Density of Simulated Americium/Curium Melter Feed Solution

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Summary

Vitrification will be used to stabilize an americium/curium (Am/Cm) solution presently stored in F-Canyon for eventual transport to Oak Ridge National Laboratory and use in heavy isotope production programs. Prior to vitrification, a series of in-tank oxalate precipitation and nitric/oxalic acid washes will be used to separate these elements and lanthanide fission products from the bulk of the uranium and metal impurities present in the solution. Following nitric acid dissolution and oxalate destruction, the solution will be denitrated and evaporated to a dissolved solids concentration of approximately 100 g/l (on an oxide basis).

During the Am/Cm vitrification, an airlift will be used to supply the concentrated feed solution to a constant head tank which drains through a filter and an in-line orifice to the melter. Since the delivery system is sensitive to the physical properties of the feed, a simulated solution was prepared and used to measure the density as a function of temperature between 20 to 70°C. The measured density decreased linearly at a rate of 0.0007 $g/cm^3/°C$ from an average value of 1.2326 g/cm^3 at 20°C to an average value of 1.1973g/cm^3 at 70°C.

Introduction

Approximately 15,000 liters of solution containing isotopes of Am/Cm are currently stored in F-Canyon Tank 17.1 at the Savannah River Site (SRS). These isotopes were recovered during plutonium-242 production campaigns in the mid and late 1970's. The continued storage of this solution was identified as an item of urgent concern in the Defense Nuclear Facility Safety Board's Recommendation 94-1. To address this concern, the SRS is planning to stabilize the Am/Cm in a lanthanide borosilicate glass. The Multi-Purpose Processing Facility in F-Canyon will be used for the vitrification process. Pretreatment operations will be performed in canyon vessels to separate the actinides and lanthanides from alkali and transition metal impurities prior to vitrification.

The pretreatment operations include a series of in-tank oxalate precipitations followed by nitric/oxalic acid washes to remove the soluble metal impurities. The oxalate precipitate is then dissolved in 8M nitric acid and the oxalate destroyed by boiling in an evaporator at total reflux. The nitric acid concentration is adjusted to nominally 0.5M by water stripping and formic acid denitration. The final treatment prior to vitrification is an evaporation step to concentrate the dissolved solids to approximately 100 g/l (on an oxide basis). The estimated solution volume and nitric acid concentration following concentration are 1131 liters and approximately 3M.[1]

Once the desired concentration of dissolved solids is reached, the Am/Cm solution is transferred by vacuum to one of two slab tanks in the MPPF. When the melter is operational, an airlift is used to supply a constant head tank above the melter. The head tank overflows back to a slab tank and feeds the melter through a filter and an in-line orifice plate. The orifice is sized to delivery the proper flowrate of solution to the melter. The design of the feed delivery system is sensitive to the physical properties of the concentrated solution such as density and viscosity. For this reason, a simulated Am/Cm solution containing nominally 100 g/l dissolved solids was prepared and used to measure the density as a function of temperature. The composition of the solution was based on material balance calculations performed for the pretreatment operations. The calculations assumed three successive oxalate precipitations followed by two 0.25M oxalic acid/0.5M nitric acid washes. The dip tube of the steam transfer jet was assumed to be 24-inches above the bottom of the tank. The estimated composition following the concentration step is shown in Table 1.

Experimental

Two liters of simulated Am/Cm feed solution were prepared by dissolving either the materials listed in Table 1 in 3M nitric acid or combinations of other starting materials to achieve the desired chemical species. Simplifying assumptions used in the solution preparation include:

1. oxide mass of terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium was redistributed as lanthanum, cerium, praseodymium, neodymium, samarium, europium, and gadolinium oxides,
2. oxide masses of americium and curium were added as erbium oxide,
3. oxide masses of uranium, neptunium, and plutonium were added as cerium oxide,
4. ferric oxalate was added as ferric nitrate and oxalic acid,
5. ferric phosphate was added as ferric nitrate and phosphoric acid,
6. ferric chloride was added as ferric nitrate and hydrochloric acid, and
7. zinc nitrate was added as zinc oxide previously dissolved in 3M nitric acid.

A summary of the starting materials, amounts of each reagent, and calculated solution concentrations is shown in Table 2.

The density of the simulated Am/Cm solution was measured by initially transferring approximately 300 ml of the simulant to a water-jacketed cell (see Figure 1). The temperature of the solution was cooled or heated using a Fisher Scientific Programmable Circulator. A calibrated mercury-filled thermometer was used to manually control the cell temperature. Once the solution was at the desired temperature, a 1 ml (cm^3) sample of the solution was removed using a calibrated pipette. A copy of the pipette calibration record is shown in Appendix A. The solution was transferred to a tared 10 ml beaker on a calibrated analytical balance. The mass of the solution was then recorded. Measurements were made at solution temperatures of 20, 30, 40, 50, 60, and 70°C.

Discussion

The mass of each 1 ml (cm^3) aliquot of the simulated Am/Cm solution at 20, 30, 40, 50, 60, and 70°C is reported in Table 3. The density reported for each measurement was calculated using a mean value of 1.0030 ml (cm^3) for the volume transferred by the calibrated pipette. The mean value, standard deviation, and 95% confidence limits for the density is also reported for each temperature. The mean value of the density as a function of the simulated solution temperature is shown on Figure 2. The error bars shown on the plot are ± 1 standard deviation for the mean densities. The regression line for the data is presented as equation (1).

$$Density(g / cm^3) = 1.2467 - 7.0078E^{-4} Temperature(^\circ C) \quad (1)$$

The three sets of ten measurements made at 20 and 30°C compared to a single set for the other temperatures (see Table 3) were the results of discovering a positive bias with the volume delivered by the calibrated pipette as the solution temperature increased. Initially the same pipette tip was reused for all the measurements at a given temperature. When measurements at 40°C were performed, the density of the solution noticeably increased from one measurement to the next. This was attributed to a slight expansion of the plastic pipette tip volume due to the solution temperature. As a result of this discovery, a new pipette tip was used for each measurement and the measurements at 20 and 30°C were repeated two additional times. Construction of 95% confidence intervals for the average densities calculated from the three data sets at 20 and 30°C (see Figures 3 and 4, respectively) shows statistical differences; however, the data sets at each temperature were pooled since there was no technical basis for discarding an outlying data set.

Conclusions

A nonradioactive solution was prepared to simulate the physical properties of the Am/Cm feed solution just prior to vitrification. The density of the simulant was measured as function of temperature between 20 and 70°C. The density decreased linearly at rate of 0.0007 $g/cm^3/°C$ from an average value of 1.2326 g/cm^3 at 20°C to an average value of 1.1973g/cm^3 at 70°C.

References

1. T. S. Rudisill, *Pretreatment of Americium/Curium Solutions for Vitrification (U),* External Report WSRC-TR-96-0074, Westinghouse Savannah River Company, Aiken, SC (March 1996).

Table 1 Composition of Melter Feed Stream

Component	Concentration (g/l)
$La(NO_3)_3$	22
$Ce(NO_3)_3$	25
$Pr(NO_3)_3$	25
$Nd(NO_3)_3$	52
$Sm(NO_3)_3$	12
$Eu(NO_3)_3$	2
$Gd(NO_3)_3$	6
$Tb(NO_3)_3$	1
$Dy(NO_3)_3$	1
$Ho(NO_3)_3$	1
$Er(NO_3)_3$	1
$Tm(NO_3)_3$	1
$Yb(NO_3)_3$	1
$Lu(NO_3)_3$	1
$Am(NO_3)_3$	16
$Cm(NO_3)_3$	4
$NpO_2(NO_3)$	$6x10^{-4}$
$Pu(NO_3)_4$	$3x10^{-1}$
$UO_2(NO_3)_2$	$2x10^{-1}$
AlF_3	$7x10^{-2}$
$Al(NO_3)_3$	1
$Al_2(SO_4)_3$	1
$Ca(NO_3)_3$	$1x10^{-3}$
$Cr(NO_3)_3$	$3x10^{-1}$
$CsNO_3$	$1x10^{-3}$
$FeCl_3$	$4x10^{-1}$
$Fe_2(C_2O_4)_3$	$4x10^{-1}$
$Fe(NO_3)_3$	1
$FePO_4$	$5x10^{-1}$
$Fe_2(SO_4)_3$	2
KNO_3	$1x10^{-1}$
$Mn(NO_3)_2$	21
$Na_2B_4O_7$	$1x10^{-2}$
$NaNO_2$	$3x10^{-1}$
$NaNO_3$	$2x10^{-1}$
Na_2SiO_3	$2x10^{-2}$
$Ni(NO_3)_2$	$2x10^{-1}$
$Zn(NO_3)_2$	$1x10^{-2}$
$Zr(NO_3)_4$	$4x10^{-3}$

Table 2 Composition of Simulated Am/Cm Solution

Compound in Solution	Reagent	Reagent Mass (g)	Compound Concentration (g/l)	Oxide Basis Concentration (g/l)
$La(NO_3)_3$	$La(NO_3)_3 \cdot 6\ H_2O$	60.3628	22.6473	11.3546
$Ce(NO_3)_3$	$Ce(NO_3)_3 \cdot 6\ H_2O$	70.3036	26.4015	13.2859
$Pr(NO_3)_3$	$Pr(NO_3)_3 \cdot 6\ H_2O$	68.4910	25.7362	12.9819
$Nd(NO_3)_3$	$Nd(NO_3)_3 \cdot 6\ H_2O$	140.6339	52.9775	26.9879
$Sm(NO_3)_3$	$Sm(NO_3)_3 \cdot 6\ H_2O$	33.9039	12.8293	6.6501
$Eu(NO_3)_3$	$Eu(NO_3)_3 \cdot 5\ H_2O$	8.6445	3.2749	1.7050
$Gd(NO_3)_3$	$Gd(NO_3)_3 \cdot 6\ H_2O$	17.6970	6.7294	3.5533
$Er(NO_3)_3$	$Er(NO_3)_3 \cdot 5\ H_2O$	60.1385	23.0244	12.4652
AlF_3	AlF_3	0.1469	0.0735	0.0446
$Al(NO_3)_3$	$Al(NO_3)_3 \cdot 9\ H_2O$	2.2394	0.6358	0.1522
$Al_2(SO_4)_3$	$Al_2(SO_4)_3 \cdot 18\ H_2O$	3.8421	0.9863	0.2939
$Ca(NO_3)_3$	$Ca(NO_3)_3 \cdot 4\ H_2O$	0.1877	0.0652	0.0223
$Cr(NO_3)_3$	$Cr(NO_3)_3 \cdot 9\ H_2O$	1.0677	0.3175	0.1014
$CsNO_3$	$CsNO_3$	0.0028	0.0014	0.0010
$FeCl_3$	$Fe(NO_3)_3 \cdot 9\ H_2O$	(1)	0.3898	0.1771
	37.2 wt% HCl	1.1 ml		
$Fe_2(C_2O_4)_3$	$Fe(NO_3)_3 \cdot 9\ H_2O$	(1)	0.4046	0.1720
	$H_2C_2O_4 \cdot 2\ H_2O$	0.8121		
$Fe(NO_3)_3$	$Fe(NO_3)_3 \cdot 9\ H_2O$	7.5764	0.5082	0.1705
$FePO_4$	$Fe(NO_3)_3 \cdot 9\ H_2O$	(1)	0.4464	0.2363
	85.5 wt% H_3PO_4	0.4 ml		
$Fe_2(SO_4)_3$	77 wt% $Fe_2(SO_4)_3$	5.3950	2.0771	0.8295
KNO_3	KNO_3	0.2696	0.1348	0.0628
$Mn(NO_3)_2$	$Mn(NO_3)_2 \cdot 6\ H_2O$	66.2899	20.6634	8.1913
$Na_2B_4O_7$	$Na_2B_4O_7 \cdot 10\ H_2O$	0.0439	0.0116	0.0036
$NaNO_2$	$NaNO_2$	0.6047	0.3024	0.1358
$NaNO_3$	$NaNO_3$	0.3916	0.1958	0.0714
Na_2SiO_3	$Na_2SiO_3 \cdot 9\ H_2O$	0.0898	0.0193	0.0098
$Ni(NO_3)_2$	$Ni(NO_3)_2 \cdot 6\ H_2O$	0.4980	0.1727	0.0527
$Zn(NO_3)_2$	ZnO	0.0157	0.0183	0.0079
$Zr(NO_3)_4$	$Zr(NO_3)_4$	0.0074	0.0037	0.0014
Total (2)				99.7211

(1) The amount of acid was the limiting reagent.
(2) The total includes 0.0117 g B_2O_5 and 0.0095 g SiO_2 from $Na_2B_4O_7$ and Na_2SiO_3, respectively.

Table 3 Density of Simulated Am/Cm Feed Solution

20°C		30°C		40°C	
Mass (g)	Density (g/cm^3)	Mass (g)	Density (g/cm^3)	Mass (g)	Density (g/cm^3)
1.2341	1.2304	1.2313	1.2276	1.2238	1.2201
1.2382	1.2345	1.2370	1.2333	1.2183	1.2147
1.2356	1.2319	1.2363	1.2326	1.2221	1.2184
1.2376	1.2339	1.2329	1.2292	1.2231	1.2194
1.2380	1.2343	1.2344	1.2307	1.2230	1.2193
1.2386	1.2349	1.2371	1.2334	1.2191	1.2155
1.2429	1.2392	1.2401	1.2364	1.2197	1.2161
1.2404	1.2367	1.2351	1.2314	1.2202	1.2166
1.2356	1.2319	1.2309	1.2272	1.2222	1.2185
1.2373	1.2336	1.2371	1.2334	1.2228	1.2191
1.2372	1.2335	1.2281	1.2244		
1.2354	1.2317	1.2280	1.2243		
1.2364	1.2327	1.2282	1.2245		
1.2379	1.2342	1.2328	1.2291		
1.2382	1.2345	1.2288	1.2251		
1.2401	1.2364	1.2305	1.2268		
1.2361	1.2324	1.2287	1.2250		
1.2403	1.2366	1.2298	1.2261		
1.2399	1.2362	1.2275	1.2238		
1.2383	1.2346	1.2240	1.2203		
1.2311	1.2274	1.2248	1.2211		
1.2327	1.2290	1.2252	1.2215		
1.2333	1.2296	1.2229	1.2192		
1.2320	1.2283	1.2250	1.2213		
1.2336	1.2299	1.2254	1.2217		
1.2335	1.2298	1.2244	1.2207		
1.2326	1.2289	1.2242	1.2205		
1.2343	1.2306	1.2261	1.2224		
1.2347	1.2310	1.2149	1.2113		
1.2345	1.2308	1.2386	1.2349		
Mean	1.2326		1.2260		1.2178
Std Dev	0.0029		0.0057		0.0019
95% CL	0.0059		0.0117		0.0039

Table 3 Continued

50°C		60°C		70°C	
Mass (g)	Density (g/cm^3)	Mass (g)	Density (g/cm^3)	Mass (g)	Density (g/cm^3)
1.2118	1.2082	1.2057	1.2021	1.1931	1.1895
1.2165	1.2129	1.2074	1.2038	1.2013	1.1977
1.2176	1.2140	1.2073	1.2037	1.1988	1.1952
1.2125	1.2089	1.2082	1.2046	1.1980	1.1944
1.2162	1.2126	1.2087	1.2051	1.2062	1.2026
1.2142	1.2106	1.2074	1.2038	1.2010	1.1974
1.2153	1.2117	1.2139	1.2103	1.2022	1.1986
1.2147	1.2111	1.2142	1.2106	1.2046	1.2010
1.2152	1.2116	1.2094	1.2058	1.1958	1.1922
1.2126	1.2090	1.2113	1.2077	1.2083	1.2047
Mean	1.2111		1.2058		1.1973
Std Dev	0.0019		0.0029		0.0047
95% CL	0.0043		0.0069		0.0106

Figure 1 Water-jacketed Density Cell

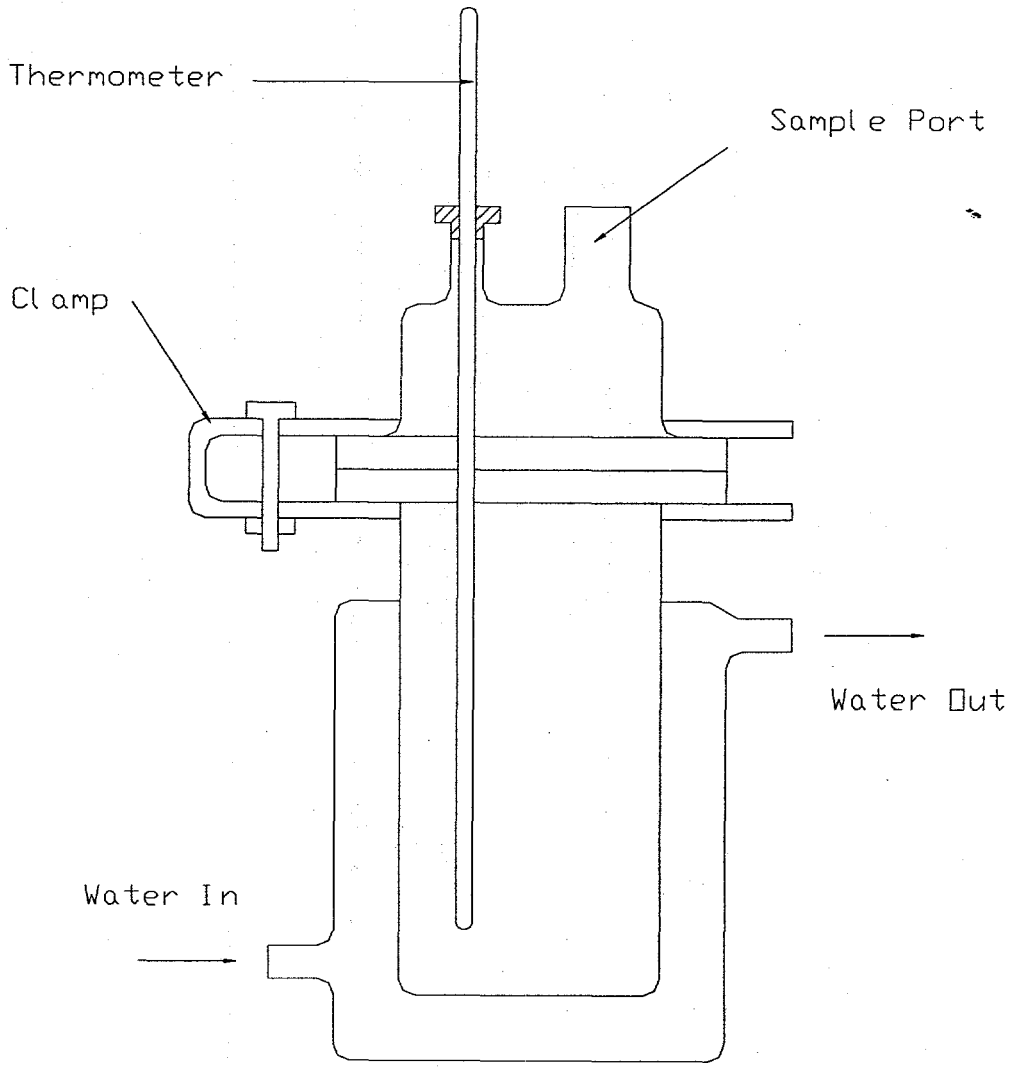


Figure 2 Density of Simulated Am/Cm Solution

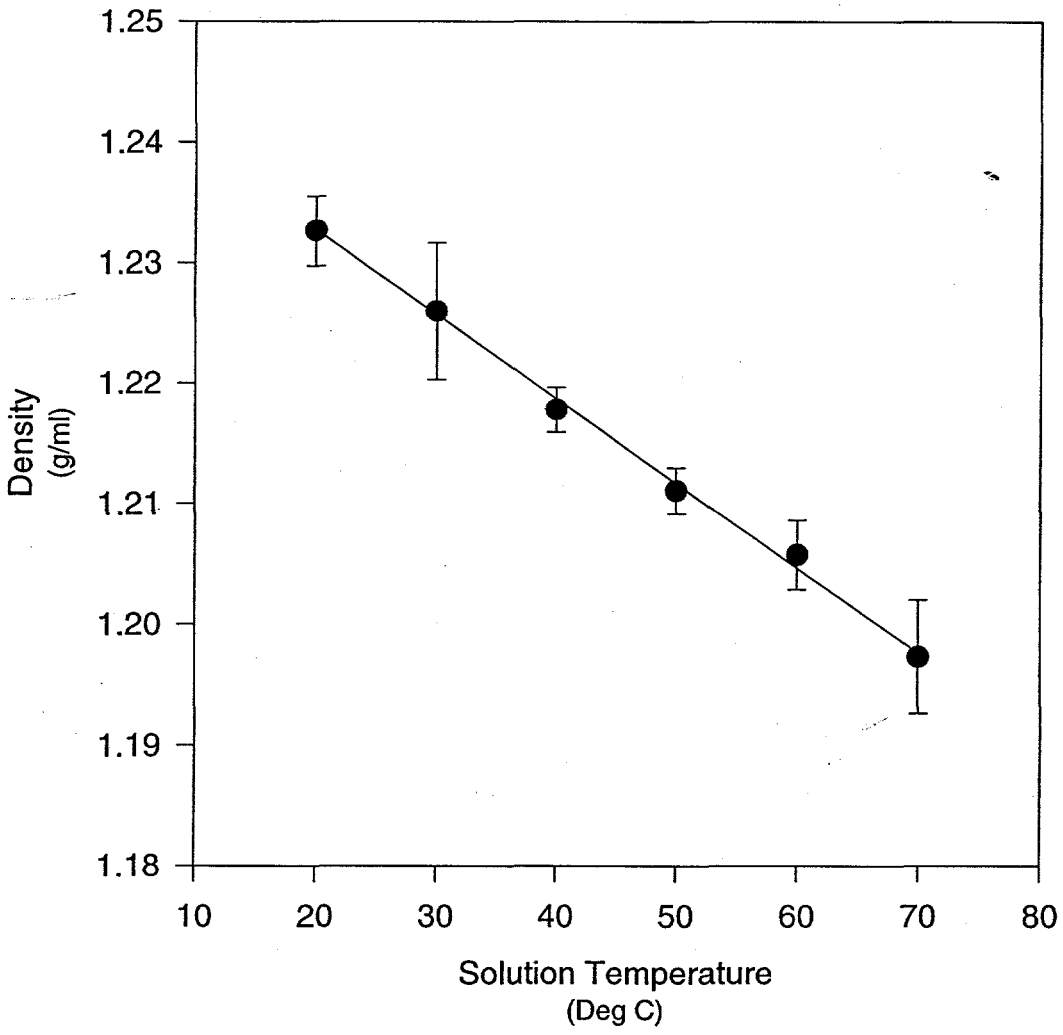


Figure 3 95% Confidence Intervals for Data Sets at 20°C

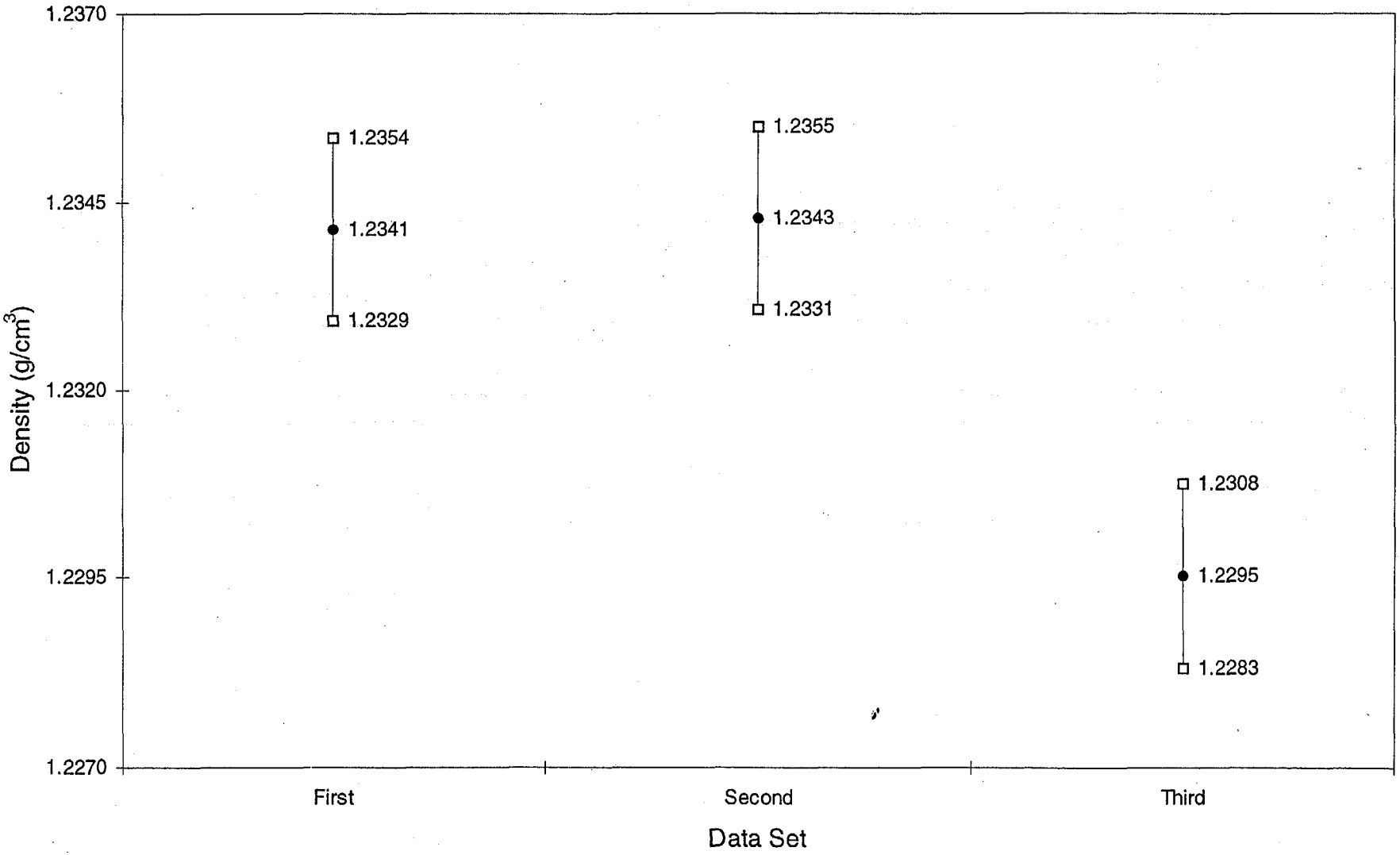
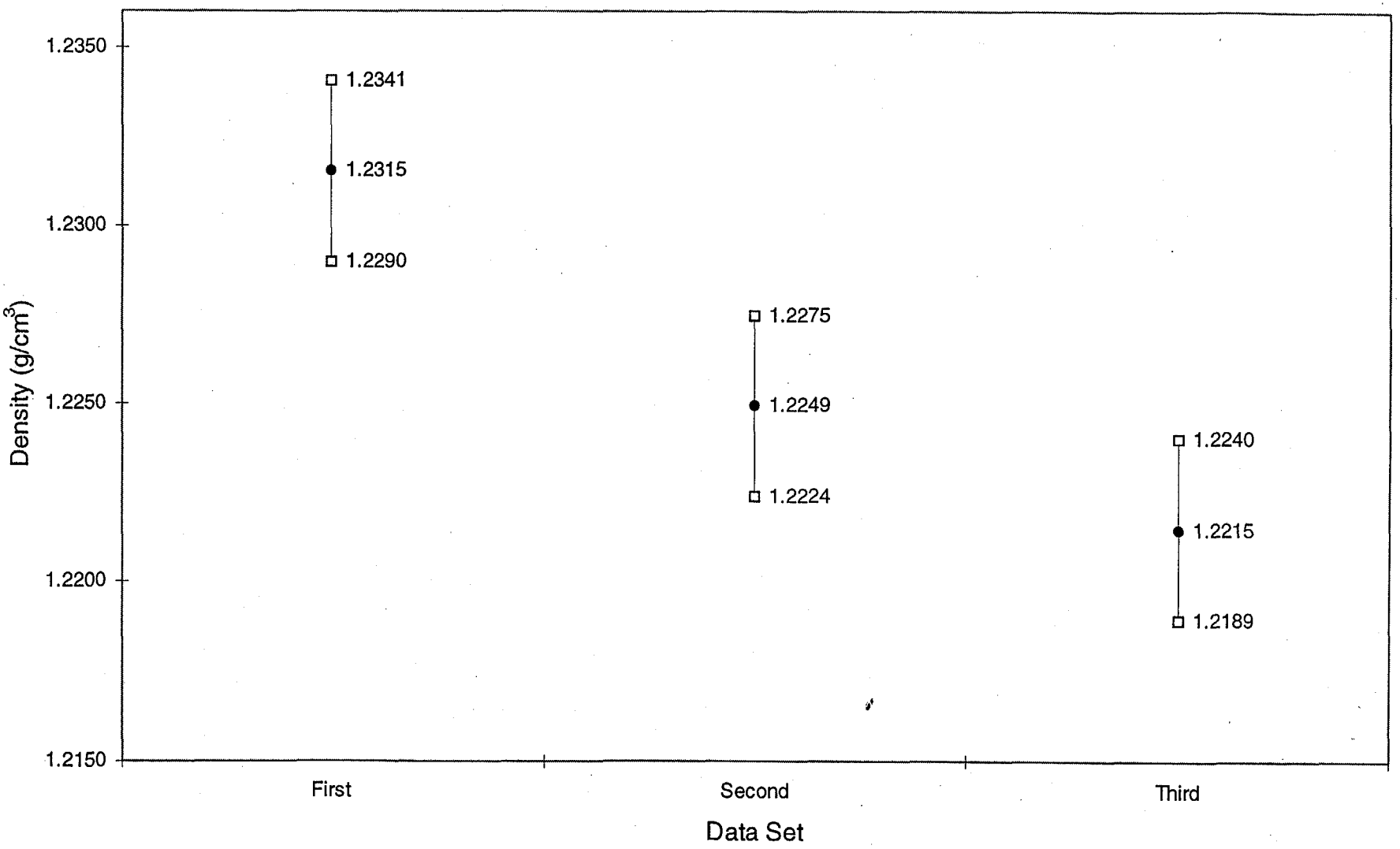


Figure 4 95% Confidence Intervals for Data Sets at 30°C



Appendix A Pipette Calibration Record

	Data Required per QAP 12-1, Rev 5.		Check One		
	M&TE # of Balance Used for Calib.:	AD0041		Pass	Fail
	Balance Calibration Expiration Date:	3/11/97	As Found Results:	X	
	Pipet Calibration Procedure:	ADS 1000, Rev. 6	As Left Results:	X	
	Pipet M&TE ID #:	J18060D		Hot	Cold
	Pipet Manufacturer:	RAININ	Lab Station:		X
	Pipet Model Number:	P1000		Yes	No
	Volume:	~ 1.0000	New Pipet?		X
	Date of this Calibration:	1/10/97			
	Lab # (where pipet is used):	B137			
	Date Pipet Calibration Expires:	4/10/97			
	Manual Calibration Results:		**QC LIMITS:**	**%BIAS**	**%RSD**
1-	1.0024	**STDEV**		0.8	0.6
2-	1.0038	0.0019			
3-	1.0049				
4-	1.0042	**MEAN**			
5-	1.0057	01.0030			
6-	1.0045				
7-	0.9995	**%BIAS**			
8-	1.0008	0.30			
9-	1.0023				
10-	1.0021	**%RSD**			
		0.19			

Pipette passes QA Limits.

Calibrated by: CY Tilley

Signature or Initial: X CYT

***** NOTICE *****

"As found" readings are when no adjustment has been made to the pipet, "as left" are if adjustment has been made. If adjustments are made, turn in both the before and after results.

*** Initial or sign the printout and any other official records turned in. ***