61
B3-5B	7.3	115	305	-62
B4-1	6.9	149	483	-69
B4-2	5.2	143	190	-25
D5-A	8.1	307	259	18
D5-B	7.5	227	207	10
D30-A	5.3	179	264	-32
D30-B	9.0	245	224	10
D15-A <sup>†</sup>	7.2	226	270	-16
D15-B <sup>†</sup>	9.7	248	333	-25

\*Based on estimated assay of 0.87 g Pu/g PuO<sub>2</sub>.

<sup>†</sup> Samples heated to ~1040 °C instead of ~1010 °C used for other samples.



## 4.0 Discussion

As shown in Figures 3-2 and 3-3, as well as in the Appendix, review of MS results for the first 15 samples in this study raised a concern that heating samples to  $\sim 1010$  °C likely does not completely volatilize the C in these samples. Increasing the heating time by five minutes and the maximum sample temperature to  $\sim 1040$  °C appeared to resolve the high-temperature Mass 44 peak, thereby yielding a more complete result for carbon content. Therefore, though TGA-MS moisture measurements only require heating samples to 1000 °C, measuring carbon in the same analysis would require slightly modifying the TGA heating profile to at least 1040 °C to ensure a more complete release of C and a more defensible value for carbon content.

A significant observation concerning the data in Table 3-1 is that ambient air exposures of three hours and greater always resulted in an increase in the carbon content of the samples. While it is well known that  $\text{PuO}_2$  adsorbs atmospheric moisture,<sup>7</sup> the affinity of  $\text{PuO}_2$  to absorb atmospheric  $\text{CO}_2$  is also well-established. A key study<sup>8</sup> of  $\text{CO}_2$  adsorption onto  $\text{PuO}_2$  found a very fast initial adsorption rate followed by very slow adsorption. It appears that in the present study, the 8-11 weeks of sample storage for the C/S analyzer samples likely allowed a slow, but appreciable level of  $\text{CO}_2$  adsorption onto the  $\text{PuO}_2$  surface.

The data in Table 3-3 show that the C determinations by TGA-MS and by the C/S analyzer did not consistently deliver similar results. For seven of the ten samples, the TGA-MS values were within 32% of the C/S analyzer values, but for three samples, the TGA-MS values were 60-70 % lower than the C/S values. In all cases where the TGA-MS values differed by more than 20% from the C/S analyzer values, the TGA-MS values were lower than the C/S analyzer values.

The knowledge that exposure to ambient air leads to  $\text{CO}_2$  adsorption and increased carbon content, and the observation that C/S analyzer results for C were generally higher than those of TGA-MS leads one to consider if the C/S analyzer samples were exposed to air for significantly longer times than the TGA-MS samples. During initial sampling, the TGA-MS samples were generally taken and sealed first, since moisture adsorption by  $\text{PuO}_2$  is well-known and concern existed as to whether or not the samples would satisfy the limit of  $<0.50$  wt % moisture. Additional sampling occurred for other analyses, including carbon, though the sampling efforts involved tens of minutes of exposure to ambient air, not hours. After sampling, the TGA-MS samples were analyzed within two weeks of calcination. The C/S analyzer tests for all samples, however, occurred on the same day, which was 8 – 11 weeks after calcination, i.e., 11 weeks for the samples at the top of Table 3-1 and 8 weeks for samples at the bottom of Table 3-1, as the samples are listed in the order in which they were generated. The C/S analyzer samples were opened the day before analysis and split into 0.25-g portions and re-sealed, and this involved an additional exposure to ambient air. Therefore, it is not clear whether the C/S analyzer generally showed higher C contents because the analysis method provides a more complete measure of the C present, or if the extended storage and longer ambient air exposures contributed to the higher C contents observed in most of the C/S analyzer samples. Notably, Table 3-3 shows that these samples all had specific surface areas in the range of 5-10  $\text{m}^2/\text{g}$ . Thus, the  $\text{PuO}_2$  surfaces had similar propensities for adsorption of  $\text{CO}_2$  (and moisture) from ambient air.

Though these methods did not consistently show the same C content for the samples tested, the C content for all samples is quite low, and is less than the MOX Feed specification for higher purity materials. For perspective on how much C is associated with these samples, consider that the Earth's atmosphere contains nominally 390 ppm  $\text{CO}_2$ . The highest C content observed in this study, 483  $\mu\text{g/g}$  Pu, equates to 105  $\mu\text{g}$  C in a 0.25 g sample, yet the volume of air containing 105  $\mu\text{g}$  C is only 0.54 L. Certainly, the adsorption of  $\text{CO}_2$  onto the  $\text{PuO}_2$  surface is a complex

process involving equilibrium and kinetics factors. But in light of the very low C content of these samples, the different handling and storage histories of the samples may have contributed significantly to the different C contents observed by the two methods.

Once production of AFS-2 PuO<sub>2</sub> in HB-Line begins, it is expected that samples for moisture and carbon will be obtained in a similar time frame, shipped together, stored in a similar manner, and analyzed in a similar time frame. Such samples would provide a better way to compare these two methods of measuring the C in these types of samples. Alternatively, sample portions of a larger batch of PuO<sub>2</sub> or of a similar material, such as cerium oxide (CeO<sub>2</sub>), could be split in a controlled manner, stored in the same manner, and analyzed in a similar time frame by both methods. Use of a larger batch of material would allow analysis of a sufficient number of replicates to better evaluate the uncertainties of the methods.

## 5.0 Conclusions

For all samples tested, measurements by both methods showed C contents below 500 µg/g Pu, which is below the standard AFS-2 purity specification<sup>1</sup> of 1000 µg/g. Measurements of C by TGA-MS showed values within 20% of the C/S analyzer values for four of the ten samples tested, lower by 25-32% for an additional three samples, and lower by 60-70% for the remaining three samples. For samples where the methods differed by more than 20%, the TGA-MS values were lower than the C/S analyzer values. Prior to analysis, the TGA-MS samples were quickly sealed in vials, had minimal exposure to ambient air, and the samples were analyzed within two weeks of being produced by calcination. In contrast, the C/S analyzer samples were not sealed up as quickly, were stored 8-11 weeks before analysis, and were opened and closed for sub-sampling the day before analysis. Thus, the higher C contents observed by the C/S analyzer may have been due in part to additional adsorption of CO<sub>2</sub> onto the surface of the PuO<sub>2</sub> during handling, storage, and sub-sampling. Measurements of C by TGA-MS showed that exposures to ambient air of three hours or longer always yielded an increase in the C content of the PuO<sub>2</sub> sample. This increase is attributed to adsorption of CO<sub>2</sub> from ambient air. In addition, to ensure a more complete release of C from this sample matrix, TGA heating profiles must be adjusted to cause sample temperatures to exceed 1040 °C.

## 6.0 Recommendations

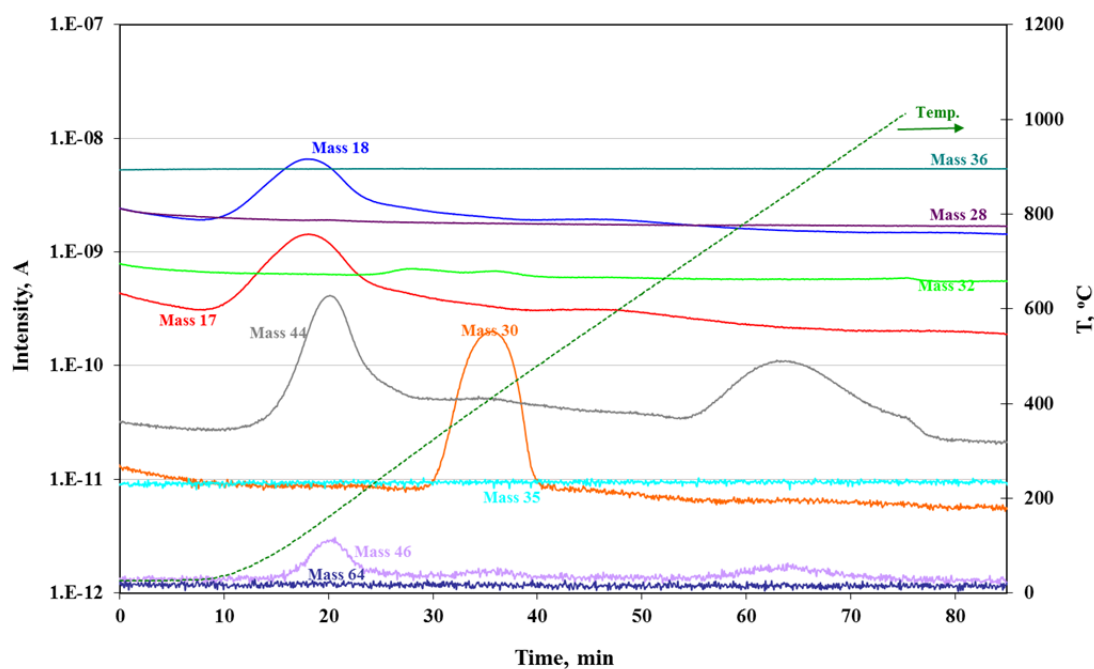
SRNL recommends that HB-Line consider having the C methods compared again using sub-samples from a larger batch of PuO<sub>2</sub> or possibly of CeO<sub>2</sub>. Alternatively, samples from early AFS-2 production batches could be evaluated for C content by both TGA-MS and by the C/S analyzer. Whichever sample types are used to evaluate these methods, it is important that the samples for the different instruments be handled and stored in similar ways and that the samples be analyzed in the same time frame, to keep the exposure to ambient air similar for the sample portions. The follow-up work to develop the C by TGA-MS method must also evaluate uncertainty and compare it to that of the C/S analyzer.

## 7.0 References

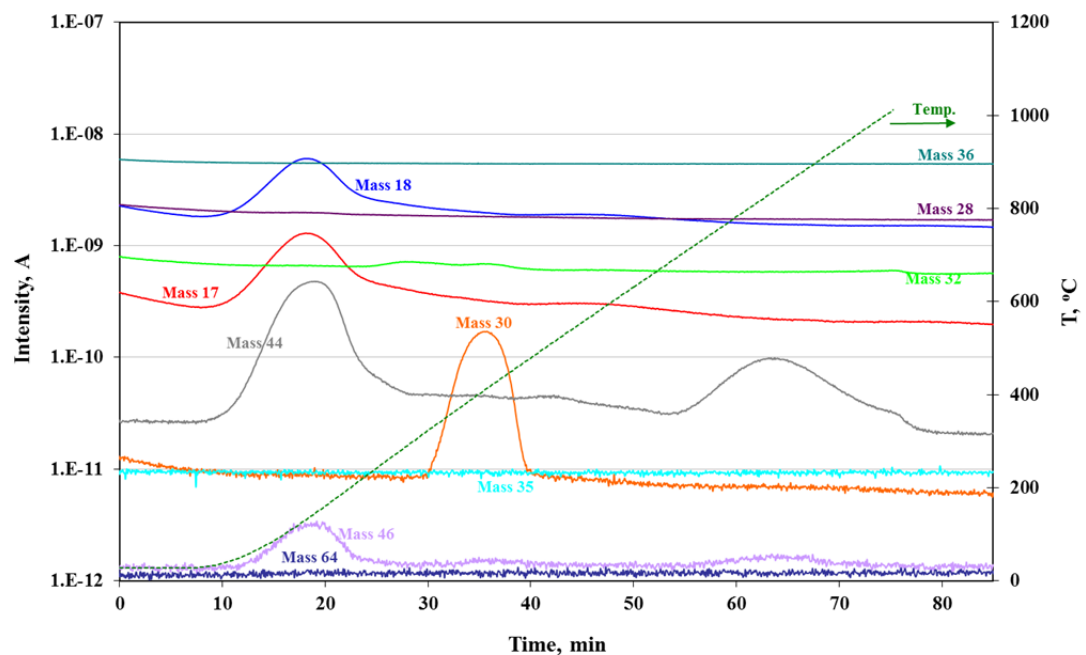
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- <sup>6</sup> Crowder, M.L., and R.A. Pierce, “Lab-Scale Demonstration of Plutonium Purification by Anion Exchange, Plutonium(IV) Oxalate Precipitation, and Calcination to Plutonium Oxide to Support the MOX Feed Mission”, SRNL-STI-2012-00422, Rev. 0, August 2012.
- <sup>7</sup> Stakebake, J.L., “The Storage Behavior of Plutonium Metal, Alloys, and Oxide”, *J. Nucl. Materials* 38, 241-259, (1971).
- <sup>8</sup> Colmenares, C.A., and K. Terada, “The Adsorption of Carbon Dioxide on Uranium and Plutonium Oxides”, *J. Nucl. Materials* 58, 336-356 (1975).

## Appendix A



**Figure A-1. MS Signals (logarithmic scale) from TGA-MS Analysis of Sample B3-5Aa**



**Figure A-2. MS Signals (logarithmic scale) from TGA-MS Analysis of Sample B3-5Ab**

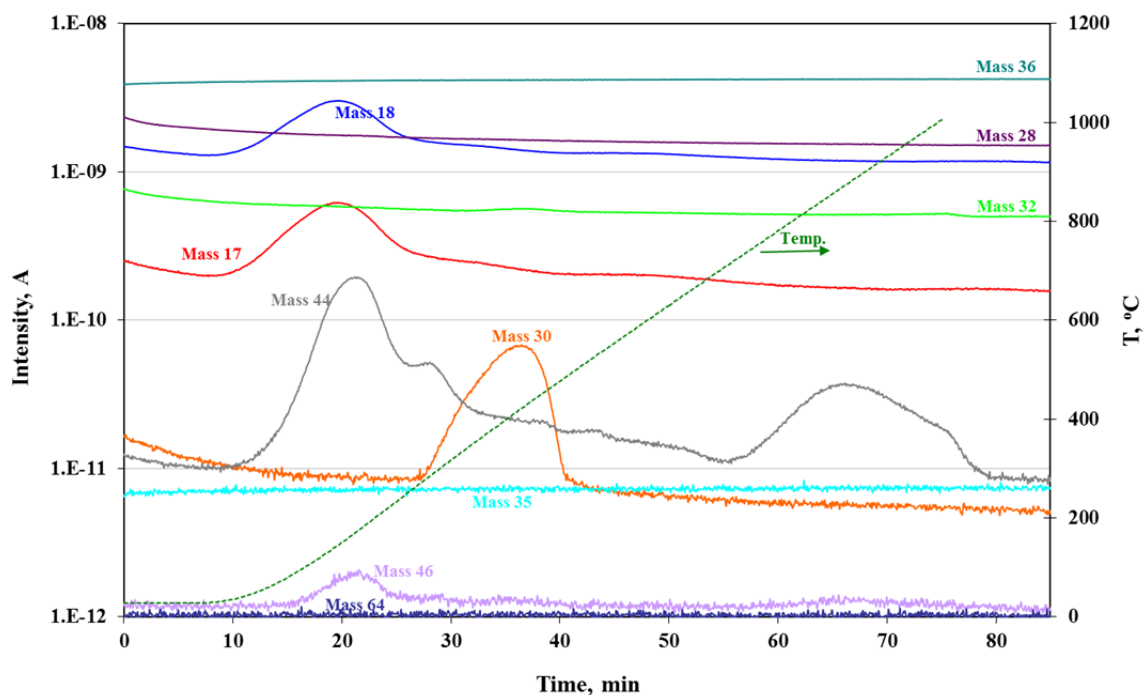


Figure A-3. MS Signals (logarithmic scale) from TGA-MS Analysis of Sample D30-A

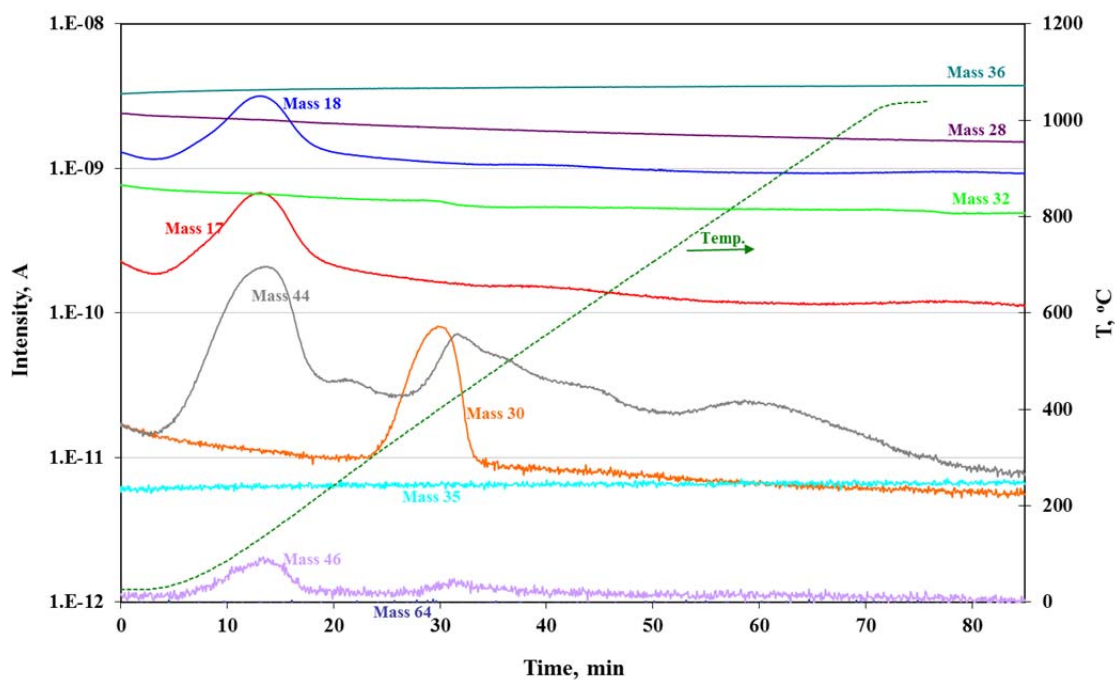


Figure A-4. MS Signals (logarithmic scale) from TGA-MS Analysis of Sample D15-Ab

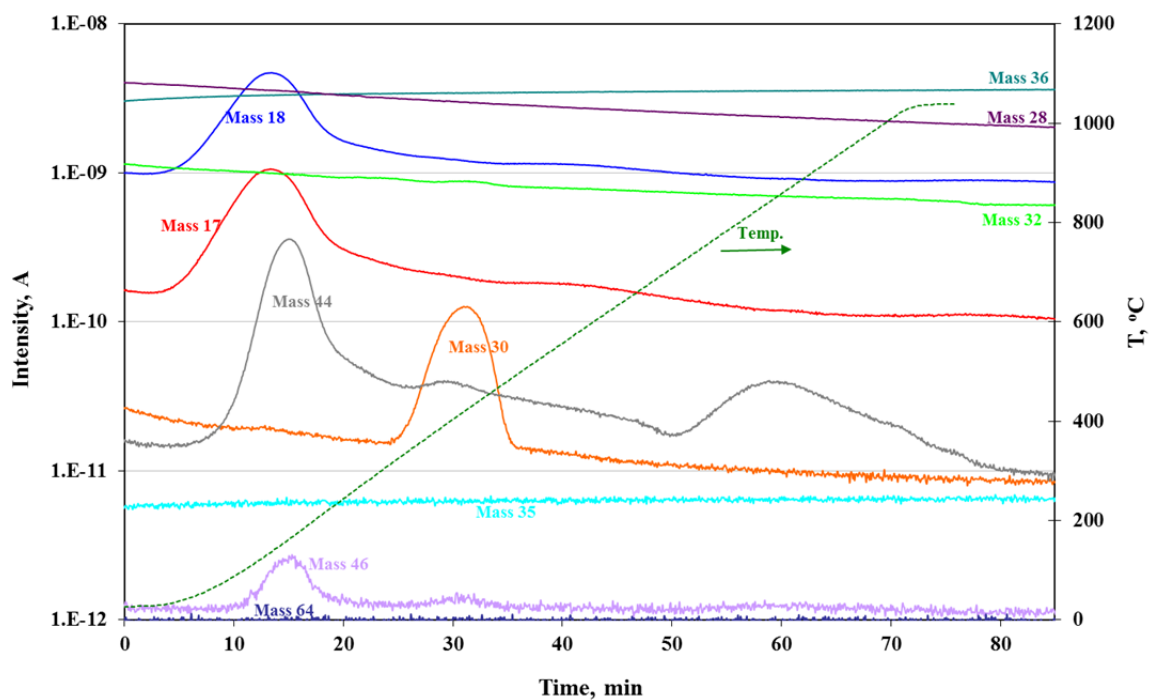


Figure A-5. MS Signals (logarithmic scale) from TGA-MS Analysis of Sample D15-Ba

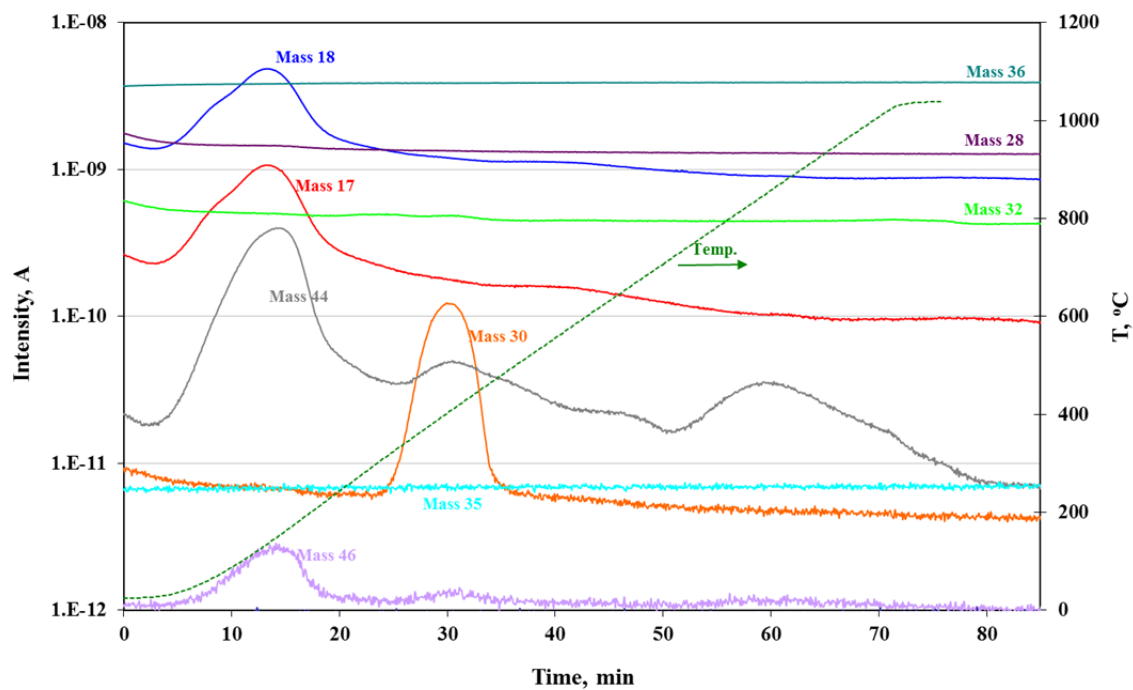


Figure A-6. MS Signals (logarithmic scale) from TGA-MS Analysis of Sample D15-Bb

**Distribution:**

T. B. Brown, 773-A  
D. H. McGuire, 999-W  
A. P. Fellingner, 773-41A  
S. D. Fink, 773-A  
E. N. Hoffman, 999-W  
S. L. Marra, 773-A  
F. M. Pennebaker, 773-42A  
W. R. Wilmarth, 773-A  
P.R. Jackson, 703-46A  
Records Administration (EDWS)  
C. Wilson, 773-A  
J. M. Duffey, 773-A  
P. M. Almond, 773-43A  
D. R. Best, 773-A  
F. F. Fondeur, 773-A

J. B. Schaade, 704-2H  
T. E. Worth, 703-H  
K. P. Burrows, 704-2H  
K. D. Scaggs, 704-2H  
S. J. Hensel, 705-K  
J. E. Therrell, 704-2H  
J. M. Jordan, 704-2H  
J. L. Varble, 704-2H  
K. E. Cheeks, 772-F  
W. L. Melton, 772-F  
R. F. Gilmore, 772-F  
M. J. Phillips, 772-F