LA-UR-98-994

Materials Identification and Surveillance Project Item Evaluation

Item: Impure Plutonium Oxide (ARF-102-85-295)

Los Alamos
NATIONAL LABORATORY

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MATERIALS IDENTIFICATION AND SURVEILLANCE PROJECT ITEM EVALUATION

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by

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ABSTRACT

In this report, we characterize properties relevant to storage of an impure plutonium oxide (26.59 mass % plutonium) in accordance with the Department of Energy (DOE) standard DOE-STD-3013-96.

Methods used to characterize the oxide include mass loss-on-calcination (LOC) measurements, mass loss-on-ignition (LOI) measurements, elemental analysis, plutonium isotopic analysis, particle analyses measurements, x-ray powder diffraction, thermal-desorption mass-spectrometry, and gas analyses. Methods used to characterize the container include x-ray radiography and photography.

Loss-on-ignition values are high due to the presence of high concentrations of chloride and stay relatively constant as the calcining temperature is increased. The material does not satisfy DOE-STD-3013-96 criteria for plutonium content and LOI.

1.0 INTRODUCTION

The requirements for extended storage of oxides containing >50 mass % plutonium are described in the Department of Energy (DOE) standard DOE-STD-3013-96.[1] Although procedures[2] are found to be valid for pure PuO_2 in accordance with this standard, questions remain for applying these methods to impure materials. This particular impure plutonium oxide item ARF-102-85-295 has 26.59 mass % plutonium and does not satisfy the criterion for plutonium content (>50 mass % plutonium). Within the DOE complex there is a large inventory of impure plutonium oxides of varying concentrations of different impurities awaiting stabilization and storage.

The objective of this study is to continue our experimental effort to characterize impure plutonium oxides and to develop preparation methods that convert these materials into forms suitable for storage.

2.0 EXPERIMENTAL METHODS

2.1 Materials

The material ARF-102-85-295 was canned for shipment at Rocky Flats about 1985 and shipped shortly thereafter. Hanford processed much of this type oxide in the mid 1980s. To support dissolution processing, some items such as this one were sampled for analysis, then returned to the vault.

Table I shows the characterization data sent from Hanford site.

Table I. Characterization Data Sent from Hanford Site for the Impure Oxide ARF-102-85-295.

Date Processed	1985
Gross weight (g)	1035.5
Net Weight (g)	635
LOI (wt.%)	<1.0
Calorimetry Date	25 June 1996
Power (watts)	0.4215

2.2 Procedures

Photography and Radiography

The canister was photographed at three different orientations, 0, 120 and 240 degrees. Also the top and bottom of the can were photographed. The photograph of the canister at 0 degrees can be seen in Fig. 1. Next the canister was radiographed, also at three different orientations, 0, 120 and 240 degrees. The radiograph of the canister at 0 degrees can be seen in Fig. 2. The radiographs suggested clumps or chunks of material but we were uncertain what form the material was really in. When the can was opened and the material was examined it became clear what we were seeing in the radiographs. The material was placed on the slip top can lid and photographed, Fig. 3. A 22-g piece of this material was calcined to determine its performance when heated in the calcining furnace. During the calcining run the furnace door was opened and the piece photographed. The temperatures in red indicate the temperature of the furnace when the photograph was taken. The last photograph is after the piece was heated at 950ºC for two hours and then cooled to room temperature, see Fig. 4.

Gas sampling and analysis

For gas sampling the puncture device was epoxied to the top of the can, see Fig. 1 of the previous report.[3] The sampling port was mated to the storage can using an O-ring and epoxy seal, which allows for a leak-tight connection to the punch assembly and volume-calibrated pressure-vacuum system (PVS). Two type-K thermocouples were also attached to the can. The can, sampling port assembly, and two gas sample vials are connected to the PVS, and the PVS is evacuated and flushed at least three times with high-purity helium gas. After the final flush, the PVS was evacuated to a pressure $5.0 \text{ X } 10^{-6}$ torr and this evacuation was monitored on a residual gas analyzer (RGA). After the helium was pumped off, a rate-of-rise leak test is performed. The leak rate is acceptable if no argon gas is detected after 5 min under static vacuum and the pressure rise in the PVS system does not exceed 5.0 millitorr. All leaks were corrected before proceeding. The gas sample vials were valved out of the system and the PVS was isolated from the vacuum pump. The punch was unlocked and the can lid punctured. The punch was then retracted and locked in its starting (volume calibrated) position. The pressure was allowed to equilibrate between the can and the PVS. The equilibrium pressure and can temperature were recorded. The

Fig. 1. Photograph of the canister at 0 degrees.

Fig. 2. Radiograph of the canister at 0 degrees.

Fig. 3. ARF-actinide material on the slip top can lid.

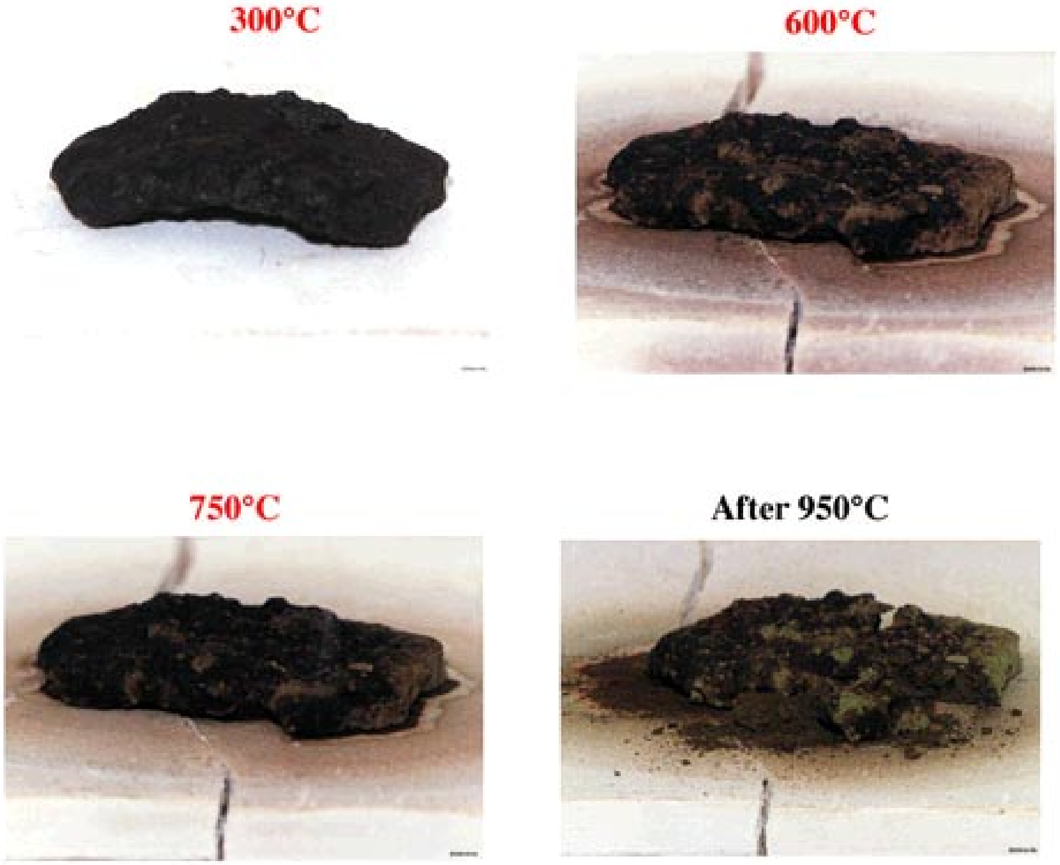


Fig. 4. **Photos of the material while the furnace was at 300ºC, 600ºC, 775ºC and after the piece was heated at 950ºC for 2h and then cooled to room temperature.**

initial can pressure was calculated based on the expanded equilibrium pressure, the can temperature, and the free volume of the food-pack can. The free volume of the food-pack can was calculated from measurements taken from radiographs of the can. A gas sample was captured in each of the two gas sample vials for future analysis, and the remaining gas in the PVS was analyzed using the RGA. The can puncturing, gas sampling and disassembly process has also been described in summary with photos in a previous report[4]. Next the can was removed from the PVS and opened, and the internal surfaces of the can were visually inspected and photographed. In nested configurations the outer surfaces of the nested can are also photographed. In cases where the nested can is another food-pack can, the puncturing process is repeated. The cycle is stopped when the inner can contains the oxide. Next the convenience container was opened and the temperature of the contents was measured in five places. The plutonium oxide was weighed on a material accountability and safeguards system (MASS) certified balance for accountability purposes. A 30-g sample of the material was then removed from the parent lot. Ten grams were used for thermal desorption mass spectrometry (TDMS), 10 g for long term storage experiments, and 10 grams held as an archive sample. The remainder of the item was sent for calcination and further tests. The experimental procedures used to measure loss on calcination, loss on ignition (LOI), specific surface area, and particle parameters are described in previous Los Alamos reports.[2,5,6,7]

The item was split into two portions, ARF102-295 remained as chunks, and ARF102-295A was rod-milled to powder. The sequence of sampling and testing is presented in Fig. 5. After samples were taken from the as-received material, (sample S), a portion of the powder was calcined at 600°C to produce sample S′. After samples were taken from the 600°C calcined powder, all of the remaining powder was calcined at 950°C to produce sample S″.

X-ray Diffraction Analysis

Samples were removed from ARF102-295 and ARF102-295A portions. From ARF102-295, sample ARF-3 was the as received material, ARF-5 was fired at 650°C, ARF-9 was fired at 900°C. From ARF102-295A, sample ARF-3a was the as received material, ARF-8 was fired at 650°C and ARF-13 was fired at 900°C. The samples were stored in screw-capped vials which were placed in an air-filled (approx. 40 % relative humidity) glovebox. The ARF samples were examined by x-ray powder diffraction using a SCINTAG XDS-2000 diffractometer. The samples were prepared for x-ray diffraction by

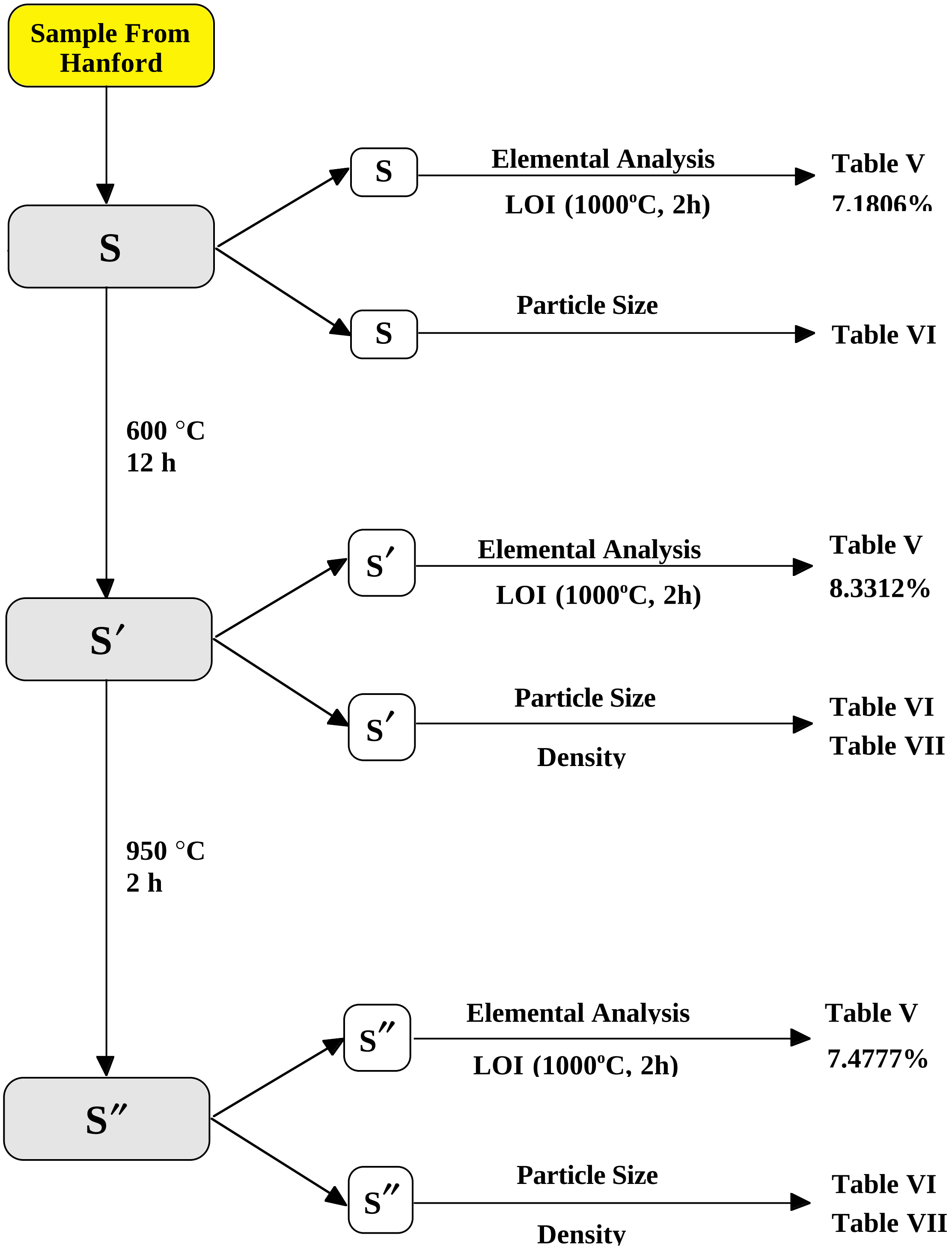


Fig. 5. Characterization of the impure plutonium oxide ARF-102-85-295.

light grinding with an Al_2O_3 mortar and pestle. A portion of the sample, approximately 50 milligrams, was then loaded on to strip of double-sided tape which was mounted on an epoxy cylinder 1.25 in diameter and 1.25 in tall. The sample and cylinder were then wrapped with plastic film, checked for contamination and then placed into a specially designed sample holder, which is mounted on to the goniometer. The correct sample height with respect to the detector-tube zero point plane was set with an external standard. Each sample was exposed to nickel filtered copper radiation; the x-ray tube settings were 45 kilovolts and 40 milliamps. A 0.05 degree beam slit, medium Soller slits, and a 0.02 degree detector slit was used. Diffraction data were collected from 25 to 135 degrees in two theta; the scan time was 6 h.

Thermal Gravimetric/Differential Thermal Analysis

The same samples were analyzed with a Rheometrics model PL-STA 2000 TGA/DSC with provided thermal gravimetric and differential thermal analysis (TGA/DTA) over a given temperature regime. The samples were consistently handled in the following way. Each sample was exposed to room air for a maximum of 15 min while that sample was weighed and then loaded into the apparatus. The samples were held in an alumina crucible. Once the sample was in the apparatus, the sample chamber, whose volume is approximately 15 cm^2, was flushed with oil-free bottled air. The flow rate was 15 ml/ min; the sample chamber was purged for 3 min before the experiment was started.

Once the sample chamber was purged, a temperature program was initiated. This program sets the temperature to 25^oC for a three minute isotherm and then ramp the temperature to 1000^oC at a rate of 10^oC /min. During this temperature ramp, the mass of the sample was monitored at a rate of one datum point per second. The experiment concluded when the temperature reached 1000^oC. These conditions were selected to closely model the LOI experiments.

3.0 RESULTS AND DISCUSSION

Before the first calcination, 48.2266 g of S in chunks form was set in a glovebox. After 2 days of exposure to the glovebox atmosphere, the weight of S increased by 0.003 mass %. For the as-received milled powder weight gain on water uptake was 108.3984 final, less 108.3908 initial or 0.0076 g or 0.007% over seven days. These results are shown in Table II. It is interesting to notice that all different powders S, S′, and S″ show very similar affinity for water. The values in Table II are most likely values for equilibrium loading of water. As we have seen before[5], for the impure plutonium dioxide ATL27960 calcined at 950°C for 2 h, one day was enough for equilibrium to be established.

Table II. Water Uptake Adsorption Measurements for the Impure Oxide ARF-102-85-295

Time & Amount of Water	Powder S[a]		Powder S′[b]		Powder S″[c]	
	Powder	**Chunks**	**Powder**	**Chunks**	**Powder**	**Chunks**
Time (days)	7	2	-	5	2	2
Mass (%)	0.007	0.003	-	0.002	0.000	0.001

[a] Powder S is the as-received material from Hanford.
[b] Powder S′ is obtained after impure oxide S is calcined at 600°C for 12 h.
[c] Powder S″ is obtained after impure oxide S′ is calcined at 950°C for 2 h.

Each time the powder was calcined, the percent mass loss was measured. During the second calcination step the percent mass loss was much more than the percent mass loss during the first calcination step. The results are shown below in Table III.

Table III. Percent Mass Loss During Calcination of Sample ARF-102-85-295

Calcination Temperature (°C)	Heating Time (h)	Mass Loss (%) Powder	Mass Loss (%) Chunks
600	12	0.41	0.21
950	2	28.82	31.14

Table IV shows that LOI values are very high and they stay about the same regardless of thermal treatment. This can be explained on the fact that this material is high in chloride. The reported Hanford-LOI value is <1.0 mass %. This very low LOI value is understood because the LOI test was done only at 600°C instead at 1000°C. This impure oxide does not conform to the DOE-STD-3013-96[1] LOI requirement of <0.5 mass % loss tested at 1000°C for 2 h, even after treatment at 950 °C.

Table IV. LOI Analyses Results of the Impure Oxide ARF-102-85-295

LOI Conditions	LOI for S[a] (mass %)		LOI for S′[b] (mass %)		LOI for S″[c] (mass %)	
	Powder	**Chunks**	**Powder**	**Chunks**	**Powder**	**Chunks**
1000°C for 2 h	7.1806	11.8452	8.3312	9.6495	7.4777	9.9484

[a] Impure oxide as-received.
[b] Impure oxide, S, was calcined at 600°C for 12 h to yield S′.
[c] Impure oxide, S′, was calcined at 950°C for 2 h to yield S″.

Table V shows the results for the elements analyzed. Carbon concentration decreased after calcination. Chloride concentration decreased slightly after the 600°C calcining step and substantially after the 950°C calcining step. The low chloride concentration for the sample calcined at 950°C is consistent with the LOI values as a function of LOI temperature conditions. Plutonium concentration slightly decreased after the 600°C calcining step and substantially increased after the 950°C calcination. Obviously, this large increase in plutonium concentration is due to the loss of chloride salts. The net amount of plutonium is understood to remain constant.

Table V. Elemental Analysis of As-Received Powder S[a] and Calcined Powders S′[b] and S″[c]

Element	Powder S (μg/g)	Powder S′ (μg/g)	Powder S″ (μg/g)
Plutonium	265900	263500	394800
Chloride	<204000	181000	77000
Carbon	3600	70	200

[a] Impure oxide as-received.
[b] Impure oxide, S, was calcined at 600°C for 12 h to yield S′.
[c] Impure oxide, S′, was calcined at 950°C for 2 h to yield S″.

The specific surface area of ARF-102-85-295 material was not measured.

Particle analysis results for the material in powder form are shown in Table VI.

Table VI. Particle Analysis Results of Precalcined Powder S[a] and Calcined Powders S′[b] and S″[c]

Property	Powder S	Powder S′	Powder S″
Spherical Equivalent Mean (μm)	17.05	18.65	18.5
Diameter-by-Volume Mean (μm)	54.75	66.3	67.65

[a] Impure oxide as-received.
[b] Impure oxide, S, was calcined at 600°C for 12 h to yield S′.
[c] Impure oxide, S′, was calcined at 950°C for 2 h to yield S″.

The tap and bulk density of the as-received oxide was not measured; however they were measured for the materials in powder form calcined at 600°C and 950°C. The values are shown in Table VII.

Table VII. Tap Density and Bulk Density of Calcined Powders S′[a] and S″[b]

Property	Powder S′	Powder S″
Tap Density (g/cc)	4.65	4.16
Bulk Density (g/cc)	5.26	4.76

[a] Impure oxide, S, was calcined at 600°C for 12 h to yield S′.
[b] Impure oxide, S′, was calcined at 950°C for 2 h to yield S″.

The results for the ARF samples of the XRD runs are summarized in Tables 1 through 6 in Appendix 1; in addition the powder patterns for each sample and the phase identification are shown in Fig. 1 through 6, Appendix 1. These results indicate that the samples are composed of PuO_{2-x}, NaCl, KCl, and chromium oxide whose stoichoimetry is not known. The exact composition of each sample could not be calculated because the composition and density of the chromium oxide could not be determined. Tables 1 through 6 contain a listing for each sample of the values for two theta, d, Miller indices, background, peak areas which reflect the intensities of the peaks, and the peak widths. At the end of each listing for a given sample, the table reports the calculated lattice constant for that sample. The lattice constant was calculated by a least squares technique in which the points were weighted by the square root of sine theta. The oxygen to plutonium ratio for each sample was calculated from the lattice constant and the data from Gardner et al.[8] The results of the TGA runs are summarized in Table 7, Appendix 1.

Interpretation of the x-ray diffraction results is complicated by the chemistry of the KCl-NaCl system. KCl and NaCl form a series of solid solutions with a miscibility gap below 500°C; upon melting KCl and NaCl are completely miscible[9]. Therefore the intensities of the KCl and NaCl lines (their amounts) in the heat treated samples depends on the temperature and the cooling rate. This statement is also true of the as received material if that material had been heat treated sometime in its history. Changes in the relative peak intensities of the phases in the ARF samples indicate that the thermal processing removes KCl and NaCl while the concentration of the phase identified as chromium oxide remains essentially unchanged. At 900°C more KCl than NaCl is removed because the vapor pressure of KCl is greater than that of NaCl[10]. The calculated lattice constants of the plutonium oxide also show that thermal processing increases the O/Pu ratio for ARF-3, 5, and 9. Sample ARF-3A, the milled powder, contained “stoichiometric” PuO_2.

The identification of chromium oxide seems questionable. Of all the chromium oxides and other known in the international center for diffraction data (ICDD), the chromium oxide selected fits the best. This oxide has Cr primarily in the +2 oxidation state although some +3 may exist, this is the reason that the composition is unknown. It seems that if CrO is the phase, the heat treatment in air would oxidize the CrO to some extent. The results show that the CrO does not change with heat treatment. This result should be checked against the elemental analysis for the starting materials. Taken together, the TGA/DTA results show that the ARF samples undergo five thermal events; although not all samples undergo all five as summarized in Table TGA/DTA-1. The thermal events between 25 and 200°C could be interpreted as the removal of water in a three stage process. The percent mass loss in the range of 25 to 500°C strongly suggests that samples ARF-9 and 13 and possibly ARF-3 and 3a picked up water during shipment for TGA analysis. The cause of the thermal event at roughly 450°C in ARF-9 and 13 is unknown. The thermal event at approximately 650°C, common to all samples, is interpreted as the melting of the KCl-NaCl. The large mass losses subsequently recorded are due to the vaporization of the KCl and NaCl. The residues that remained after thermal treatment at 900°C could only be removed from the crucible by scrapping. The melting of the salt at 650°C will impact the processing of this material in two ways, (1) the as processed material will not be a free flowing powder, and (2) large quantities of salt will be deposited in the processing equipment.

The gas analysis results for the outer and inner can are shown in Table VIII. Since the outer can was open to the atmosphere it is understandable that the gas analysis is very close to that of the air. The differences are attributed to error in the RGA calibration.

Table VIII. Can Puncturing Results and the Gas Composition for the Outer and Inner Can Gas Phase.

Property	Outer Can	Inner Can	Air
Temperature (°C)	19.9	21.5	
Equilibrium Pressure (Torr)	578.9	475 (584.24)	
Calculated Pressure (Torr)	NA	456.2	
Can Seal	leaking	leaking	
Gas Species (mole %)			
N_2	80.5	97.1	78.08
O_2	18.6	0.0042	20.94
Ar	0.75	0.91	0.934
CO_2	0.043	1.27	0.0314
He	0.0022	0.44	5.24×10^{-4}
H_2	0.0058	0.0054	5.0×10^{-5}
H_2O	0.05	0.02	not listed
CH_4	not present	0.052	not listed
45	not present	0.14	not listed

The 1996 isotopic distribution of plutonium is shown in Table IX.

Table IX. Isotopic Distribution of Plutonium for the "As-received" Powder S.

Isotope	Hanford Analysis	Los Alamos Analysis
Pu-238	0.0077	0.0076
Pu-239	94.1925	94.1808
Pu-240	5.673	5.6858
Pu-241	0.107	0.1069
Pu-242	0.0199	0.0189
Total	100	100

4.0 CONCLUSION

This particular impure plutonium oxide item ARF-102-85-295 has 26.59 mass % plutonium. The very high LOI value is a result of the very high concentration of chloride. The material does not satisfy DOE-STD-3013-96 criteria for plutonium content and LOI.

REFERENCES

1. “Criteria for Preparing and Packaging Plutonium Metals and Oxides for Long-Term Storage,” Department of Energy document DOE-STD-3013-96 (September 1996).
2. J. M. Haschke and T. E. Ricketts “Plutonium Dioxide Storage: Conditions for Preparation and Handling”, Los Alamos National Laboratory Report LA-12999-MS, Los Alamos National Laboratory, Los Alamos, NM, August 1995.
3. Andreas Toupadakis, Thomas Allen, Quentin Appert, Charles Davis, Lynn Foster, David Horrell, Richard Mason, Louis Morales, Michael Ramos, John Telford, and Jeremy Trujillo, “Materials Identification and Surveillance Project Item Evaluation: Impure Plutonium Oxide (PPSL-365),” Los Alamos National Laboratory report LA-UR-97-4436.
4. Thomas Allen, David Horrell, Richard Mason, Luis Morales, and Andreas Toupadakis, “Materials Identification and Surveillance Project Item Evaluation: Impure Plutonium Oxide (HRA905191),” Los Alamos National Laboratory report LA-UR-97-2141 (June 1997). http://lib-www.lanl.gov/la-pubs/00326312.pdf
5. Tom Allen, Quentin Appert, Charles Davis, John Haschke, William Hollis, David Horrell, Aaron Martinez, Richard Mason, Louis Morales, Tom Ricketts, Jim Rubin, Craig Taylor, Andreas Toupadakis, “Materials Identification and Surveillance Project Item Evaluation: Impure Plutonium Oxide ATL27960 and Pure Plutonium Oxide PEOR3258,” Los Alamos National Laboratory report LA-13246-MS (March 1997). http://lib-www.lanl.gov/la-pubs/00326225.pdf
6. Tom Allen, Quentin Appert, Charles Davis, John Haschke, William Hollis, David Horrell, Aaron Martinez, Richard Mason, Louis Morales, Jim Rubin, Craig Taylor, John Telford, Andreas Toupadakis, Jeremy Trujillo, “Materials Identification and Surveillance Project Item Evaluation: Impure Mixture of Plutonium Oxide and Uranium Oxide (PUUOXBCO5),” Los Alamos National Laboratory report LA-13295-MS (June 1997). http://lib-www/la-pubs/00326289.pdf
7. Andreas Toupadakis “Evaluation of the Loss-on-Ignition Measurement for Storage of Legacy Plutonium-Bearing Materials,” Los Alamos National Laboratory report LA-UR-97-3753-Rev.1 (December 1997). http://lib-www.lanl.gov/la-pubs/00326374.pdf

8. E. R. Gardner, T. L. Markin and R. S. Street, J. Inorg. Nucl. Chem., **27**, (1965), 541.
9. D. D. Gohil, T. G. Chart and M. H. Rand, NPL Report DMA (D) 519, March 1986.
10. L. Morales, vapor pressure calculations with JANAF data.

Appendix 1. XRD and TGA results.

Table 1. X-ray Diffraction Results for Sample ARF-3

2-Theta	d(A)	Int	I%	FWHM	Phase-ID	h	k	l
27.322	3.2614	5	4.9	0.214	Halite, syn	1	1	1
28.353	3.1451	102	100.0	0.315	Sylvite, syn	2	0	0
30.087	2.9677	6	5.9	0.360	Cr-O	2	2	0
31.611	2.8280	37	36.3	0.206	Halite, syn	2	0	0
33.139	2.7010	25	24.5	0.417	PuO2	0	0	2
35.507	2.5262	13	12.7	0.308	Cr-O	3	1	1
40.498	2.2256	30	29.4	0.287	Sylvite, syn	2	2	0
43.134	2.0955	5	4.9	0.150	Cr-O	4	0	0
45.400	1.9960	15	14.7	0.241	Halite, syn	2	2	0
47.468	1.9138	20	19.6	0.327	PuO2	0	2	2
50.127	1.8183	5	4.9	0.100	Sylvite, syn	2	2	2
52.704	1.7353	2	2.0	0.067				
56.331	1.6319	28	27.5	0.406	Halite, syn	2	2	2
57.040	1.6133	1	1.0	0.100	Cr-O	5	1	1
58.341	1.5804	5	4.9	0.110				
58.679	1.5721	10	9.8	0.818	Sylvite, syn	4	0	0
59.041	1.5633	8	7.8	0.514	PuO2	2	2	2
62.681	1.4810	7	6.9	0.262	Cr-O	4	4	0
66.320	1.4083	9	8.8	0.338	Sylvite, syn	4	2	0
73.783	1.2832	2	2.0	0.164	Sylvite, syn	4	2	2
75.263	1.2616	6	5.9	0.300	Halite, syn	4	2	0
76.833	1.2396	10	9.8	0.818	PuO2	1	3	3
78.217	1.2211	3	2.9	0.084				
79.133	1.2093	5	4.9	0.409	PuO2	0	2	4
83.584	1.1558	2	2.0	0.078	Halite, syn	4	2	2
88.693	1.1020	5	4.9	0.090	PuO2	2	2	4
89.210	1.0969	5	4.9	0.250				
89.604	1.0931	1	1.0	0.045				
95.314	1.0422	9	8.8	0.506	PuO2	1	1	5
102.891	0.9850	2	2.0	0.069				
108.604	0.9485	2	2.0	0.067	Sylvite, syn	6	2	2
110.358	0.9383	6	5.9	0.089	Halite, syn	6	0	0
115.328	0.9117	3	2.9	0.104	PuO2	1	3	5
118.774	0.8950	1	1.0	0.082				

122.789	0.8774	3	2.9	0.077				
129.102	0.8531	3	2.9	0.245	PuO2	0	2	6

Calculated lattice constant for PuO2: 5.4081(3)

Calculated O/Pu: 1.967

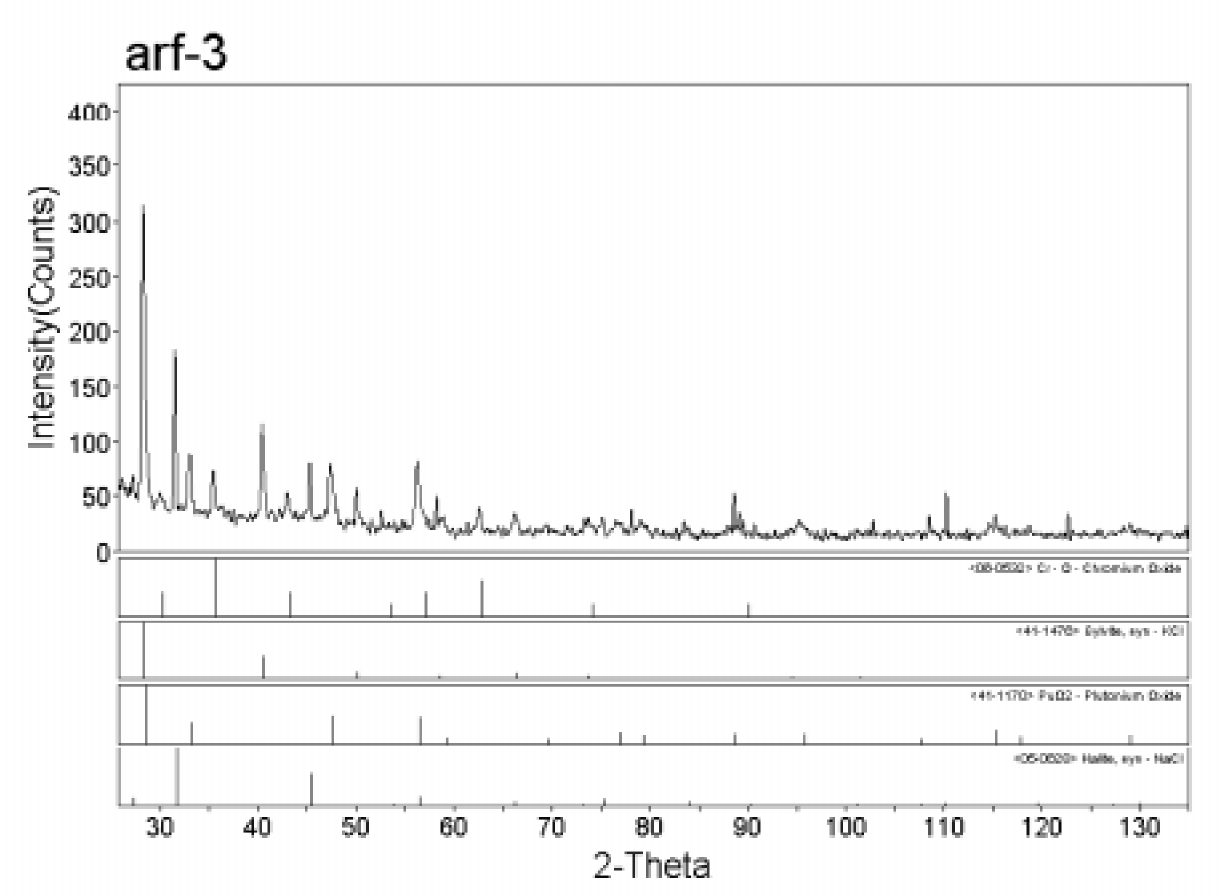
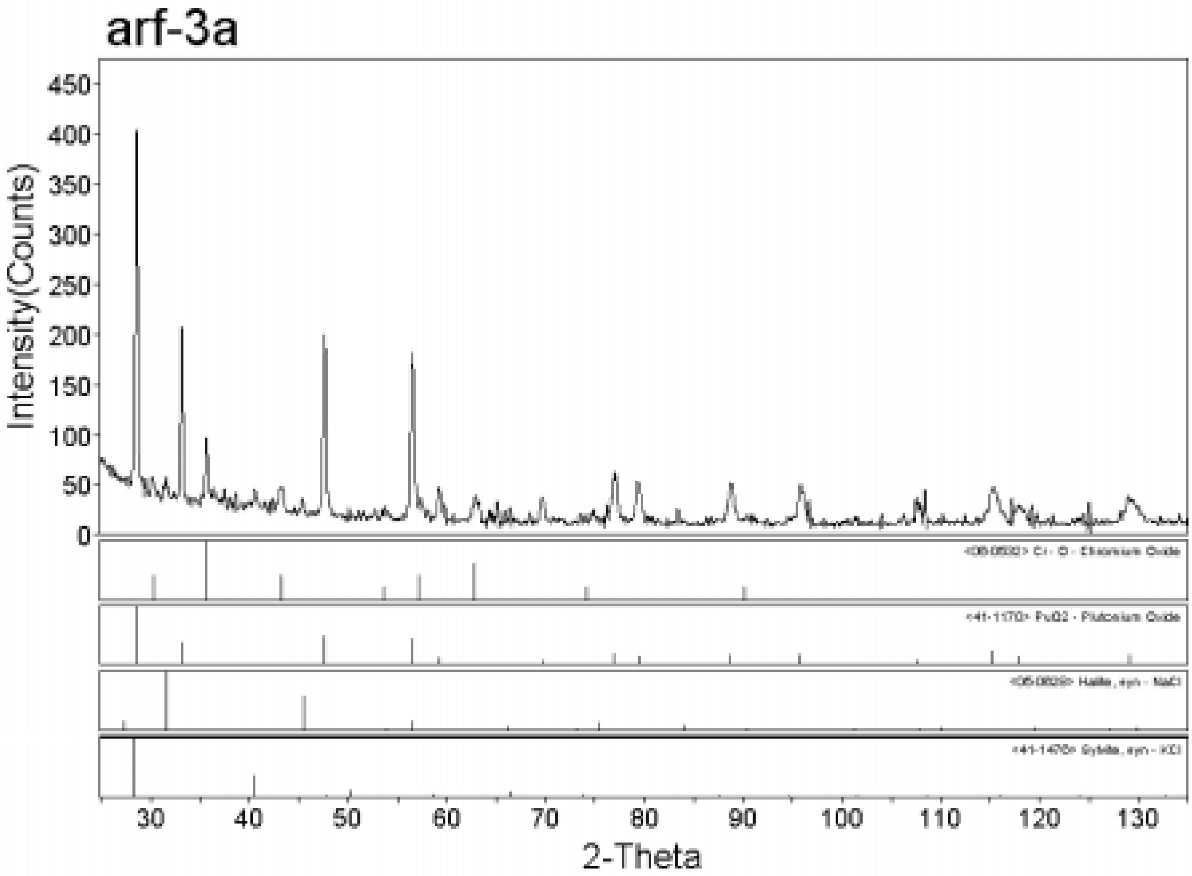


Table 2. X-ray Diffraction Results for Sample ARF-3A

2-Theta	d(A)	Int	I%	FWHM	Phase-ID	h	k	l
28.580	3.1207	107	100.0	0.267	PuO2	1	1	1
30.154	2.9613	5	4.7	0.250	Cr-O	2	2	0
31.600	2.8290	6	5.6	0.235	Halite, syn	2	0	0
33.143	2.7007	46	43.0	0.238	PuO2	0	0	2
35.644	2.5168	17	15.9	0.243	Cr-O	3	1	1
40.512	2.2249	7	6.5	0.332	Sylvite, syn	2	2	0
43.241	2.0906	15	14.0	0.587	Cr-O	4	0	0
45.341	1.9985	5	4.7	0.265	Halite, syn	2	2	0
47.602	1.9087	71	66.4	0.349	PuO2	0	2	2
50.097	1.8193	3	2.8	0.208	Sylvite, syn	2	2	2
53.741	1.7042	7	6.5	0.420	Cr-O	4	2	2
56.483	1.6278	64	59.8	0.360	Halite, syn	2	2	2
57.359	1.6051	12	11.2	0.491	Cr-O	5	1	1
59.190	1.5597	11	10.3	0.291	PuO2	2	2	2
62.885	1.4766	16	15.0	0.514	Cr-O	4	4	0
63.198	1.4701	9	8.4	0.368				
65.071	1.4322	5	4.7	0.196				
66.412	1.4065	3	2.8	0.169	Sylvite, syn	4	2	0
69.590	1.3499	10	9.3	0.333	PuO2	0	0	4
69.816	1.3460	5	4.7	0.225				
76.962	1.2379	33	30.8	0.594	PuO2	1	3	3
79.325	1.2068	22	20.6	0.495	PuO2	0	2	4
88.707	1.1018	21	19.6	0.497	PuO2	2	2	4
95.746	1.0386	14	13.1	0.371	PuO2	1	1	5
107.530	0.9550	5	4.7	0.173	PuO2	0	4	4
108.370	0.9499	5	4.7	0.145	Sylvite, syn	6	2	2
115.358	0.9115	25	23.4	0.776	PuO2	1	3	5
117.185	0.9025	4	3.7	0.171				
119.169	0.8932	2	1.9	0.100				
125.030	0.8683	4	3.7	0.157				
129.000	0.8534	19	17.8	0.658	PuO2	0	2	6

Calculated lattice constant for PuO2: 5.3974(4)
Calculated O/Pu: 1.996


arf-3a
Intensity(Counts)
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400
350
300
250
200
150
100
50
0
<06-0532> Cr - O - Chromium Oxide
<41-1170> PuO2 - Plutonium Oxide
<05-0628> Halite, syn - NaCl
<41-1476> Sylvite, syn - KCl
30
40
50
60
70
80
90
100
110
120
130
2-Theta

Table 3. X-ray Diffraction Results for Sample ARF5

2-Theta	d(A)	Int	I%	FWHM	Phase-ID	h	k	l
27.279	3.2665	3	2.8	0.208	Halite, syn	1	1	1
28.289	3.1522	92	86.0	0.427	Sylvite, syn	2	0	0
28.452	3.1345	107	100.0	0.544	Halite, syn	2	0	0
31.525	2.8355	25	23.4	0.179	Halite, syn	2	0	0
33.067	2.7068	23	21.5	0.287	PuO2	0	0	2
35.638	2.5172	4	3.7	0.327	Cr-O	3	1	1
40.441	2.2286	22	20.6	0.257	Sylvite, syn	2	2	0
45.249	2.0023	10	9.3	0.180	Halite, syn	2	2	0
47.541	1.9110	27	25.2	0.426	PuO2	0	2	2
50.044	1.8211	6	5.6	0.164				
50.280	1.8131	6	5.6	0.169	Sylvite, syn	2	2	2
56.363	1.6310	33	30.8	0.530	Halite, syn	2	2	2
56.797	1.6196	11	10.3	0.330	PuO2	1	1	3
57.180	1.6097	1	0.9	0.100	Cr-O	5	1	1
58.558	1.5750	2	1.9	0.164	Sylvite, syn	4	0	0
59.151	1.5606	2	1.9	0.129	PuO2	2	2	2
66.330	1.4081	10	9.3	0.500	Sylvite, syn	4	2	0
73.807	1.2828	3	2.8	0.193	Sylvite, syn	4	2	2
74.270	1.2759	1	0.9	0.090	Cr-O	5	3	3
74.967	1.2658	3	2.8	0.129				
76.683	1.2417	3	2.8	0.129				
76.984	1.2376	4	3.7	0.144	PuO2	1	3	3
77.957	1.2246	4	3.7	0.129				
80.938	1.1868	3	2.8	0.123				
88.705	1.1019	3	2.8	0.135	PuO2	2	2	4
101.764	0.9928	3	2.8	0.123	Sylvite, syn	6	2	0
104.904	0.9715	4	3.7	0.133				
111.646	0.9311	4	3.7	0.120				
115.076	0.9129	3	2.8	0.123	PuO2	1	3	5
119.189	0.8931	6	5.6	0.164				
133.401	0.8387	5	4.7	0.132				

Calculated lattice constant for PuO2: 5.4016(3)
Calculated O/Pu: 1.985

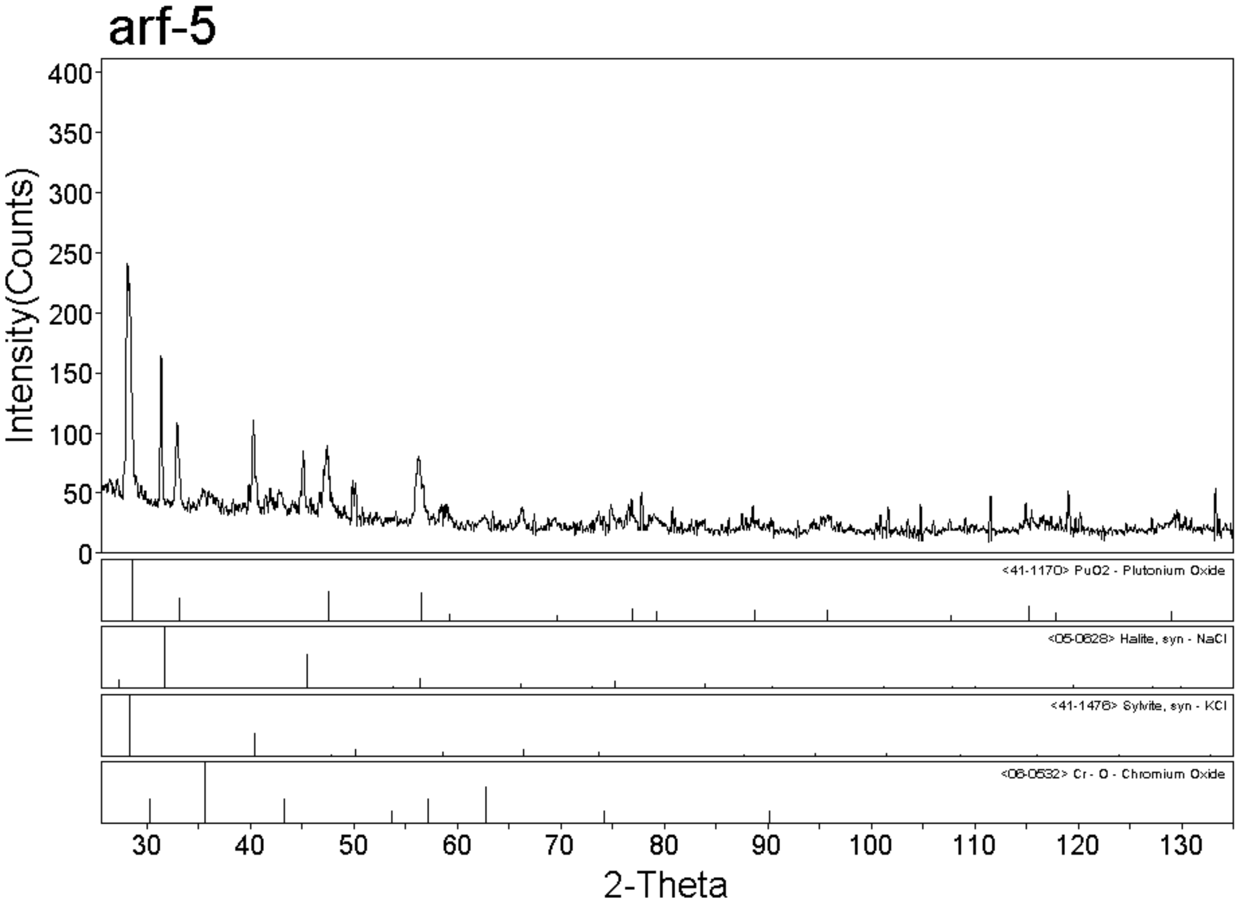

arf-5
Intensity(Counts)
400
350
300
250
200
150
100
50
0
<41-1170> PuO2 - Plutonium Oxide
<05-0628> Halite, syn - NaCl
<41-1476> Sylvite, syn - KCl
<06-0532> Cr - O - Chromium Oxide
30
40
50
60
70
80
90
100
110
120
130
2-Theta

Table 4. X-ray Diffraction Results for Sample ARF8

2-Theta	d(A)	Int	I%	FWHM	Phase-ID	h	k	l
27.322	3.2614	3	2.5	0.093	Halite, syn	1	1	1
28.300	3.1509	95	78.5	0.441	Sylvite, syn	2	0	0
28.495	3.1298	121	100.0	0.500	PuO2	1	1	1
31.560	2.8325	28	23.1	0.176	Halite, syn	2	0	0
33.079	2.7058	29	24.0	0.284	PuO2	0	0	2
35.433	2.5313	6	5.0	0.180	Cr-O	3	1	1
40.467	2.2272	20	16.5	0.222	Sylvite, syn	2	2	0
40.617	2.2194	16	13.2	0.257				
42.852	2.1086	4	3.3	0.150				
43.081	2.0980	11	9.1	0.396	Cr-O	4	0	0
45.270	2.0014	18	14.9	0.198	Halite, syn	2	2	0
47.578	1.9096	52	43.0	0.532	PuO2	0	2	2
50.128	1.8183	5	4.1	0.145	Sylvite, syn	2	2	2
56.399	1.6301	39	32.2	0.444	Halite, syn	2	2	2
56.687	1.6225	23	19.0	0.493	PuO2	1	1	3
59.064	1.5627	5	4.1	0.225	PuO2	2	2	2
62.719	1.4802	9	7.4	0.405	Cr-O	4	4	0
66.290	1.4088	4	3.3	0.133	Halite, syn	4	0	0
74.905	1.2667	6	5.0	0.216				
76.885	1.2389	12	9.9	0.450	PuO2	1	3	3
78.739	1.2143	3	2.5	0.108				
81.030	1.1857	3	2.5	0.100				
86.401	1.1252	2	1.7	0.100				
88.663	1.1023	4	3.3	0.300	PuO2	2	2	4
90.414	1.0854	2	1.7	0.095	Halite, syn	5	1	1
95.845	1.0378	11	9.1	0.900	PuO2	1	1	5
108.919	0.9466	3	2.5	0.123				
112.239	0.9278	2	1.7	0.086				
115.064	0.9130	4	3.3	0.150	PuO2	1	3	5
121.453	0.8830	5	4.1	0.132				
125.409	0.8668	2	1.7	0.082				
129.147	0.8529	3	2.5	0.123	PuO2	0	2	6

Calculated lattice constant for PuO2: 5.3985(4)
Calculated O/Pu: 1.993

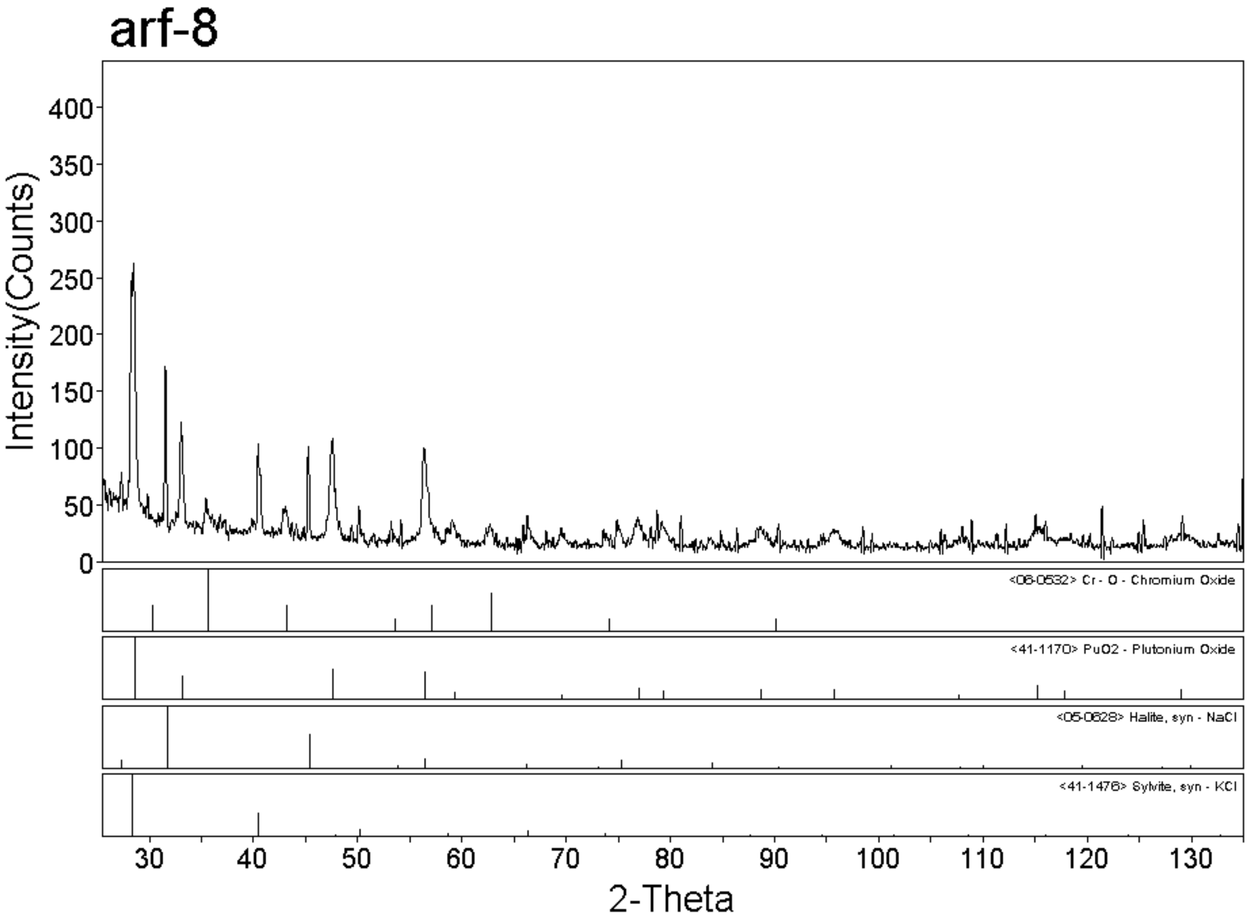

arf-8
Intensity(Counts)
0
50
100
150
200
250
300
350
400
<06-0532> Cr - O - Chromium Oxide
<41-1170> PuO2 - Plutonium Oxide
<05-0628> Halite, syn - NaCl
<41-1476> Sylvite, syn - KCl
30
40
50
60
70
80
90
100
110
120
130
2-Theta

Table 5. X-ray Diffraction Results for Sample ARF9

2-Theta	d(A)	Int	I%	FWHM	Phase-ID	h	k	l
28.541	3.1249	103	100.0	0.255	PuO2	1	1	1
29.888	2.9870	4	3.9	0.129				
30.163	2.9604	5	4.9	0.150	Cr-O	2	2	0
31.524	2.8357	8	7.8	0.157	Halite, syn	2	0	0
33.116	2.7028	41	39.8	0.225	PuO2	0	0	2
35.545	2.5236	23	22.3	0.252	Cr-O	3	1	1
40.534	2.2237	7	6.8	0.286	Sylvite, syn	2	2	0
43.205	2.0922	13	12.6	0.292	Cr-O	4	0	0
47.561	1.9103	51	49.5	0.319	PuO2	0	2	2
56.478	1.6280	51	49.5	0.335	Halite, syn	2	2	2
57.228	1.6084	22	21.4	0.600	Cr-O	5	1	1
58.687	1.5718	3	2.9	0.129	Sylvite, syn	4	0	0
59.188	1.5597	12	11.7	0.318	PuO2	2	2	2
62.441	1.4861	3	2.9	0.135				
62.937	1.4755	13	12.6	0.355	Cr-O	4	4	0
69.556	1.3504	9	8.7	0.261	PuO2	0	0	4
76.921	1.2384	24	23.3	0.502	PuO2	1	3	3
77.131	1.2356	11	10.7	0.291				
78.118	1.2224	2	1.9	0.095				
79.376	1.2062	16	15.5	0.424	PuO2	0	2	4
85.156	1.1385	6	5.8	0.132				
88.650	1.1024	14	13.6	0.371	PuO2	2	2	4
95.873	1.0375	17	16.5	0.546	PuO2	1	1	5
96.147	1.0353	6	5.8	0.257				
99.784	1.0071	2	1.9	0.090				
103.603	0.9802	2	1.9	0.095				
105.016	0.9708	4	3.9	0.129				
107.186	0.9571	2	1.9	0.090				
115.151	0.9125	10	9.7	0.429	PuO2	1	3	5
115.475	0.9109	13	12.6	0.390				
118.121	0.8981	4	3.9	0.157	PuO2	2	4	4
121.106	0.8846	3	2.9	0.129				
126.485	0.8627	3	2.9	0.104				
129.746	0.8508	3	2.9	0.108	Halite, syn	6	2	2

Calculated lattice constant for PuO2: 5.3969(4)
Calculated O/Pu: 1.997

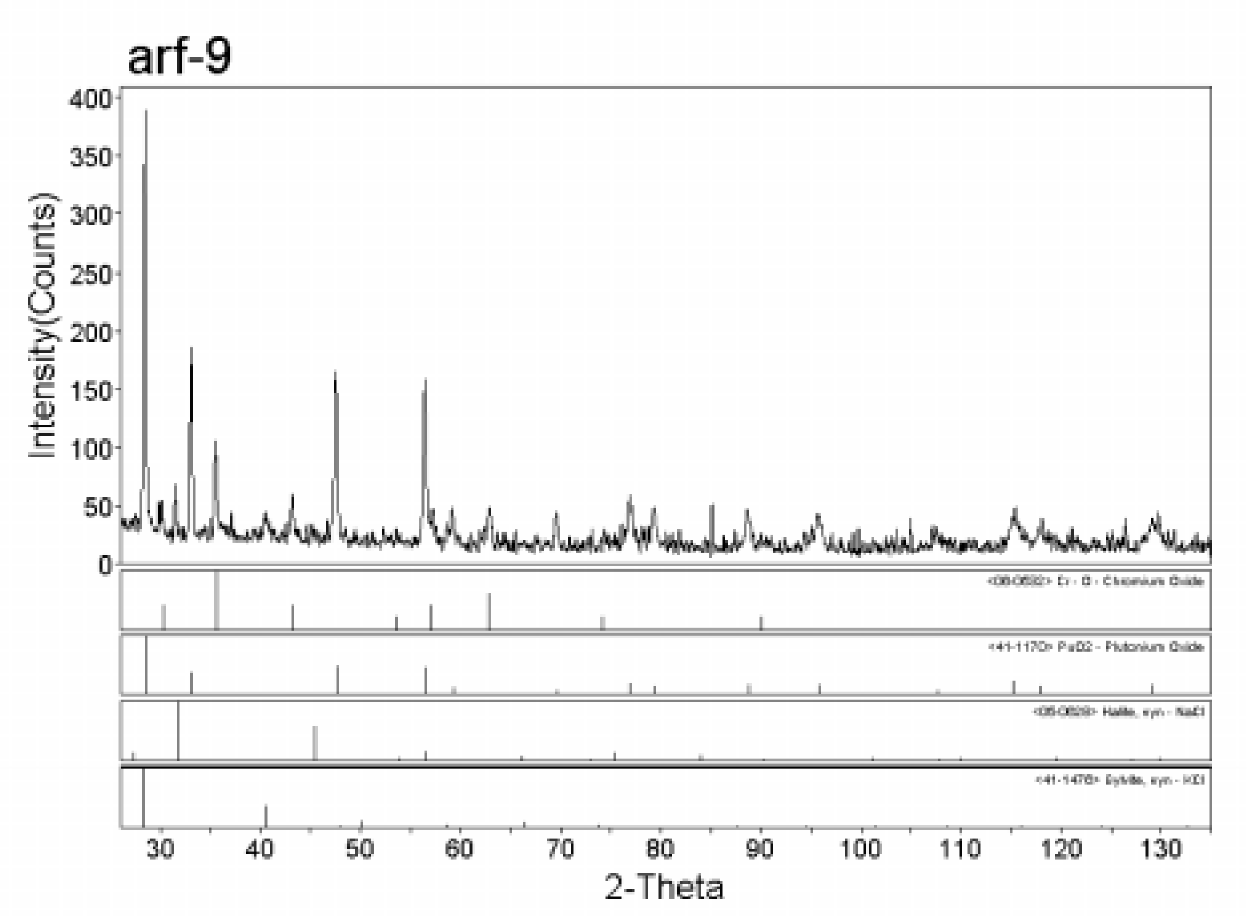
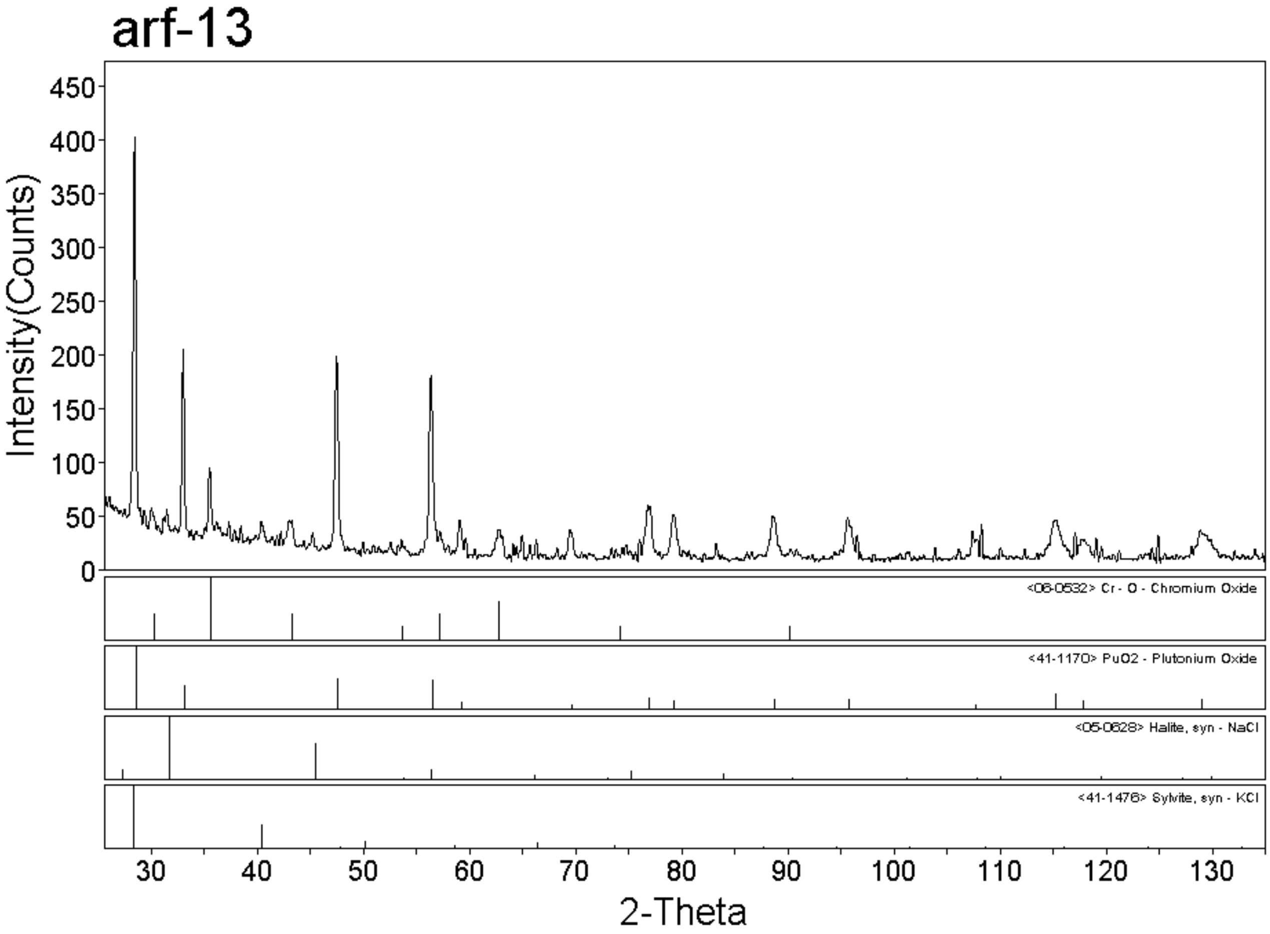

arf-9
Intensity(Counts)
400
350
300
250
200
150
100
50
0
<06-0532> Cr - O - Chromium Oxide
<41-1170> PuO2 - Plutonium Oxide
<05-0628> Halite, syn - NaCl
<41-1476> Sylvite, syn - KCl
30
40
50
60
70
80
90
100
110
120
130
2-Theta

Table 6. X-ray Diffraction Results for Sample ARF13

2-Theta	d(A)	Int	I%	FWHM	Phase-ID	h	k	l
28.577	3.1210	106	100.0	0.266	PuO2	1	1	1
30.197	2.9571	7	6.6	0.315	Cr-O	2	2	0
31.579	2.8309	7	6.6	0.286	Halite, syn	2	0	0
33.145	2.7006	46	43.4	0.239	PuO2	0	0	2
35.646	2.5166	17	16.0	0.247	Cr-O	3	1	1
40.528	2.2240	6	5.7	0.284	Sylvite, syn	2	2	0
43.228	2.0912	15	14.2	0.614	Cr-O	4	0	0
45.336	1.9987	7	6.6	0.371	Halite, syn	2	2	0
47.604	1.9086	70	66.0	0.346	PuO2	0	2	2
50.087	1.8197	2	1.9	0.164	Sylvite, syn	2	2	2
53.722	1.7048	8	7.5	0.514	Cr-O	4	2	2
56.498	1.6274	64	60.4	0.362	PuO2	1	1	3
57.357	1.6051	10	9.4	0.409	Cr-O	5	1	1
59.212	1.5592	12	11.3	0.318	PuO2	2	2	2
62.889	1.4766	17	16.0	0.567	Cr-O	4	4	0
63.188	1.4703	8	7.5	0.343				
65.074	1.4322	5	4.7	0.196				
66.419	1.4064	3	2.8	0.142	Sylvite, syn	4	2	0
69.590	1.3499	10	9.4	0.333	PuO2	0	0	4
76.971	1.2378	34	32.1	0.612	PuO2	1	3	3
79.379	1.2062	23	21.7	0.517	PuO2	0	2	4
83.380	1.1581	3	2.8	0.180	PuO2	2	2	4
88.733	1.1016	24	22.6	0.554	PuO2	2	2	4
95.754	1.0385	14	13.2	0.382	PuO2	1	1	5
107.533	0.9550	6	5.7	0.216	PuO2	0	4	4
108.378	0.9499	5	4.7	0.150	Sylvite, syn	6	2	2
115.374	0.9114	22	20.8	0.683	PuO2	1	3	5
117.182	0.9025	3	2.8	0.129				
119.187	0.8931	3	2.8	0.142				
125.026	0.8683	4	3.8	0.157				
128.973	0.8535	19	17.9	0.684	PuO2	0	2	6

Calculated lattice constant for PuO2: 5.3966(3)
Calculated O/Pu: 1.998


arf-13
Intensity(Counts)
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400
350
300
250
200
150
100
50
0
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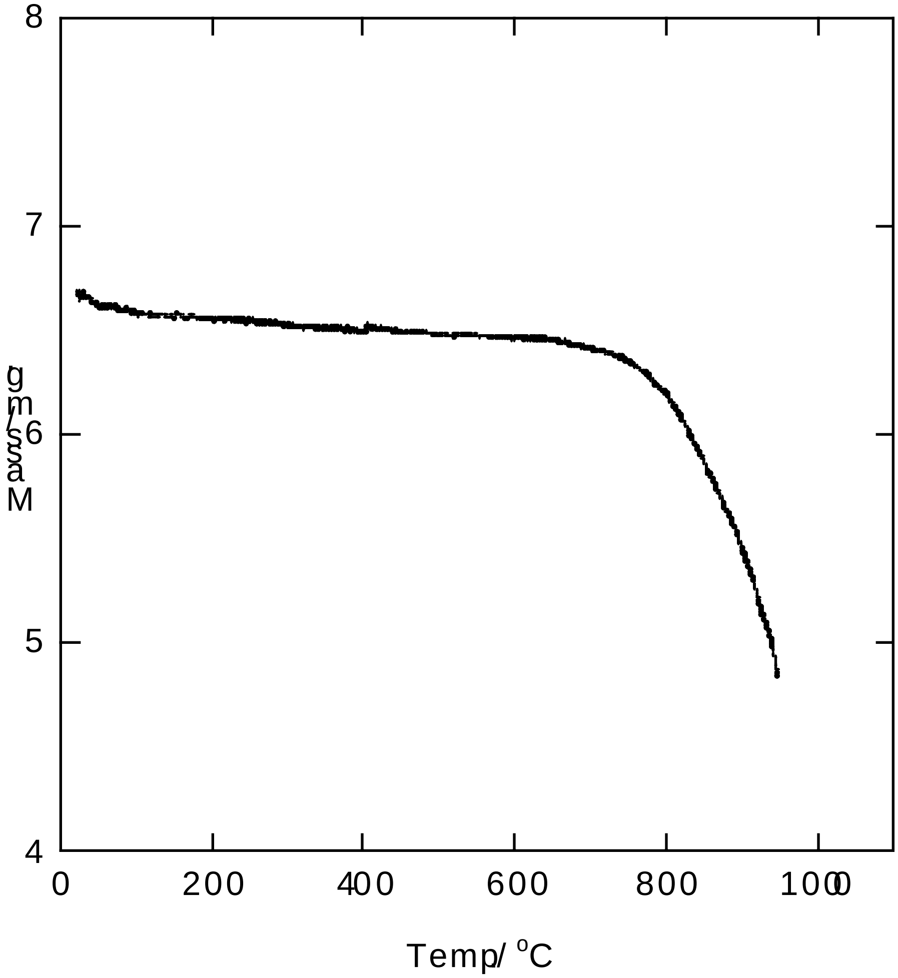
<41-1170> PuO2 - Plutonium Oxide
<05-0628> Halite, syn - NaCl
<41-1476> Sylvite, syn - KCl
30
40
50
60
70
80
90
100
110
120
130
2-Theta

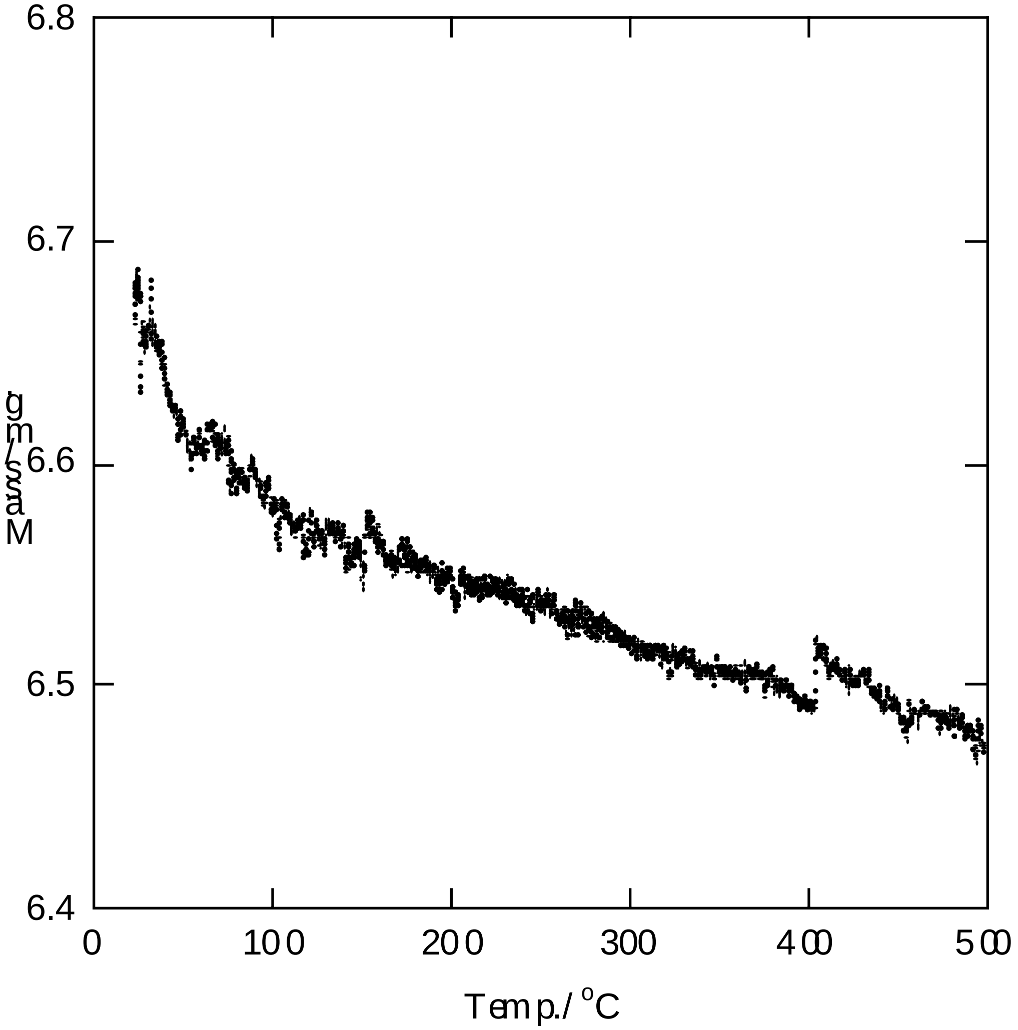
Table 7. Summary of TGA/DTA Results for the ARF Samples.

Sample ID	Mass Loss / % Range 25 to 1000°C	Mass Loss / % Range 25 to 500°C	Thermal Events/ C
ARF-3	27.62	2.9	41.8 96.9 651.4
ARF-3A	29.61	1.9	37.4 99.8 149.3 649.1
ARF-5	28.46	0.32	88.3 649.4
ARF-8	26.30	0.35	92.8 648.9
ARF-9	11.74	0.99	99.6 146.8 447.8 646.3
ARF-13	13.63	2.0	38.5 104.3 152.3 458.9 648.4

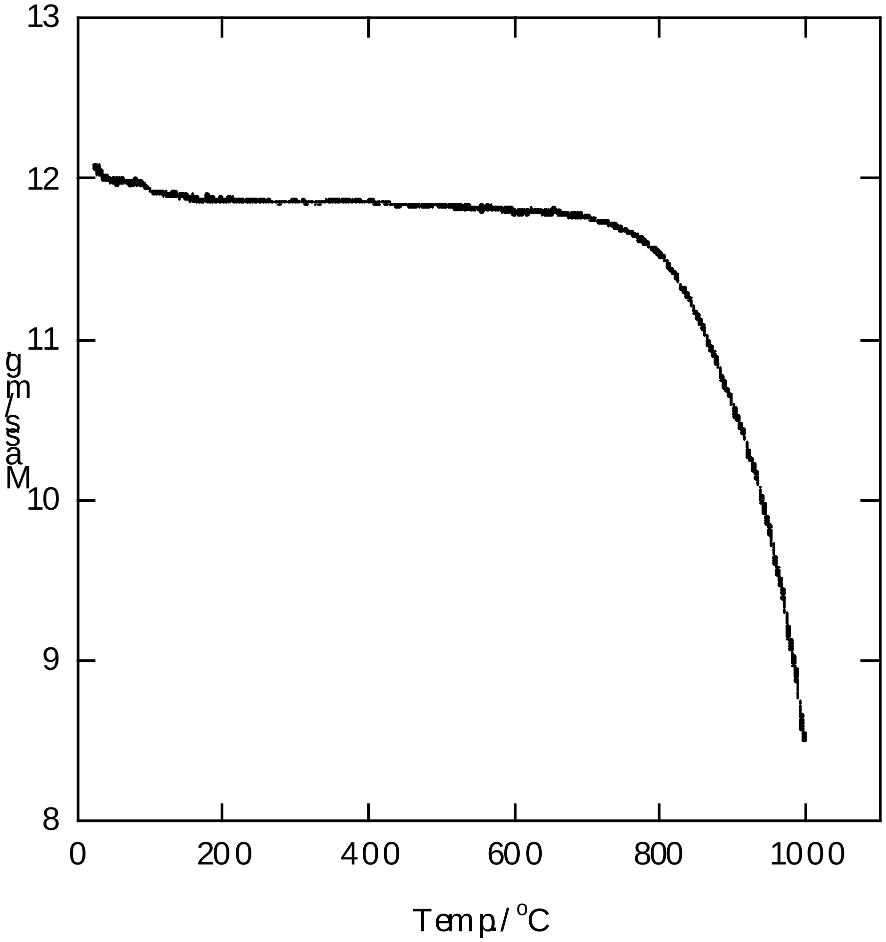
TGA of ARF-3

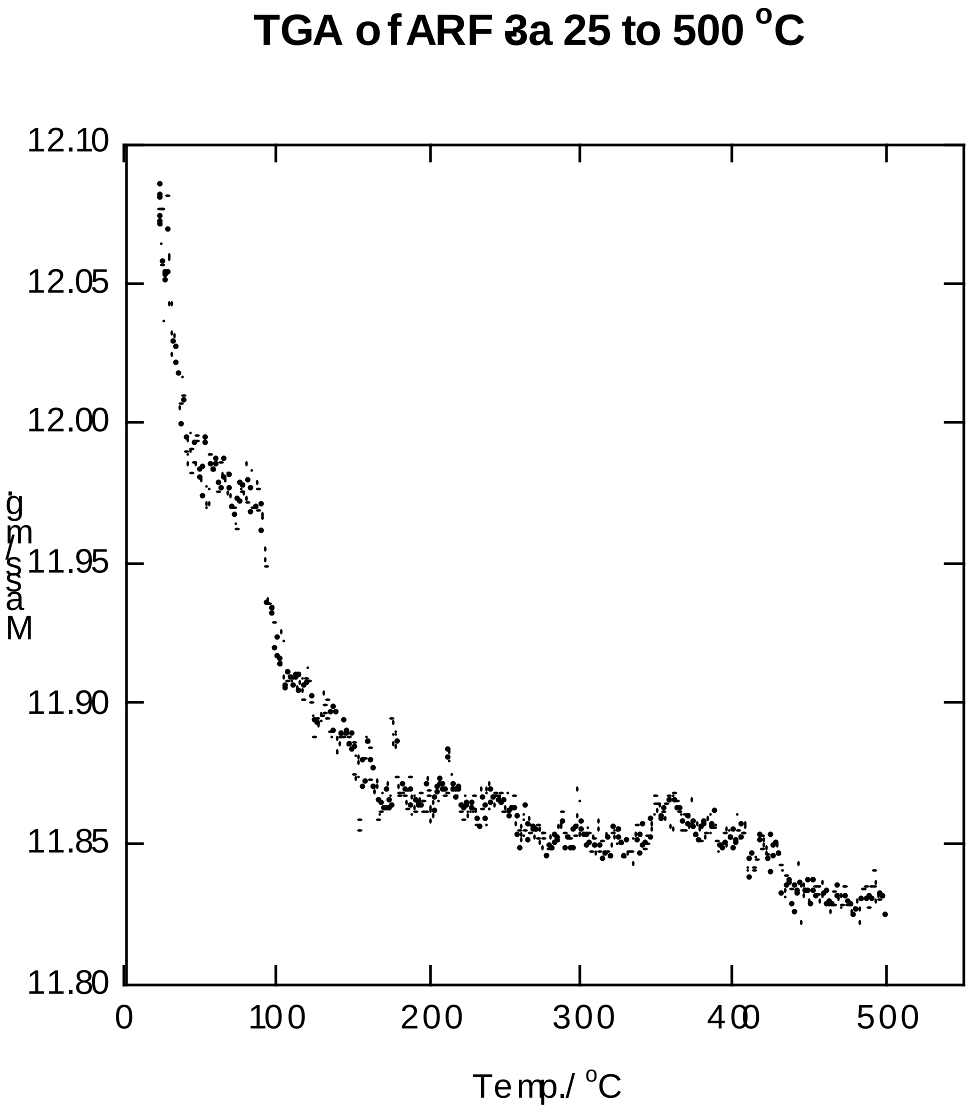


TGA of ARF-3 25 to 500 °C

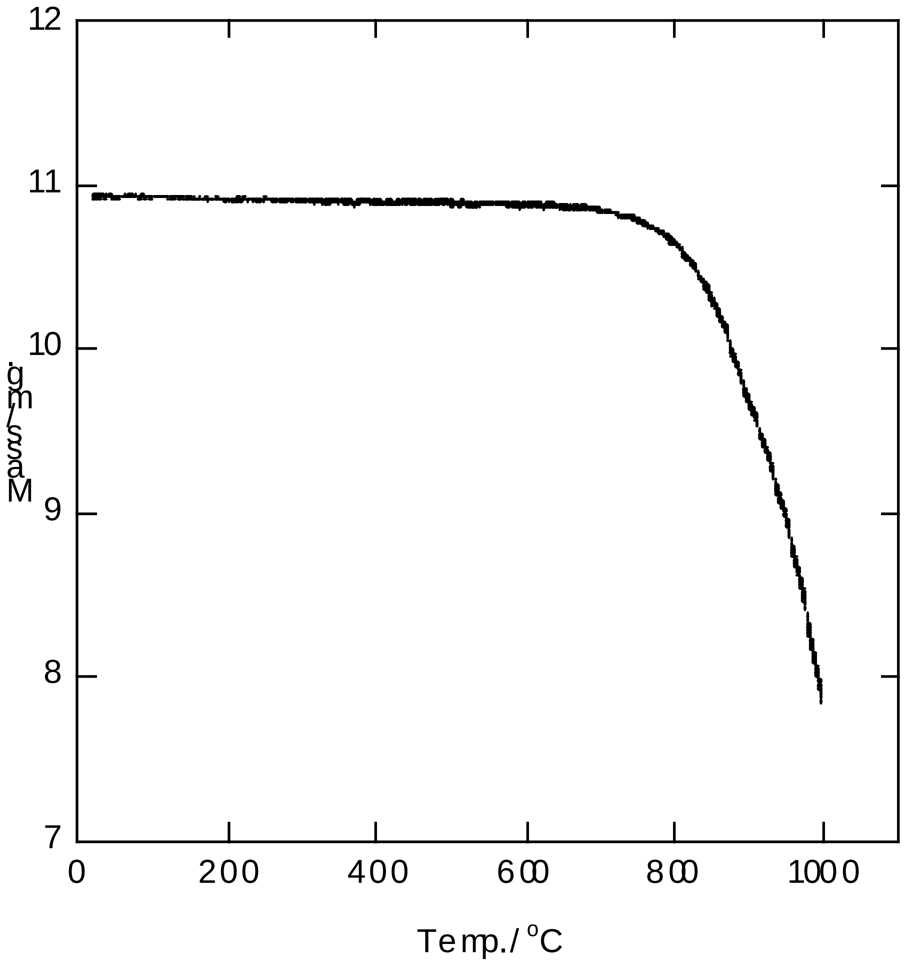


TGA of ARF-3a

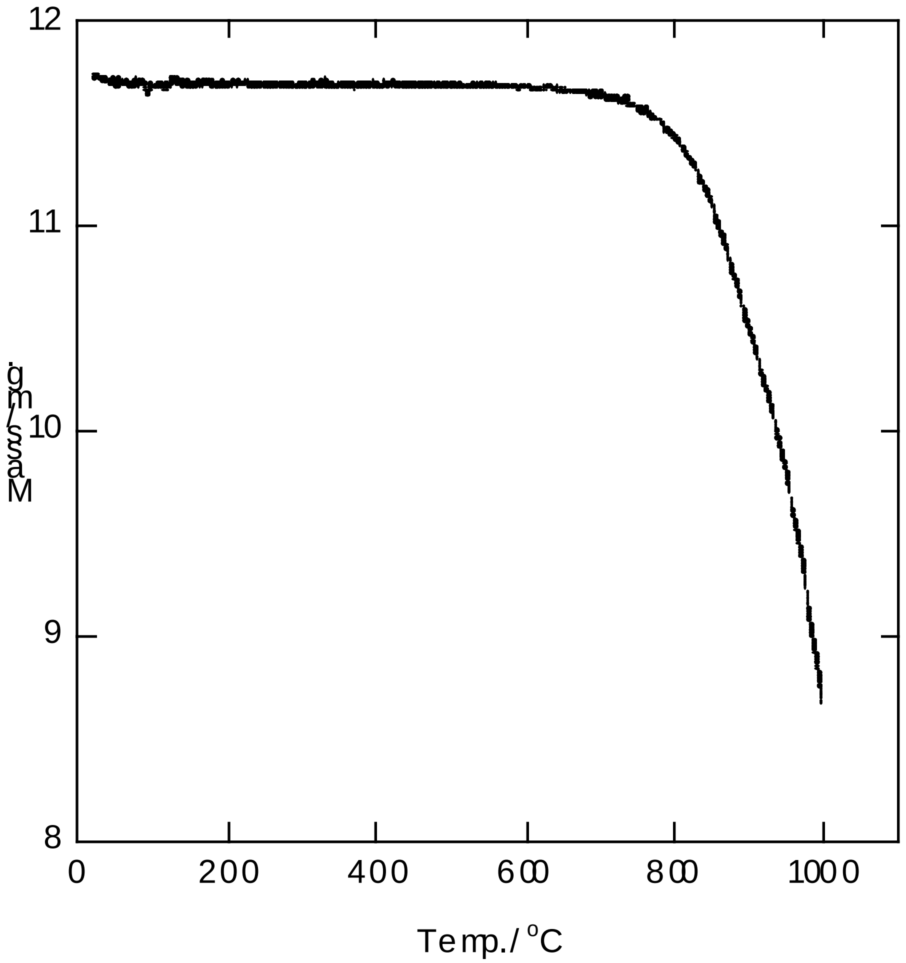


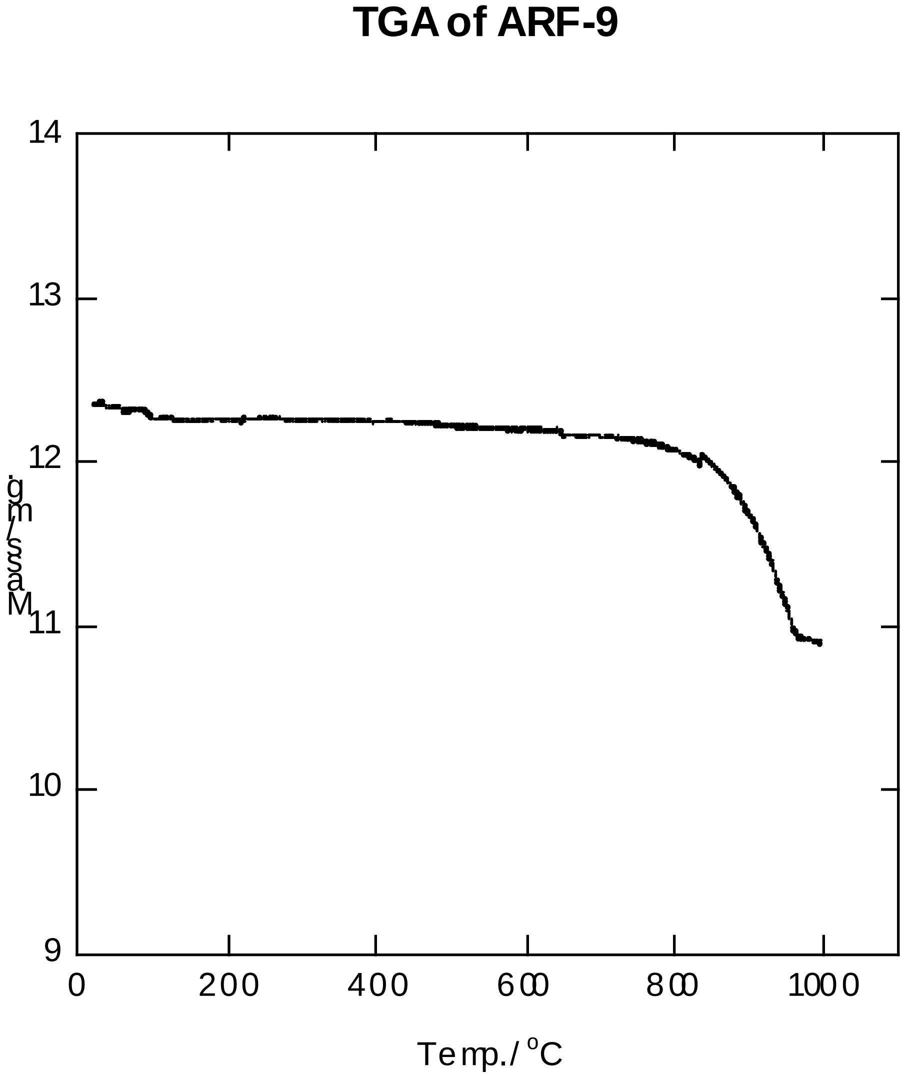

TGA of ARF-3a 25 to 500 ^oC
12.10
12.05
12.00
11.95
11.90
11.85
11.80
Mass/mg
0
100
200
300
400
500
Temp./ ^oC

TGA of ARF-5

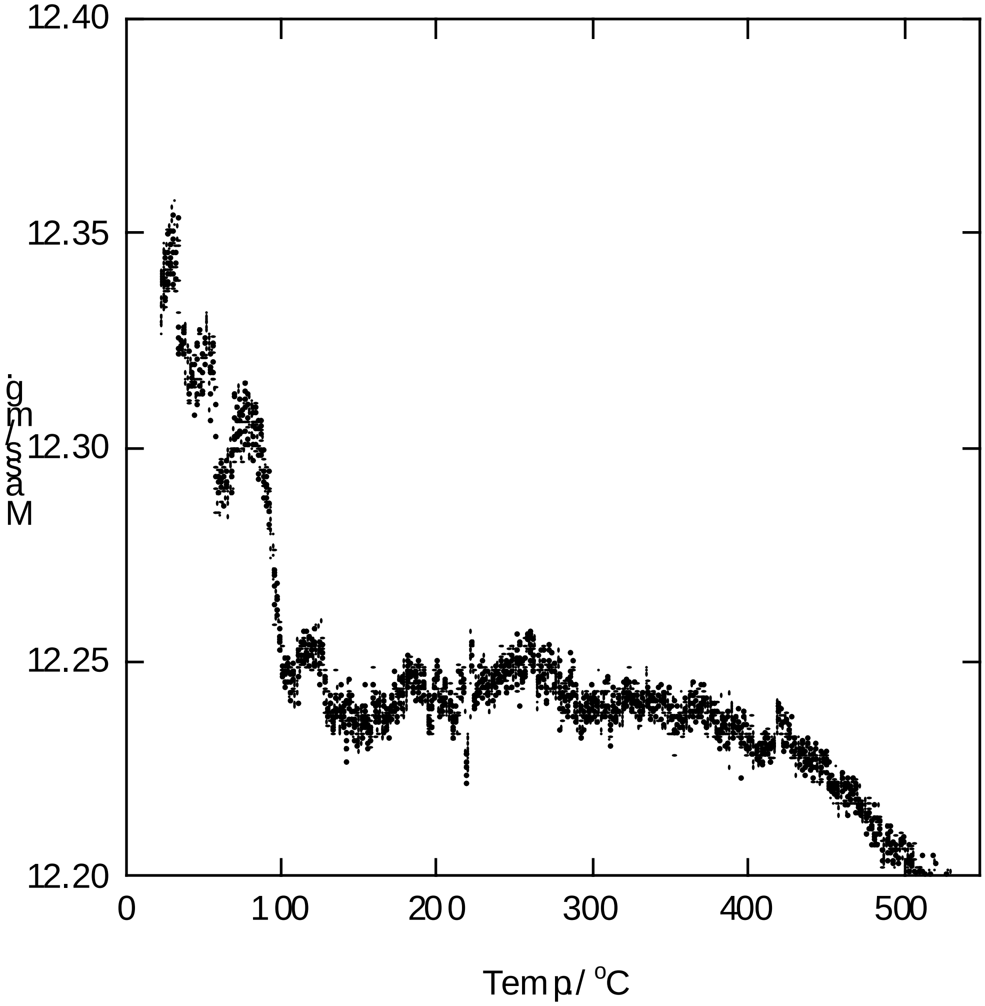


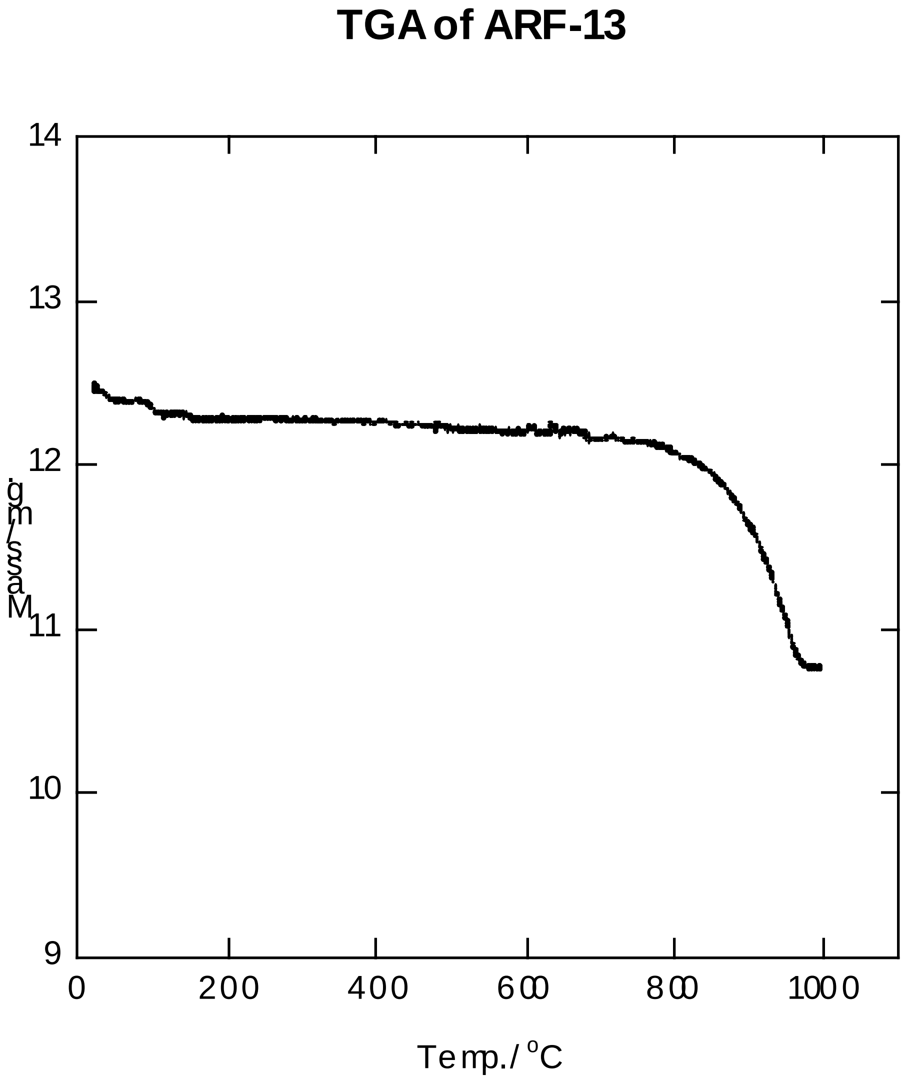
TGA of ARF-8




TGA of ARF-9
14
13
12
11
10
9
Mass/mg.
0
200
400
600
800
1000
Temp./ ^{o}C

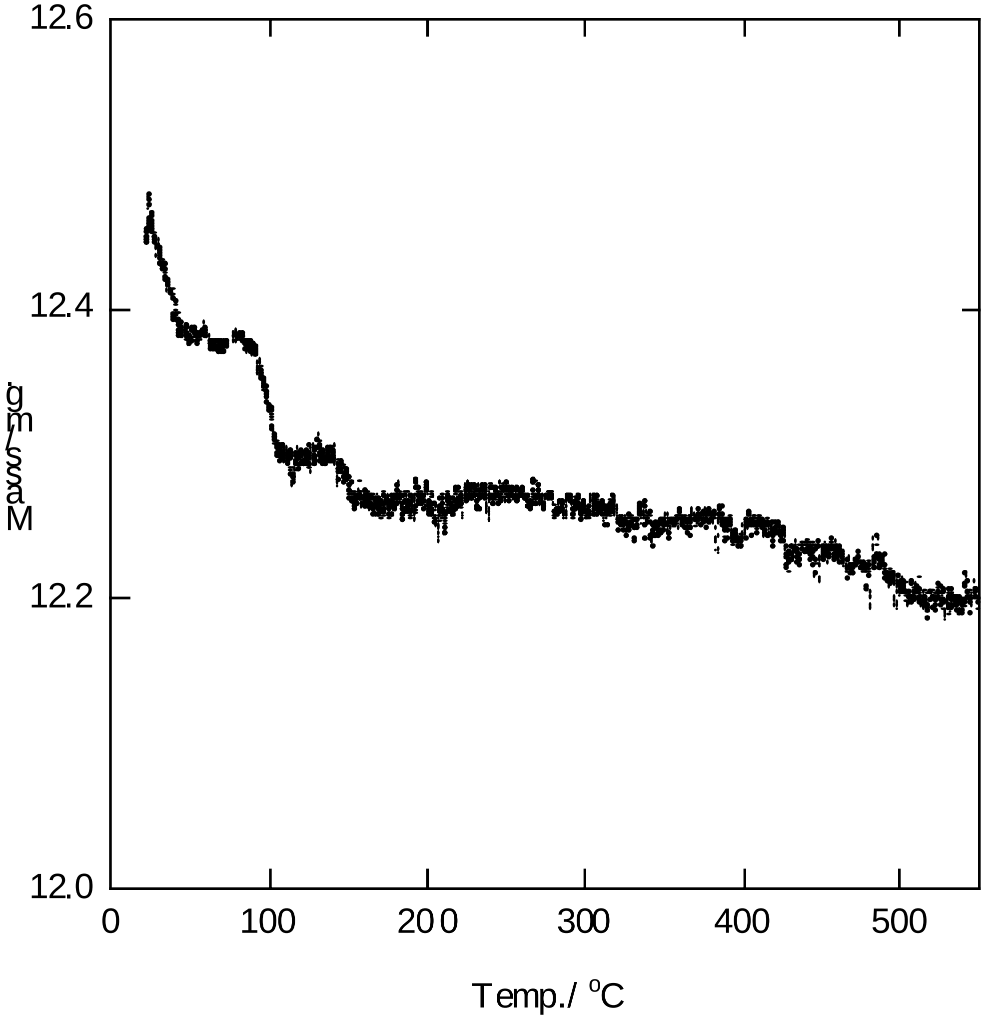
TGA of ARF 9 25 to 500 ^{o}C



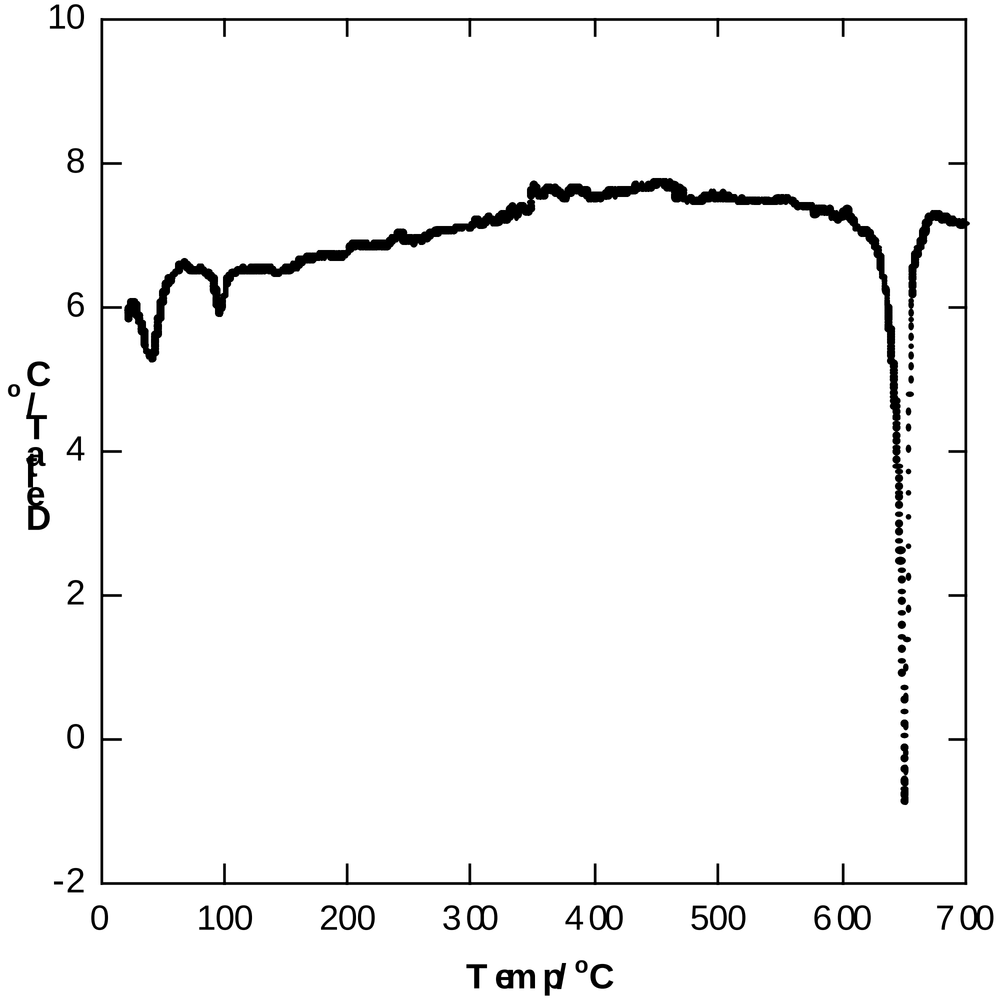


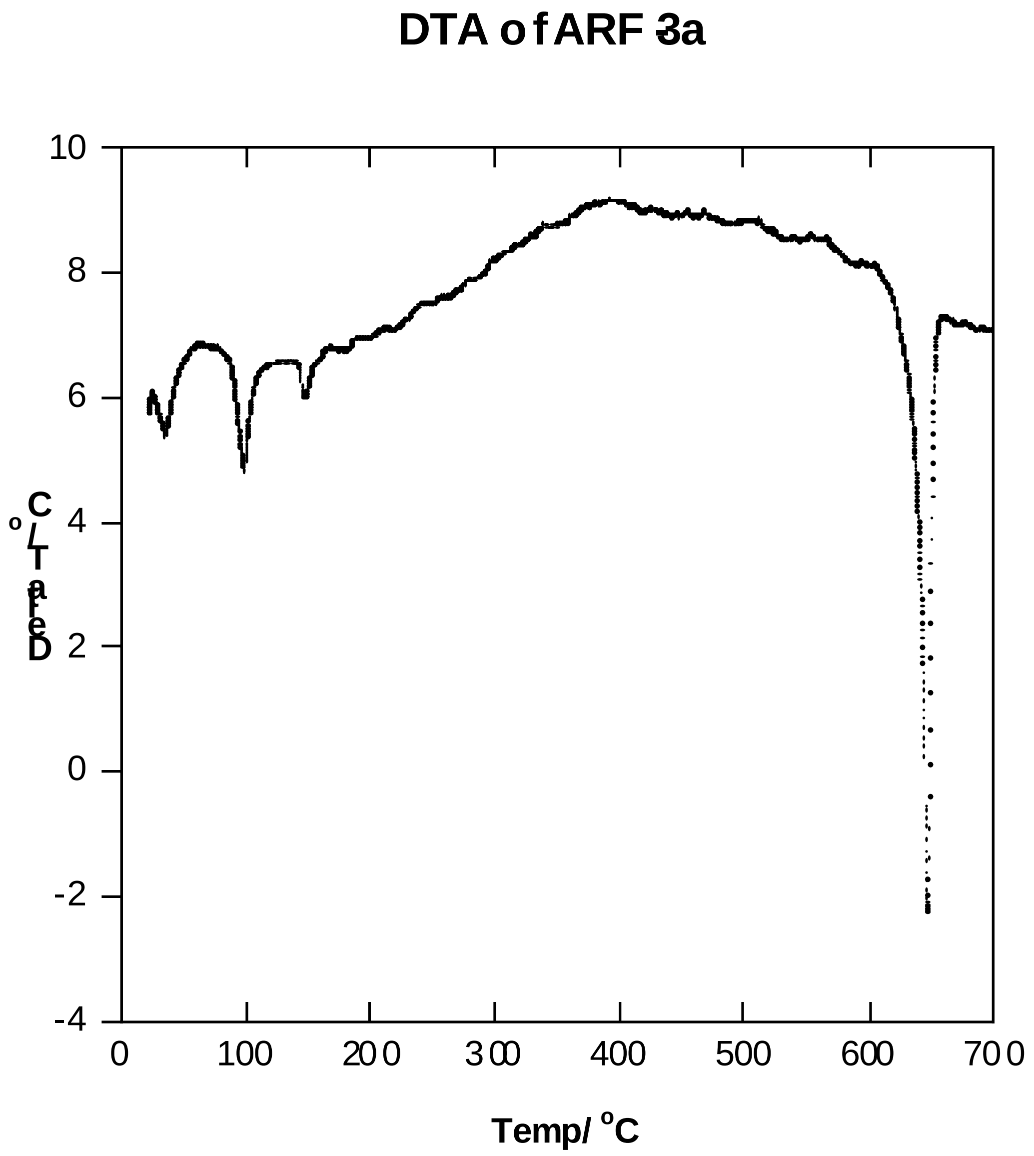
TGA of ARF-13

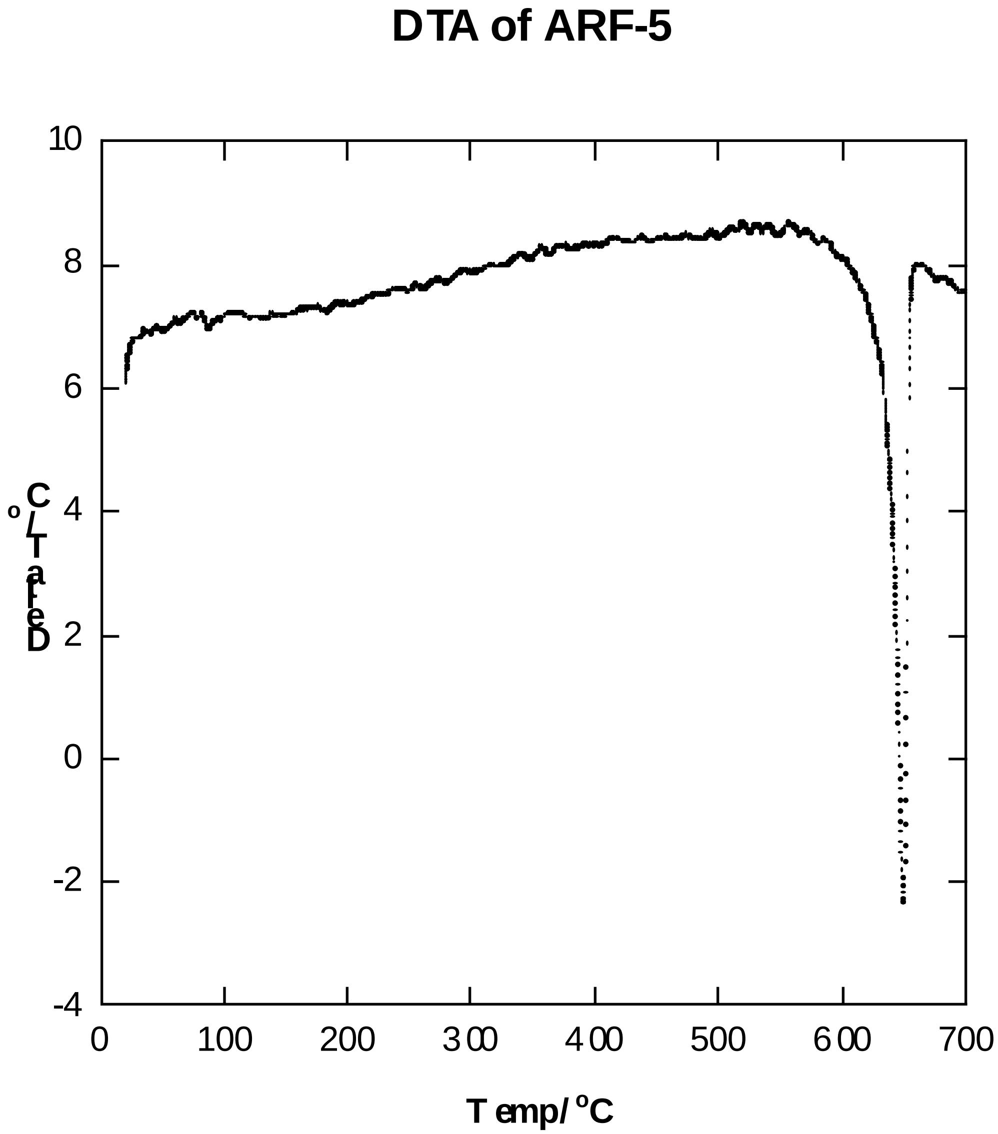
TGA of ARF-13 25 to 500 ^{o}C



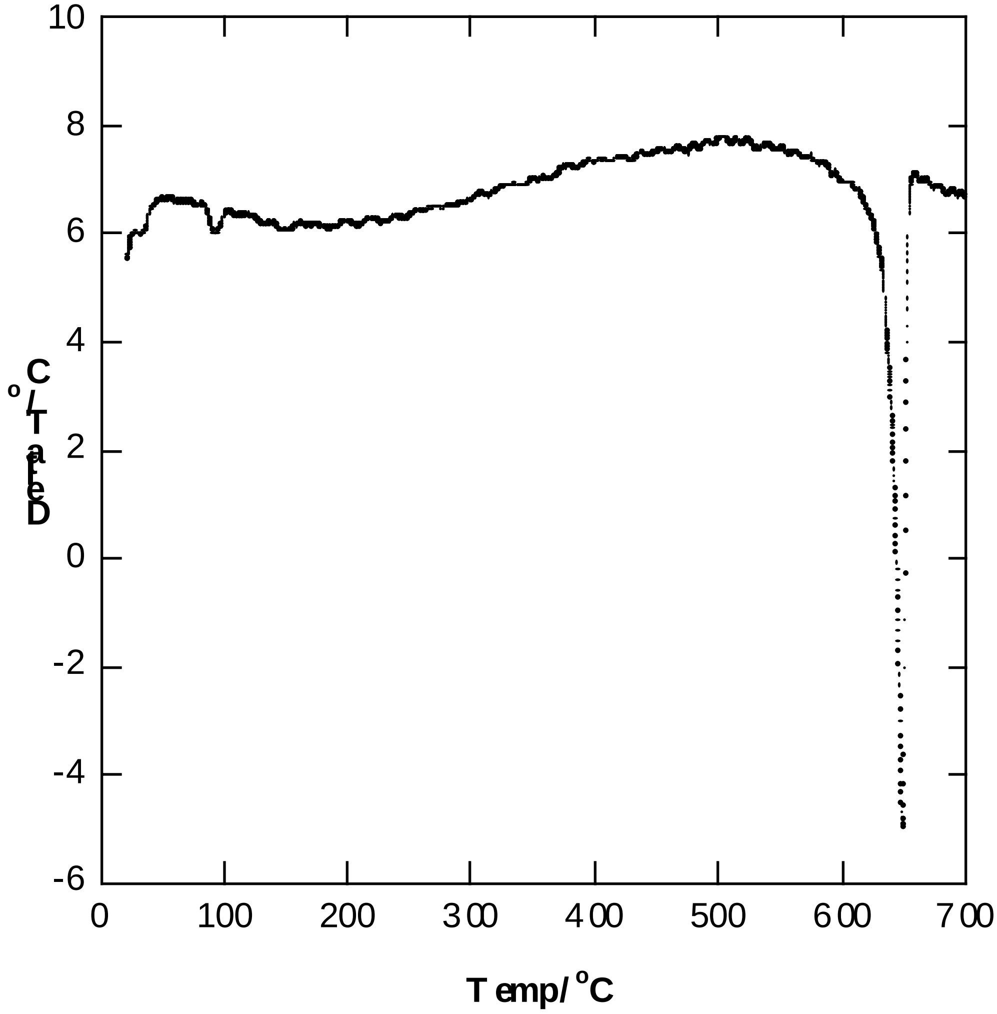
DTA of ARF-3



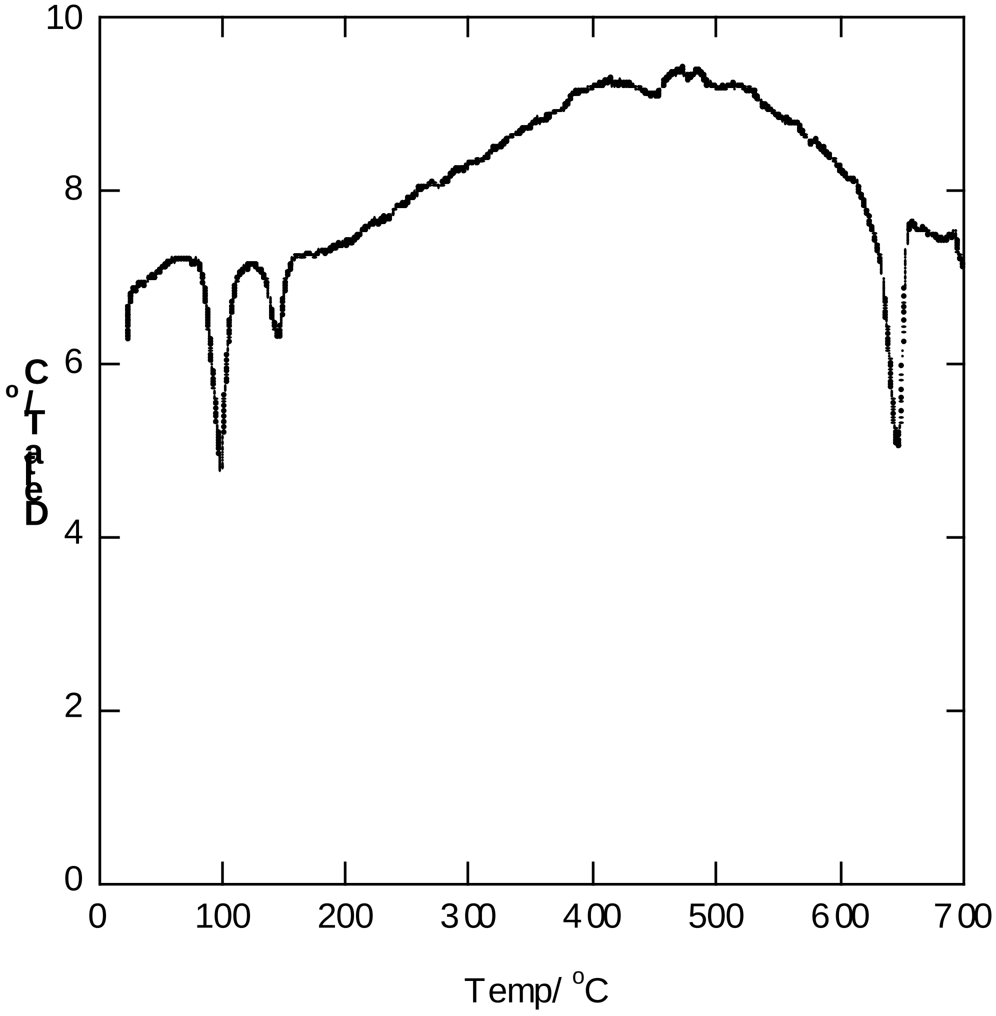

DTA of ARF-3a
10
8
6
4
2
0
-2
-4
0
100
200
300
400
500
600
700
DeltaT/ °C
Temp/ °C

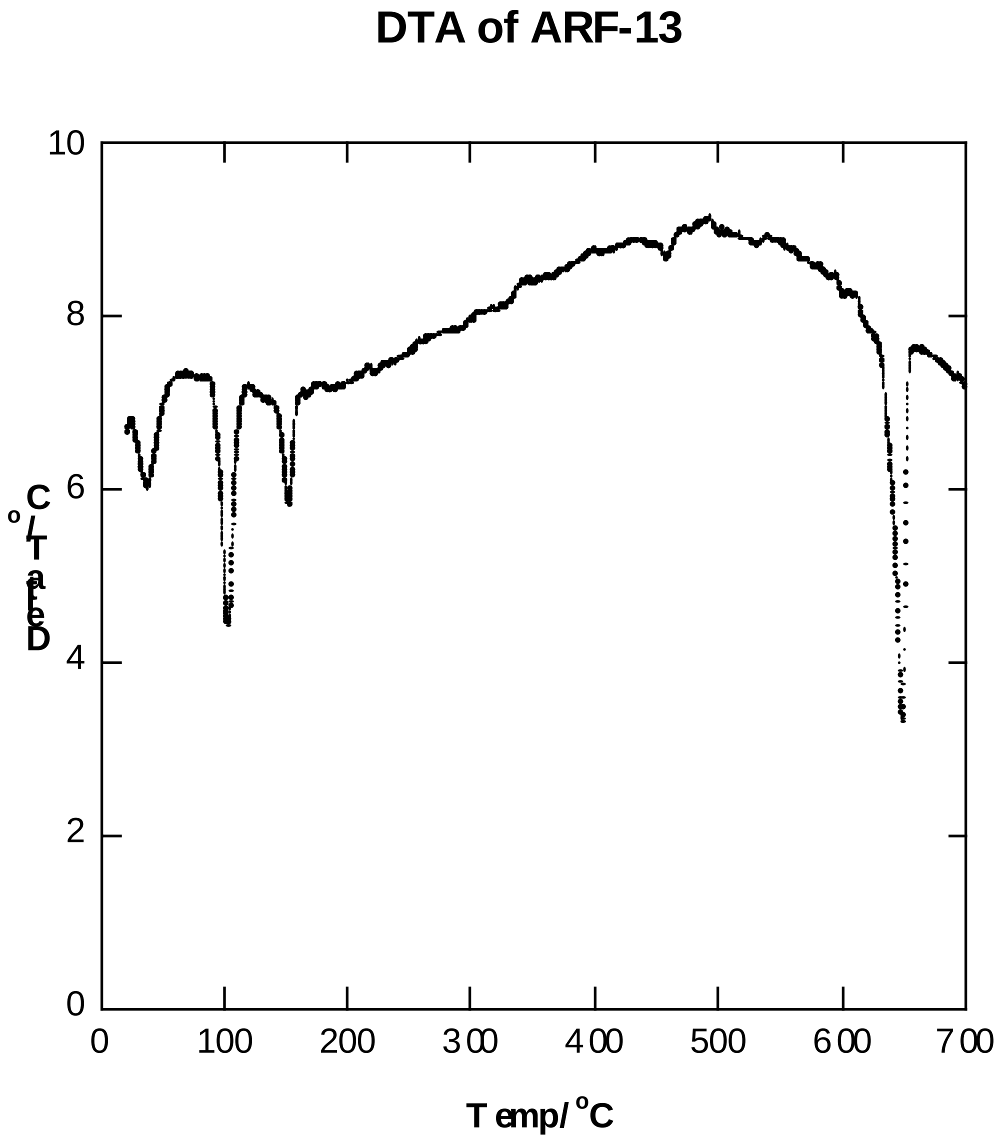

DTA of ARF-5
10
8
6
4
2
0
-2
-4
Delta T/°C
0
100
200
300
400
500
600
700
Temp/°C

DTA of ARF-8



DTA of ARF-9




DTA of ARF-13
10
8
6
4
2
0
0
100
200
300
400
500
600
700
DelT/°C
Temp/°C

APPENDIX 2. TD-MS results.

These results will be added later.

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