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Solubility Limits of Dibutyl Phosphoric Acid in Uranium Solutions at SRS

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Abstract

The Savannah River Site has enriched uranium (EU) solution which has been stored for almost 10 years since being purified in the second uranium cycle of the H area solvent extraction process. The concentrations in solution are ~6 g/L U and about 0.1 M nitric acid. Residual tributylphosphate in the solutions has slowly hydrolyzed to form dibutyl phosphoric acid (HDBP) at concentrations averaging 50 mg/L. Uranium is known to form compounds with DBP which have limited solubility. The potential to form uranium-DBP solids raises a nuclear criticality safety issue.

SRTC tests have shown that U-DBP solids will precipitate at concentrations potentially attainable during storage of enriched uranium solutions. Evaporation of the existing EUS solution without additional acidification could result in the precipitation of U-DBP solids if DBP concentration in the resulting solution exceeds 110 ppm at ambient temperature. The same potential exists for evaporation of unwashed 1CU solutions. The most important variables of interest for present plant operations are HNO_3 and DBP concentrations. Temperature is also an important variable controlling precipitation. The data obtained in these tests can be used to set operating and safety limits for the plant. It is recommended that the data for 0°C with 0.5 M HNO_3 be used for setting the limits. The limit would be 80 mg/L which is 3 standard deviations below the average of 86 observed in the tests. The data shows that super-saturation can occur when the DBP concentration is as much as 50% above the solubility limit. However, super-saturation cannot be relied on for maintaining nuclear criticality safety.

The analytical method for determining DBP concentration in U solutions was improved so that analyses for a solution are accurate to within 10 %. However, the overall uncertainty of results for periodic samples of the existing EUS solutions was only reduced slightly. Thus, sampling appears to be the largest portion of the uncertainty for EUS sample results, although the number of samples analyzed here is low which could contribution to higher uncertainty. The analytical method can be transferred to the plant analytical labs for more routine analysis of samples.

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Introduction

The Savannah River Site has enriched uranium (EU) solution which has been stored for almost 10 years since being purified in the second uranium cycle of the H area solvent extraction process. The concentrations in solution are ~6 g/L U and about 0.1 M nitric acid. After reprocessing, the solution contained about 200 μg of dissolved tributyl phosphate (TBP) per gram of solution and a thin film of 7.5 vol.% TBP in n-paraffin diluent floating on top of the solution. The dissolved TBP has slowly hydrolyzed to dibutyl phosphoric acid (DBP) giving an average concentration of DBP in solution of 50 mg/L. The hydrolysis reaction is slow at ambient temperature and low acid concentration so that all the TBP has not yet hydrolyzed. Uranium is known to form compounds with DBP which have limited solubility.[1-9] The solubility of $UO_2(DBP)_2$ has been reported to be 5.6×10^{-4} in 0.2 M HNO_3 and a solubility product constant was calculated to be 6.1×10^{-11}.[5,7] Previous unpublished studies at SRTC have shown that at ambient temperature U does not precipitate from 6 g/L U solutions with 100 mg DBP/L solution, but does precipitate when the concentration reaches 125 mg DBP/L solution.[9] If all the dissolved TBP were converted to DBP, the solution could reach 158 mg DBP/L solution. However, DBP is also hydrolyzed slowly to MBP which reduces the maximum attainable concentration. In addition, U will precipitate at lower concentrations. The present concentration is 50-60 mg/L based on analyses of past samples of the solution with high uncertainty. Possible precipitation represents a nuclear criticality concern. A better understanding and measurement of the solubility limits for the U-HNO_3-DBP system are needed to establish safety and operating limits for storage and operations.

Another concern is the large variability in analyses for DBP in the EU solution. Measurement of the concentration of DBP in the stored EU solution has been tracked over the past several years and found to average about 60 mg/L ± 20 mg/L. This large variability in analytical results affects the setting of operating limits and could result in uncertainty in whether the operating limit has been exceeded or not. Work was done to identify the uncertainty in analyses for DBP in the existing EU solutions.

Experimental

Solutions were prepared with reagent grade HNO_3 and uranyl nitrate hexahydrate (UNH) and with 98 % pure DBP solution obtained from Aldrich. Stock solutions of UNH and DBP were prepared in glass volumetric flasks with 0.5 M HNO_3 prepared from 15.7 M acid. The UNH solution containing 150 g/L U was prepared by dissolving 79.13 g of UNH solids in a 250 mL volumetric flask using 0.5 M HNO_3 and diluting to the mark. The DBP solution was prepared by dissolving 0.2792 g of DBP in a 100 mL glass volumetric flask using 0.5 M HNO_3 and diluting to the mark. The concentration of DBP based on 98 % purity is 2736 mg/L. Duplicate analyses of the DBP stock solution gave an average concentration of 2700±10 mg/L. The stock solutions were then used to prepare test solutions. Solubility in the $UO_2(NO_3)_2$- HNO_3-H_2O system was approached in two principal ways: precipitation and dissolution of known solids.

Precipitation Tests

Precipitation tests were done at ambient temperature (22-23°C) and at 0°C. Tests were carried out by preparing the solutions, and by allowing the solutions to sit in a hood at ambient temperature or in a constant temperature bath at 0°C. The samples were examined daily to see if precipitation had occurred. If precipitation of solids occurred in the test, samples were taken to analyze the DBP concentration remaining in solution. The quantity of solids precipitated was small so that the concentrations of U and acid should not be significantly affected. The intent of the test is to add enough DBP to be near or above the solubility limit. If the components are near the solubility limit, super-saturation can occur, which results in slow solids formation. Solution preparation is shown below for two 0°C tests and one ambient temperature test. In all cases, the HNO_3 added was solution with the desired final concentration, either 0.1M, 0.3M, or 0.5M.

The solutions were prepared in glass vials with Teflon liners in the caps to prevent adsorption of DBP by the plastic. The total solution volume in the vials was 25 mL in all cases. Table 1 shows preparation of the first 0°C test. The quantity of DBP, added during the first attempt at preparing samples for the 0°C test, was too high and resulted in immediate precipitation in all cases where U was present. The samples were placed in the constant temperature bath at 0°C for several days before sampling and analysis. The DBP analyses are shown in the table as well. Two blanks were included as checks on the analyses.

Table 1. Solution Preparation for First 0°C Temperature Tests

Solution Preparation				Calculated Concentrations			Analyses
mL HNO3	mL U	mL DBP	mL H2O	HNO3,M	U, g/L	DBP, ppm	DBP, ppm
20	0	1	4	0.1	0	109	108
15	1	1	8	0.1	6	109	69
13.125	1	1.375	9.5	0.1	6	150	71
11.25	1	1.75	11	0.1	6	192	67
7.5	2	1.5	14	0.1	12	164	74
5	2	2	16	0.1	12	219	63
2.5	2	2.5	18	0.1	12	274	72
23.25	0	1.75	0	0.5	0	192	200
21.75	1	2.25	0	0.5	6	246	99
21.25	1	2.75	0	0.5	6	301	99
20.75	1	3.25	0	0.5	6	356	93
20.75	2	2.25	0	0.5	12	246	84
20.25	2	2.75	0	0.5	12	301	88
19.75	2	3.25	0	0.5	12	356	87

The second test at 0°C was prepared by first diluting the 2736 mg/L solution to 1000 mg/L to allow more accurate volume measurement. Table 2 shows solution preparation along with the calculated concentrations and the precipitation results to date. Precipitation has not occurred in most of the samples.

Table 3 shows solution preparation and calculated values along with the observed precipitation times at ambient temperature.

Dissolution of Solids

Solid $UO_2(DBP)_2$ was prepared by dissolving 9.97 g of UNH in 50 mL of deionized (DI) water and adding DBP prepared by washing 30 mL of a 50-50 mixture of DBP/MBP (monobutyl phosphate) three times with 10 mL portions of DI water. The MBP is highly water soluble compared to DBP and should be removed by the water washes. The small volume of water washes minimizes the loss of DBP due to solubility. Yellow solids separated immediately upon addition of DBP. The solids were sticky and were separated from the solution by filtration. The solids were dissolved in a small quantity of hot 2-ethylhexanol and reprecipitated by cooling

Table 2. Solution Preparation for Second 0°C Temperature Tests

Solution Preparation				Calculated Concentrations			Time to
mL HNO3	mL U	mL DBP	mL H2O	HNO3,M	U, g/L	DBP, ppm	Precipitate
20	0	1	4	0.1	0	40	Blank
15	1	1	8	0.1	6	40	No Ppt
13.125	1	1.375	9.5	0.1	6	55	No Ppt
11.25	1	1.75	11	0.1	6	70	No Ppt
7.5	2	1.5	14	0.1	12	60	No Ppt
5	2	2	16	0.1	12	80	No Ppt
2.5	2	2.5	18	0.1	12	100	No Ppt
23.25	0	1.75	0	0.5	0	70	Blank
21.75	1	2.25	0	0.5	6	90	No Ppt
21.25	1	2.75	0	0.5	6	110	No Ppt
20.75	1	3.25	0	0.5	6	130	7 days
20.75	2	2.25	0	0.5	12	90	No Ppt
20.25	2	2.75	0	0.5	12	110	No Ppt
19.75	2	3.25	0	0.5	12	130	8 days

* No Ppt in 32 days at temperature

Table 3. Solution Preparation for Ambient Temperature Tests

Solution Preparation				Calculated Concentrations			Time to
mL HNO3	mL U	mL DBP	mL H2O	HNO3,M	U, g/L	DBP, ppm	Precipitate
15	1	1	8	0.1	6	109	No Ppt
10	2	1	12	0.1	12	109	56 days
5	3	1	16	0.1	18	109	56 days
0	15	1	9	0.1	90	109	35 days
18.33	1	3	2.67	0.3	6	328	Immediate
16.67	2	3	3.33	0.3	12	328	Immediate
15	3	3	4	0.3	18	328	Immediate
0	15	3	7	0.3	90	328	16 days
19	1	5	0	0.5	6	547	Immediate
18	2	5	0	0.5	12	547	Immediate
17	3	5	0	0.5	18	547	Immediate
5	15	5	0	0.5	90	547	Overnight

* No Ppt in >60 days at temperature

with an ice bath. The resulting solids were filtered and dried in air. Yellow powder was obtained after drying (9.5 g, 72 % yield). The x-ray pattern of the solids was similar to that of Pu DBP with no indication of more than one phase. Thermogravimetric analysis of the solids resulted in a weight loss of 34.4 % starting at 210°C and complete by 274°C. The total weight loss was 37.2 % at 315°C. Thermogravimetric studies show that TBP decomposes when heated with loss of butyl groups complete at about 268°C.[10] The product resulting from pyrolysis was given as $H_4P_2O_7$.[10] Based on that information the weight loss associated with formation of $UO_2H_2P_2O_7$ would be 35.2 % and loss of a water molecule from that compound to give $UO_2P_2O_6$ could occur at higher temperatures resulting in a weight loss of 37.8 %. The data indicated the desired compound had been prepared. These solids were then used in subsequent dissolution tests at 10°C and 30°C.

One half gram of solids were placed in glass vials with various amounts of UNH stock solution, the appropriate concentration of acid, and DI water to obtain the desired concentrations. In addition, vials were prepared with water and the three acid concentrations without any U present. The total volume, added to each vial was 25 mL. The vials were placed in a constant temperature bath at the desired temperature. Periodic samples were taken for DBP analysis to determine if equilibrium had been reached. When equilibrium was attained, samples were taken and analyzed for DBP, U, and free acid. The samples taken for analysis from the bath at 30°C were diluted with an equal volume of 0.5 M HNO_3 to ensure that precipitation did not occur when the samples cooled to ambient temperature. Solution preparation for both tests was the same as shown in Table 4. Blank samples of DI water were submitted with all samples from this set. In addition, some solutions with known initial amounts of DBP in 6-18 g/L U were prepared as standards and submitted along with the samples.

Table 4. Solution Preparation for UO_2 $(DBP)_2$ Solid Dissolution

Solution Preparation			Calculated Concentrations	
mL HNO3	mL U	mL H2O	HNO3,M	U, g/L
0	0	25	0	0
25	0	0	0.1	0
25	0	0	0.3	0
25	0	0	0.5	0
20	1	4	0.1	6
15	2	12	0.1	12
10	3	16	0.1	18
0	15	9	0.1	90
23.30	1	0.67	0.3	6
21.70	2	1.33	0.3	12
20	3	2	0.3	18
0	15	10	0.3	90
24	1	0	0.5	6
23	2	0	0.5	12
22	3	0	0.5	18
10	15	0	0.5	90

Analyses

Analysis for U in solution was done by the Chem Check instrument, which utilizes U phosphorescence. Free acid analyses were done by the standard method in Analytical Development Section. DBP analyses were done by ion chromatographic analysis (IC). Considerable effort was made to improve the DBP analysis method to obtain reproducible results with the lowest uncertainty. Samples without U or high nitrate ion can be run without significant pretreatment. However, U and high nitrate can interfere with the analysis. Nitrate is also an anion which at high concentrations binds with more ion exchange sites on the analytical column causing DBP^- to elute in the void volume. Uranium complexes DBP so strongly ($\beta_1 = 1 \times 10^4$)[8] that a portion of the DBP is not present as an anion in the eluant, causing the results to be low. Both effects were overcome by pretreatment involving extraction of DBP from the aqueous samples with 2-ethylhexanol followed by back-extraction into 1 M NaOH. The back-extracted solution was then put through ion exchange cartridges to remove the sodium ion and protonate DBP^- to HDBP. Optimum instrumental analysis was achieved in a pH range between 0 and 3. A check for U and NO_3^- effects. Spike recovery was also done on random samples. Spike recoveries of 83 to 91 % were consistently observed with most of the recoveries being between 87 and 89 %.

Results and Discussion

The solubility of U in HNO_3 solutions containing DBP is expected to be a function of acid concentration, and U concentration as can be seen from the reaction governing precipitation (equation 1).

$$UO_2^{2+} + 2\,HDBP \leftrightarrow UO_2(DBP)_{2\,solid} + 2\,H^+ \quad (1)$$

Temperature is also a variable since soubility generally increases with increasing temperature. The reaction given above is the overall reaction to yield a precipitate. There are actually several reactions and associated equilibrium constants involved as shown in equations 2-4.[3]

$$HDBP \leftrightarrow H^+ + DBP^- \qquad K_a = [H^+][DBP^-]/[HDBP] \quad (2)$$
$$UO_2^{2+} + DBP^- \leftrightarrow UO_2(DBP)^{1+} \qquad \beta_1 = [UO_2(DBP)^{1+}]/[UO_2^{2+}][DBP^-] \quad (3)$$
$$UO_2(DBP)^{1+} + DBP^- \leftrightarrow UO_2(DBP)_{2\,solution} \qquad \beta_2 = [UO_2(DBP)_2]/[UO_2(DBP)^{1+}][DBP^-] \quad (4)$$

where the brackets in the equilibrium constants are for molal activity. At low concentrations of reactants, the activity is the same as the molal concentration because the activity coefficients are equal to one. The activity coefficients are not equal to one for the solutions being studied especially at the highest acid and U concentrations. The stability constant for the first step (β_1) is reported to be 10^4, but no value is reported for the second step.[9] The equation to define the solubility of the solid and solubility product constant (K_{sp}) for this reaction are shown in equation 5.

$$UO_2(DBP)_{2\,solid} \leftrightarrow UO_2^{2+} + 2\,DBP^- \qquad K_{sp} = [UO_2^{2+}]\,[DBP^-]^2 \quad (5)$$

Two values have been reported for K_{sp} in the literature which differ by a factor of 10.[7,8] A further complication is that two values are also reported for the acid dissociation constant (K_a) for HDBP, which differ by a factor of >5.[11,12] One of the values for K_{sp} was calculated using the higher value for K_a (equation 5), although the lower value is believed to be correct. Consequently, the literature data could not be used for calculation of the information required here.

The results from work on improvement of DBP analyses by ion chromatography will be presented first since the uncertainties shown in the analyses affect the interpretation of the solubility studies. Significant improvements were made during the course of these studies in the reproducibility and accuracy of DBP analyses. The principal problem was encountered only when U was present in solution. Initial results were scattered and could not be replicated at times. Replicates of 14 samples ranged from no difference to almost 26 % difference. A DI water blank was reported to contain 64 mg/L DBP and samples where DBP was known to be 110 mg/L varied from 58 to 95 mg/L. Submission of blanks with only DBP and standards with known quantities of U and DBP were included with other solubility samples to determine when problems were occurring and to establish a basis for reproducibility and uncertainty. Improvements made in sample pretreatment and elution have improved overall results although periodic variations do require samples to be analyzed a second time. Table 5 shows the results from analysis of standard samples nominally containing 50 mg/L DBP with 6 g/L U and 0.1 M HNO3 and 75 mg/L DBP with 18 g/L U and 0.5 M HNO_3. These results are very good because they were analyzed soon after submission, a standard sample was analyzed at the same time for spike recovery, and attention was paid to the chromatogram from the instrument to insure the correct peak is evaluated. Experience with the pretreatment method has also led to improved results.

Table 5. Analytical Results for Standard Samples

DBP in Standard, mg/L	DBP Analysis, mg/L	DBP in Standard, mg/L	DBP Analysis, mg/L
50	52	75	71
50	53	75	74
50	53	75	77
50	53	75	77
50	54	75	77
50	54	75	78
50	54	75	80
50	54	75	81
Average	53.4	Average	76.9
Standard Deviation	0.7	Standard Deviation	3.2
% Standard Deviation	1.4	% Standard Deviation	4.1

Table 6 shows the results of analysis of plant solutions taken at two different times which were split into five separate samples and interspersed with each other as well as some other plant samples. Note that one sample in each set was replicated so that six results are presented in the table. These samples had not been analyzed previously.

Table 6. Replicate Analyses of Plant EUS Samples

EUS Sample Date 2/7/98		EUS Sample Date 3/29/98	
Sample Number	DBP, mg/L	Sample Number	DBP, mg/L
3-107238	34	3-107240	45
3-107239	32	3-107241	39
3-107458	35	3-107462	48
3-107460	37	3-107462	44
3-107460	35	3-107463	44
3-107461	40	3-107464	43
Average	35.5	Average	43.8
Standard Deviation	2.7	Standard Deviation	2.9
Percent Std. Dev.	7.6	Percent Std. Dev.	6.6

Note that the percent standard deviation is slightly different for the two sets of samples, but is less than 10 % in both cases. Table 7 shows the averages of the split samples combined with several samples taken last year, two of which were analyzed earlier. The percent standard deviation is much higher and is attributed to a combination of small number of samples analyzed by the improved method, difference in samples, and the analytical error for the improved method. This does not appear to be a significant improvement in the overall uncertainty observed previously, even though the analytical error for the method is low. It should be possible to reduce the uncertainty in EUS sample results by submitting multiple samples instead of a single sample to allow averaging of the results. Three samples will allow statistics to be used to discard analyses or to signal that the sample should be reanalyzed. Submission of a known standard along with the samples can help determine whether problems are being encountered in the analytical method or in sampling and sample handling.

Table 7. Combined Error for EUS Samples

Sample Date	DBP Analysis, mg/L	Comments
6/4/97	43	One sample
8/6/97	57	One Sample
12/2/97	67	One sample
2/7/98	35.5	Average
3/29/98	43.8	Average
Average	49.3	
Standard Deviation	12.6	
Percent Std. Dev.	25.5	

The results from tests at 0 and 23°C were shown in Tables 1-3. The results from the first set of 0°C tests show that within the analytical uncertainties there is no difference in the DBP concentrations with 6 or 12 g/L U at 0.1 M HNO_3. The final DBP concentration is the same regardless of the starting DBP concentration. Reif noted that within his experimental conditions there was no difference in precipitation threshold for 3 or 6 g/L U solutions with 0.1 M HNO_3.[9] The concentration of DBP which can result in precipitation then is about 70 mg/L for both 6 and 12 g/L U solutions at 0°C. If this value is used as the safety limit with the operating limit set lower, the operating limit would be exceeded by one of the samples shown in Table 7. Therefore, the acidity must be increased to 0.5 M to allow existing freeze protection measures to define the low temperature for the tanks. It is uncertain whether the data at 0.5 M HNO_3 is different for 6 and 12 g/L U. The 6 g/L data has an average of 97 mg/L with a standard deviation of 3.5 mg/L. The 12 g/L data has an average of 86 mg/L with a standard deviation of 2.1 mg/L. There is no difference in the numbers at 2 standard deviations.

Tables 2 and 3 show that super-saturation occurs in the solutions such that actual formation of solids is delayed for as much as several months when the DBP concentration exceeds the solubility limit. For example, the second set of 0°C samples has been in the constant temperature bath for more than 4 weeks with only two of the five samples, which should precipitate actually having solids present (this assumes Table 1 analyses are correct). The samples, which precipitated took 7 to 8 days before solids appeared although the solubility limit was exceeded by 34 % and 50 %, respectively. Samples at 0.5 M HNO_3 with 110 mg/L DBP added initially have 13 % and 27 % excess DBP, but show no solids yet. This data confirms that super-saturation is not a steady state condition and precipitation will eventually occur.

The analytical data for DBP in the solutions at 23°C were not reliable having been analyzed prior to recent improvements in the analytical method; they are not reported. Observations about the time of precipitation are valid. Figures 1-4 summarize remaining data for different temperatures and acid concentrations. The data for 90 g/L U is not shown in these figures to provide clarity. The DBP concentrations required for precipitation at 90 g/L are higher than for the lower concentrations shown in the figures. This phenomenon is due either to the increased ionic strength or to the formation of the charged complex ion shown in equation 3 above. The ionic strength will change the activity coefficients affecting the activities in the system. High U concentration increases the amount of DBP present in solution as the complex ion, $UO_2(DBP)^{1+}$, thus more DBP is needed in solution to initiate precipitation.

Figures 1 and 2 show there is little change in DBP concentration required for precipitation as the U concentration changes at a constant acid concentration except for samples with no initial U present. Figures 3

Figure 1.

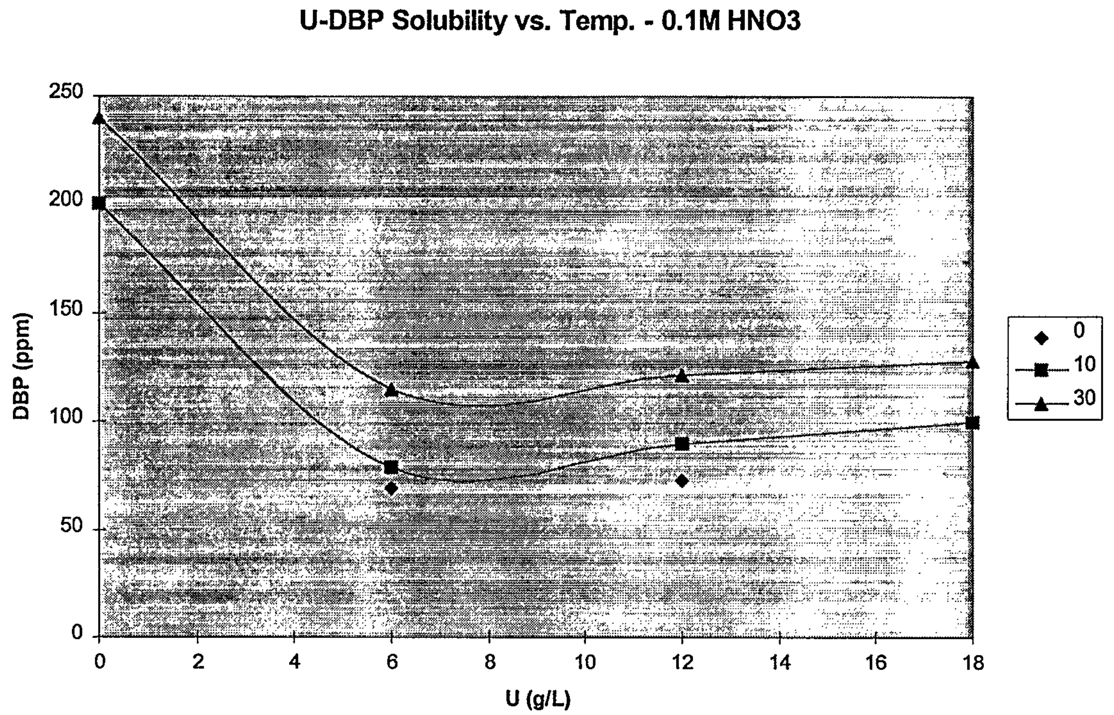


Figure 2.

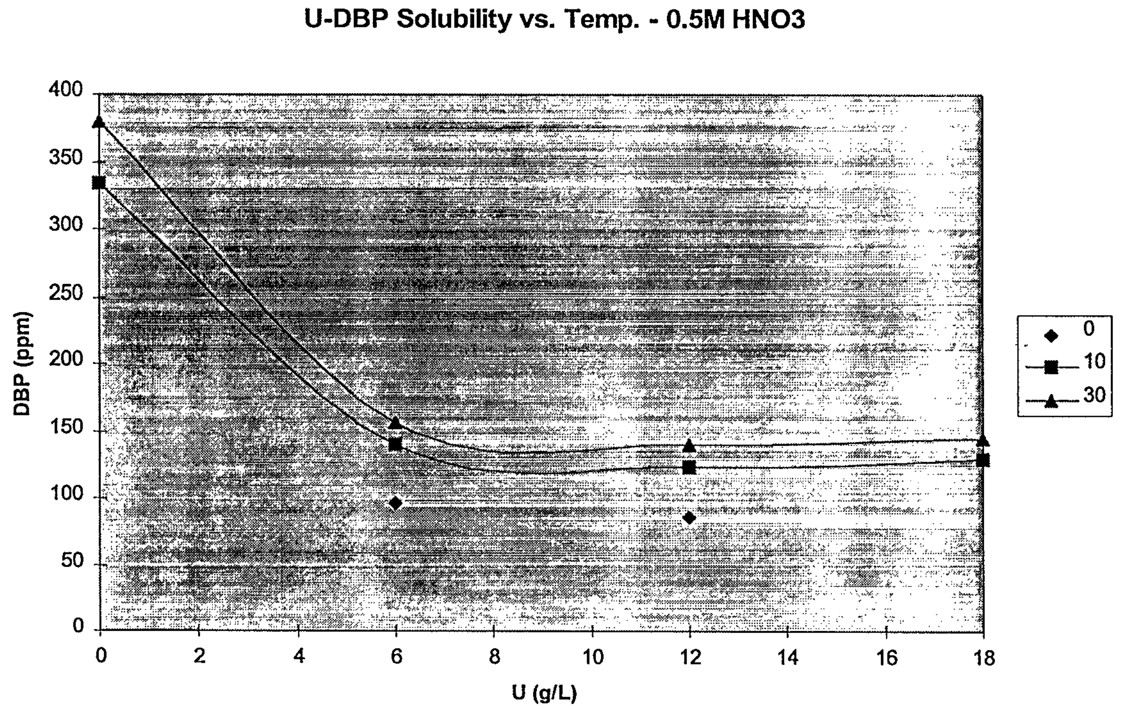


Figure 3.

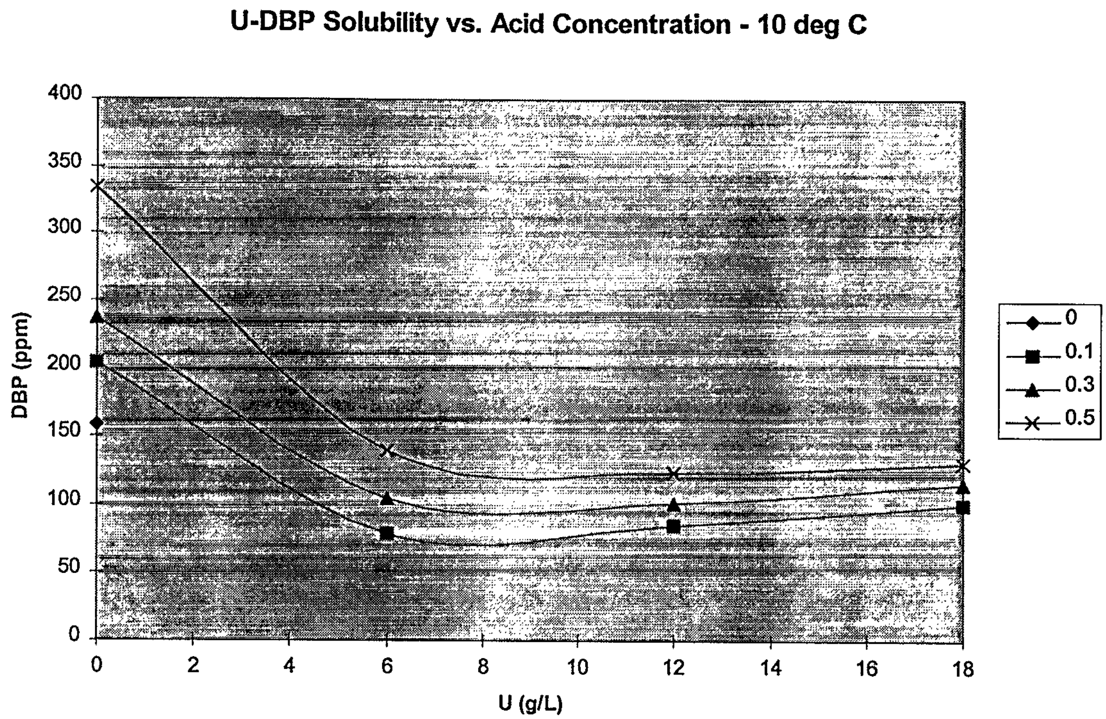
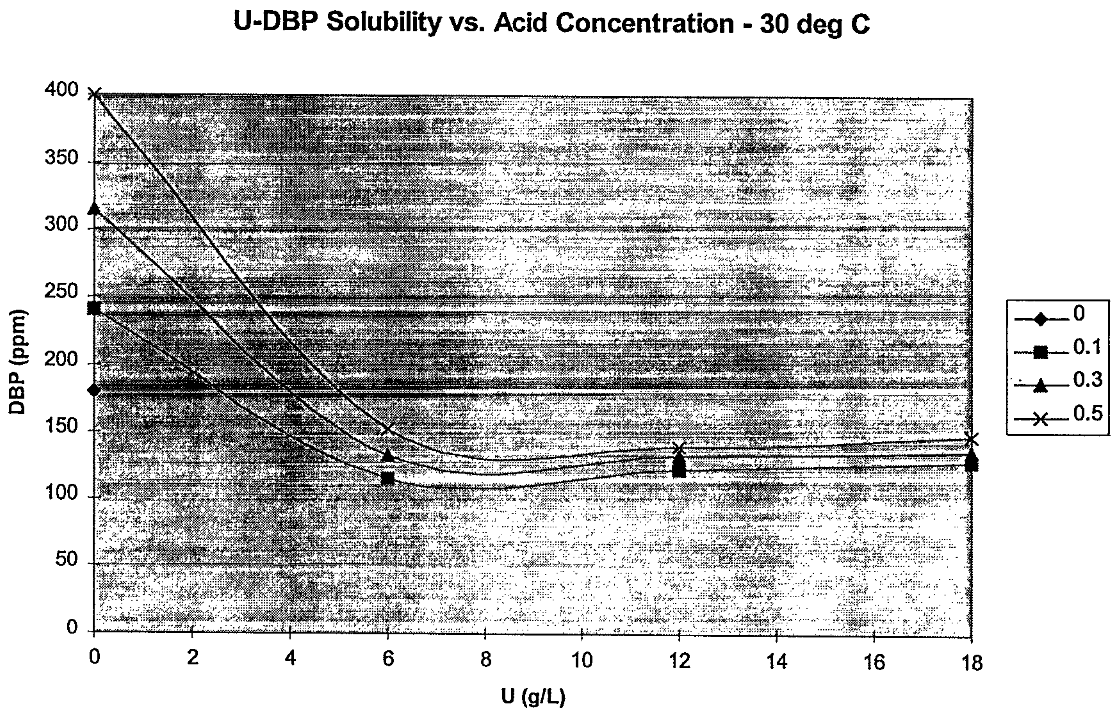


Figure 4.



and 4 show that the shape of the curves change slightly at higher acidity such that the apparent minimum concentration of DBP occurs at 12 g/L in 0.5 M HNO_3 instead of 6 g/L in 0.1 M HNO_3. In the range of acid concentration tested, increasing the acid concentration by a factor of 5 from 0.1 M to 0.5 M increases the DBP concentration required for precipitation by a maximum factor of 2. That much increase is only observed at the lowest concentration. The increase is less at 12 and 18 g/L U. Temperature appears to have the largest effect at low acidity, but the effect is reduced at higher acidity.

The data in the figures and tables can be used to establish limits for temperature, acid concentration and DBP concentration required to maintain safety during storage. It is clear from Figures 1 and 2 that in the range of uranium concentrations anticipated during storage and processing, 6-12 g/L, the data at 0.5 M HNO_3 and 0°C should be used to establish safety limits. Establishing limits based on this data allows existing freeze protection measures to ensure that precipitation will not occur.

Conclusions and Recommendations

The tests have shown that U-DBP solids will precipitate at concentrations potentially attainable during storage of enriched uranium solutions. Evaporation of the existing EUS solution without additional acidification will result in the precipitation of U-DBP solids; the same potential exists for evaporation of unwashed 1CU solutions. The most important variables of interest for present plant operations are HNO_3 and DBP concentrations. Uranium concentrations of 6 to 18 g/L do not significantly affect the DBP concentration at which precipitation can occur. Temperature is also an important variable controlling precipitation. Existing freeze protection measures should be relied on to maintain temperature above freezing. The data obtained in these tests can be used to set operating and safety limits for the plant. It is recommended that the data for 0°C with 0.5 M HNO_3 be used for setting the limits. A safety limit (Double Contingency Analysis) of 80 mg/L is 3 standard deviations below the average at 12 g/L and should be adequate to ensure that precipitation will not occur. The data shows that super-saturation can occur when the DBP concentration is as much as 50% above the solubility limit. However, super-saturation is not a steady state condition and precipitation will eventually occur. Therefore, super-saturation cannot be relied on for maintaining nuclear criticality safety.

The analytical method for determining DBP concentration in U solutions was improved so that analyses for a solution are accurate to within 10 %. However, the uncertainty of analytical results for periodic samples of the existing EUS solutions was only reduced from 30 % to 25 %. Thus, sampling appears to be the largest portion of the uncertainty for EUS sample results. The analytical method can be transferred to the plant analytical labs for more routine analysis of samples. It is recommended that more frequent sampling of the EUS tank be done. More than one sample (preferably 3) should be submitted in conjunction with a standard containing both 6-18 g/L U and 50-80 mg/L DBP. The analytical results obtained should be treated statistically to obtain an average value with outlying values excluded based on statistical tests.

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