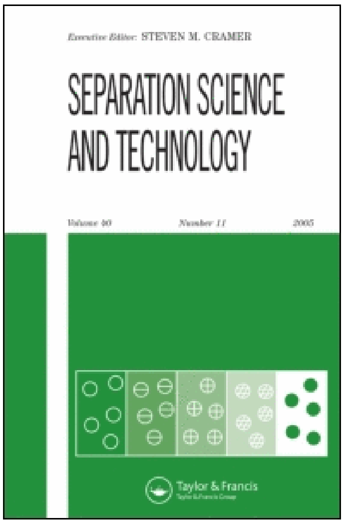

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URANIUM EXTRACTION SELECTIVITIES OF DIBUTYL CARBITOL AND TRIBUTYL PHOSPHATE IN THE SYSTEM $UO_2(NO_3)_2$-HNO_3-H_2O-$Al(NO_3)_3$-SOLVENT *

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ABSTRACT

Historically, both the BUTEX (dibutyl carbitol–based) and PUREX (tributyl phosphate–based) processes have been used for uranium recovery and purification. Currently, BUTEX- and PUREX-type extraction processes are being used in series for recovery of isotopically enriched uranium at the Oak Ridge Y-12 Plant. The use of two solvents is predicated on the differing selectivities of each with regard to the contaminant elements present in the uranium source stream. As part of efforts to streamline plant operations in response to decreasing throughput requirements, the Y-12 Development Division is evaluating options for converting the existing two-solvent operation to a single-solvent process.

At the request of the Y-12 Development Division, the Robotics and Process Division at the Oak Ridge National Laboratory has undertaken evaluation of solvents for use in a single-solvent recovery process. Initial efforts have been directed toward development of a single-solvent, dibutyl carbitol– or tributyl phosphate–based process that produces a product with purity equal to or exceeding what is currently obtained in the two-cycle, two-solvent operation. The test effort has

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involved both laboratory equilibrium determinations and engineering-scale process demonstrations in multistage flowsheets using centrifugal solvent extraction contactors. Excellent uranium recovery results have been obtained from both dibutyl carbitol– and tributyl phosphate–based solvent extraction flowsheets. Contaminant rejection performance by the two solvents is similar for many of the elements considered. Extraction of some contaminant elements by tributyl phosphate is significant enough to conclude that the solvent is not as selective for uranium as is dibutyl carbitol. This determination does not necessarily eliminate tributyl phosphate from consideration for use in a single-solvent process but does indicate a need for effective scrubbing of contaminants from uranium-loaded tributyl phosphate, possibly by partial reflux of the purified, aqueous uranyl nitrate product solution.

INTRODUCTION

Both dibutyl carbitol (diethylene glycol dibutyl ether) and tri-*n*-butyl phosphate are used in multistage operations for the selective extraction of uranium from aqueous nitric acid solutions. Tri-*n*-butyl phosphate (TBP) diluted with a hydrocarbon fraction is the solvent of choice for the vast majority of uranium recovery and purification operations, most of which are based on the PUREX (Plutonium and URanium EXtraction) process concept. Dibutyl carbitol (DBC) is the solvent used in processes based on the BUTEX concept, which was developed primarily by Atomic Energy of Canada, Ltd., and by the United Kingdom Atomic Energy Authority.[1,2]

At present, the BUTEX process is applied domestically at production scale only at the United States Department of Energy's (U.S. DOE) Oak Ridge Y-12 Plant. In fact, the Y-12 facility utilizes both DBC- and TBP-based extraction processes to purify isotopically enriched uranium from various machining and casting operations. The two processes are configured in series, with the DBC-based primary process receiving aqueous dissolvates and leachates from low-purity-uranium recovery processes (e.g., the leaching of ash produced by the incineration of combustible, contaminated waste). Uranium purified by extraction with DBC is recovered as aqueous uranyl nitrate by contacting the uranium-loaded solvent with dilute nitric acid. The product solution is then concentrated and combined with aqueous solutions from higher-purity–uranium recovery operations, including the dissolution of uranium machining and casting remnants. The combined solution becomes the aqueous feed stream for the TBP-based secondary extraction system.

The rationale for applying two sequential extraction steps using different solvents is to take advantage of the different selectivities of the solvents for contaminant elements, thereby obtaining a more nearly pure uranium product. For example, DBC has little affinity for zirconium. Therefore, zirconium present in feed to a DBC-based extraction system is rejected to the raffinate stream. By comparison, TBP is less effective for zirconium/uranium separation. In addition, zirconium forms strong complexes with the degradation products of TBP—dibutyl and monobutyl phosphoric acids—which are formed by the acid-catalyzed hydrolysis of TBP. As zirconium is difficult to remove from these compounds, it tends to accumulate in the solvent, leading to a loss in uranium loading capacity by the solvent. In this instance, placement of a DBC-based extraction process upstream of a TBP-based purification step improves the uranium recovery performance of the latter process and may mitigate the need to regenerate the TBP solvent. While DBC does degrade somewhat, regeneration is not required as a fraction of the solvent is constantly removed from the process as a result of its solubility in aqueous solutions. MacKay[3] has reported the solubility of DBC in water to be 3.27 g/liter, versus a TBP solubility in water of 0.25 g/liter. DBC lost to aqueous streams is replaced with clean solvent, which results in continuous renewal of the process solvent inventory.

The work reported is part of an effort to eliminate the use of the DBC-based extraction process from the existing two-solvent processing configuration used at the Y-12 facility, both to simplify overall process operation and to reduce costs. In the subject effort, equilibrium tests have been performed to evaluate the significance of nitric acid and aluminum nitrate salting, uranium concentration, and solvent type on the coextraction of contaminants during uranium transfer.

Alternatives to the existing extraction process configuration currently under consideration are the use of the TBP/diluent solvent in two systems in series, or use of the solvent in a single expanded process. Due to the uniqueness of the Y-12 Plant's role in the U.S. DOE's nuclear materials complex, the performance of any replacement alternative to the existing process must be demonstrated conclusively prior to implementation. Of primary concern is the ability of a single TBP-based extraction system to provide the same contaminant rejection capability currently provided by the two-extraction, two-solvent process.

TESTING CONSIDERATIONS

Pure TBP has a specific gravity of 0.982 at 20°C, which differs only slightly from the specific gravities of the aqueous solutions (water and dilute nitric acid) which are used to strip extracted uranium from the solvent. Typically, lower density hydrocarbon fractions are blended with the TBP to obtain organic/aqueous phase density differences which will promote effective phase separation. The literature indicates that a 30 vol % blend of TBP in a hydrocarbon diluent is the formulation most commonly used in uranium recovery processes.[4] Diluents used are *n*-dodecane, normal paraffin hydrocarbon (a predominantly C_{12} fraction), and kerosene-like hydrocarbon fractions (including those sold under the tradenames "odorless mineral spirits" and AMSCO). AMSCO, which is used in the secondary extraction system at the Oak Ridge Y-12 Plant, was used as the diluent in the reported work.

The extractions of uranium by DBC and TBP are generally accepted to be described by the expressions

$$UO_2^{2+} + 2NO_3^- + 4H_2O + 2DBC \Leftrightarrow UO_2(NO_3)_2 \cdot 4H_2O \cdot 2DBC \qquad \text{and}$$

$$UO_2^{2+} + 2NO_3^- + 2TBP \Leftrightarrow UO_2(NO_3)_2 \cdot 2TBP,$$

respectively. Results of several studies indicate that uranium is extracted into the organic phase only in the neutral (associated) form.[5] Published uranium extraction equilibrium data indicate that DBC is an effective uranium extractant only when nonextracting nitrate salting agents are present in the aqueous phase. Particularly effective salting agents are the nitrates of aluminum and calcium. In addition to enhancing uranium extraction, the cations of these salts complex fluoride ions, which are typically present in the feed to the primary extraction process due to the use of hydrofluoric acid in dissolution processes. Free fluoride ions in the feed solution are undesirable from an equipment corrosion standpoint. Use of nonextracting salting agents is not required to obtain high uranium extraction efficiencies with TBP/diluent blends—salting by nitric acid at aqueous-phase concentrations in the 3 to 5 *M* range is sufficient. However, due to the fluoride complexation consideration, aluminum nitrate was added to the aqueous feed solutions used in extract tests using TBP.

EXPERIMENTAL

Procedure

Feed solution conditions were selected which (1) are representative of optimal conditions for multistage uranium extraction and stripping operations and (2) include contaminants at levels that are similar to those encountered in uranium recovery operations. Aqueous feeds were formulated by blending concentrated uranyl nitrate, aluminum nitrate, nitric acid, and contaminant spike solutions in carefully measured proportions. The effects of four variables—solvent, $Al(NO_3)_3$ concentration, nitric acid concentration, and uranium concentration—were evaluated. Each variable was applied at two levels, resulting in a total of 2^4 possible treatment combinations. To reduce the amount of data requiring processing, a half-factorial experiment design was used. Therefore, the total number of outcomes obtained was 2^{4-1}. Variable levels and treatment combinations are listed in Table 1. Nominal contaminant element concentrations in initial aqueous feed solutions are presented in Table 2.

In each test, equal volumes of aqueous feed solution and extractant were combined and agitated such that a fine dispersion of phases was maintained for a minimum of five minutes. (Results of tests performed outside the current study verified that this mixing period is sufficient to achieve equilibrium in the chemical systems under consideration.) After mixing, the dispersions were allowed to separate by gravity for not less than 10 min. Equilibrium distribution determinations between aqueous and organic solutions were made at ambient conditions (25°C). Samples of each phase were then withdrawn using a pipettor. Aqueous solutions which contained

Table 1. Treatment Combinations Used in Testing

Test number	HNO_3 conc. (*M*)	$Al(NO_3)_3$ conc. (*M*)	Uranium conc. (g/L)	Solvent used
1	0.4	0.07	0	DBC
2	0.4	0.36	54	DBC
3	1.0	0.07	0	DBC
4	1.0	0.36	54	DBC
5	0.4	0.07	54	30% TBP
6	0.4	0.36	0	30% TBP
7	1.0	0.07	54	30% TBP
8	1.0	0.36	0	30% TBP

Table 2. Nominal Contaminant Concentrations in Contaminant Feed Solutions

Element	Concentration, mg/L (ppm)	Element	Concentration, mg/L (ppm)
Arsenic	35	Calcium	700
Lanthanum	35	Manganese	35
Thorium	35	Cobalt	35
Lead	35	Nickel	70
Vanadium	35	Beryllium	35
Copper	700	Lithium	35
Potassium	70	Zinc	70
Boron	70	Erbium	70
Magnesium	70	Strontium	35
Chromium	350	Barium	35
Cadmium	700	Sodium	700
Tungsten	35	Iron	700
Tantalum	35	Zirconium	70
Molybdenum	35	Tin	35
Silicon	35	Titanium	35

no uranium were analyzed directly for contaminant concentrations. Samples containing uranium were first stripped by repeated contact (up to five times) with 0.1 *M* trioctyl phosphine oxide (TOPO) in cyclohexane. Stripping of uranium was required prior to contaminant analysis by atomic emission spectroscopy to prevent signal interference due to uranium decay emissions. Organic samples were not analyzed because the instrument used was configured for aqueous samples only.

In a side experiment, a single control contaminant formulation was subdivided and samples were contacted with the 0.1 *M* TOPO extractant to determine if the sample preparation step resulted in removal of contaminant elements. These samples were analyzed, and the results were compared with those obtained from control samples (i.e., samples which had not been treated with the TOPO blend). Neither uranium nor aluminum nitrate were present in the control formulation, and there was no variation in the initial, aqueous-phase nitric acid concentration.

Materials

Dibutyl carbitol and tri-*n*-butyl phosphate were of reagent-grade purity (99+%) and were used as received from the Aldrich Chemical Company (product numbers 20562-1 and 240494, respectively). The diluent used in TBP blends was Mineral Spirits 66, obtained from Ashland Chemical Company. Nitric acid used to formulate aqueous feed solutions was Tracepure (TM) grade (ultra-high purity), from J. T. Baker Company. All water used for the preparation of solutions was passed through a Barnstead Nanopure (TM) filtration/deionization system prior to use.

Uranyl nitrate solutions used in testing were produced by dissolving uranyl nitrate hexahydrate that had been evaporated to dryness after purification in a multistage, liquid-liquid extraction system. Aluminum nitrate was added to aqueous solutions by dissolution of reagent-grade aluminum nonahydrate crystals, which were obtained from the J. T. Baker Company. Contaminant elements were added as nitrates to the aqueous feed solutions using analytical chemistry standard solutions supplied by High Purity Standards of Charleston, South Carolina. Chemical analysis materials were obtained as American Chemical Society reagent-grade materials and were used as received.

Chemical Analysis Procedures

Analysis for contaminant concentrations was performed by Inductively Coupled Plasma/Atomic Emission Spectroscopy (ICP/AES). The instrument used was a Perkin-Elmer

Optima 3000 DV spectrophotometer, operating under an ICP Winlab version 1.0 software interface. Spectra were observed with the instrument operated in the axial position. Preliminary tests were performed to evaluate spectra for interelement interferences. Where necessary, wavelengths evaluated were changed to eliminate these interferences. A listing of the contaminant elements analyzed for, and the emission wavelengths examined, is presented in Table 3.

Acid concentration determinations were made by titrations with a certified, standardized sodium hydroxide solution, using bromothymol blue as the endpoint indicator. A solution of sodium fluoride and potassium oxalate was used to complex metals present in solution which could otherwise interfere with the determination.

RESULTS AND DISCUSSION

Contaminant Rejection

Contaminant rejection fractions are presented in Table 4. The rejection fraction defined as that fraction of an element initially present in the aqueous solution which remains in the aqueous phase after contact with an organic solvent. Conversely, the rejection fraction may be interpreted as the fraction of an element which is not extracted (i.e., is rejected) by a solvent. Rejection fractions were calculated by dividing aqueous raffinate concentration values by the concentration in the aqueous solution prior to extraction. Only aqueous phase results were used to evaluate contaminant rejection in order to compensate for sample preparation effects which were identified as part of current study. These effects were corrected for by application of identical pretreatment of corresponding feed and raffinate samples. Use of identical pretreatments and description of results as fraction (ratios) effectively eliminates preparation effects from the rejection fraction values.

Results from extraction using DBC (Tests 1 through 4) indicate that the solvent is a poor extractant for most of the contaminants considered. Exceptions to this general observation occur primarily at conditions of higher aqueous aluminum nitrate, uranyl nitrate, and nitric acid

Table 3. Contaminant Elements and Emission Wavelengths Examined

Element	Wavelength (nm)	Element	Wavelength (nm)
Arsenic	193.696	Calcium	317.933
Lanthanum	379.478	Manganese	257.610
Thorium	283.730	Cobalt	228.616
Lead	220.353	Nickel	232.003
Vanadium	292.402	Beryllium	313.107
Copper	324.754	Lithium	460.286
Potassium	766.491	Zinc	213.856
Boron	249.773	Erbium	337.721
Magnesium	279.079	Strontium	460.733
Chromium	205.552	Barium	233.527
Cadmium	214.438	Sodium	330.237
Tungsten	207.911	Iron	238.204
Tantalum	226.230	Zirconium	343.823
Molybdenum	202.030	Tin	235.484
Silicon	251.611	Titanium	334.941

concentrations, and are limited to the elements lanthanum, thorium, arsenic, copper, zinc, cadmium, chromium, and silicon. Increased contaminant extractions by DBC at higher $Al(NO_3)_3$ and nitric acid conditions are an expected result of increased salting. (Increased nitrate ion concentration in the aqueous phase increases the degree to which aqueous cations are associated into extractable nitrate forms.) At the 54-g/L concentration applied as the higher uranium condition, uranium loading of the solvent can be no greater than 11% of saturation, which is apparently not high enough to retard extraction of contaminants present at relatively low concentrations. Instead, the presence of uranyl nitrate in the aqueous phase may supplement salting from the other major nitrate sources (aluminum nitrate and nitric acid).

The results in Table 4 indicate the 30% TBP/diluent solvent is a more effective solvent for the contaminants under consideration than is DBC. Greater than 20% extraction of thorium, zinc, erbium, and zirconium is indicated over a range of test conditions. Contaminant rejection

Table 4. Rejection of Contaminants by DBC and 30% TBP/diluent[a]

Element	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	Test 8
As	0.965	0.788	0.997	0.776	1.029	0.612	1.014	0.972
Ca	1.027	1.098	0.943	0.920	0.993	0.773	0.991	0.942
La	1.052	1.018	0.988	0.814	0.945	0.727	0.805	0.974
Mn	1.035	1.076	0.978	0.923	0.963	0.749	0.961	0.996
Th	1.048	0.671	1.008	0.222	0.493	0.014	0.034	0.025
Co	1.031	1.066	0.975	0.920	0.991	0.761	1.006	0.968
Pb	1.037	1.099	0.977	0.959	0.967	0.777	0.971	0.924
Ni	1.044	1.088	0.965	0.824	0.982	0.764	0.980	0.890
V	1.039	1.040	0.977	0.885	0.691	0.743	0.951	0.959
Be	1.020	1.116	0.955	0.912	0.954	0.742	0.915	1.060
Cu	1.058	0.977	0.955	0.792	1.011	0.716	1.113	1.097
Li	1.041	1.131	0.968	0.981	0.988	0.754	0.991	0.909
K	1.068	1.175	0.978	1.015	0.946	0.756	0.844	1.026
Zn	1.037	1.924	0.972	0.422	0.746	0.730	0.735	0.975
B	1.012	0.951	0.934	0.872	0.969	0.731	0.985	0.975
Er	1.051	1.121	1.000	0.743	0.637	0.714	0.672	0.939
Mg	1.048	1.183	0.952	1.126	0.987	0.775	1.169	0.927
Sr	1.061	1.246	0.986	1.120	0.922	0.791	0.813	0.989
Cr	1.038	0.986	0.995	0.817	1.013	0.748	1.076	0.998
Ba	1.028	1.086	0.971	0.913	0.994	0.745	0.984	0.976
Cd	1.028	0.860	0.955	0.685	1.043	0.726	1.284	0.963
Na	1.033	1.215	0.958	1.141	0.913	0.842	0.771	0.980
W	0.827	1.142	0.992	1.017	0.880	0.558	0.719	0.860
Fe	1.039	1.027	0.972	0.872	0.985	0.735	1.034	0.930
Ta	0.911	1.000	0.970	1.084	0.933	0.538	0.751	1.149
Zr	1.026	1.422	0.993	1.230	0.801	0.349	0.424	0.543
Mo	1.003	1.217	1.000	0.929	0.812	0.717	0.757	0.916
Sn	1.026	1.139	1.000	1.018	0.939	0.766	0.874	0.937
Si	0.895	0.933	0.923	0.805	1.020	0.736	1.158	0.997
Ti	1.028	1.180	0.992	1.021	0.898	0.748	0.816	0.981

[a] DBC was used as the solvent in Tests 1 through 4. In Tests 5 through 6, 30% TBP in a hydrocarbon diluent was used. Aqueous solution compositions used in testing were as described in Table 1.

performance under conditions of Test 6 (high aluminum nitrate, low uranium, and low nitric acid concentrations) are poor for all elements evaluated. On first inspection, the uniformly low rejection fractions from Test 6 might be attributed to experimental or analytical error. However, Test 6 results do not deviate from results from other tests by any constant proportion as they might be expected to do if a dilution error had been made during sample preparation. The possibility of error due to sample contamination is discounted as no analysis procedures were performed on the Test 6 feed sample which were not also performed on the raffinate sample, and contamination of the raffinate sample alone would result in artificially high rejection fractions. In any case, it is unlikely that a contamination error would result in uniformly decreased rejection fractions for all elements.

The conditions of Test 6 can reasonably be considered to be optimal for extraction of contaminant elements. Higher $Al(NO_3)_3$ concentration in the aqueous phase results in a salting effect without any corresponding solvation site occupation by the nitrate, which is essentially inextractable by either DBC or TBP. Similarly, occupation of solvation sites by extractable nitric acid and uranium is minimal, as uranium was not present in the test and the nitric acid concentration was at the lower value condition.

The experiment performed was designed to permit evaluation of the test variables solvent, $Al(NO_3)_3$ concentration, and uranium concentration on contaminant element rejection (or extraction) As designed, analysis of parameter (effect) significance required dividing (blocking) the data according to nitric acid concentration. As a result, the significance of the acid concentration effect cannot be determined directly. The experiment design used reflects practical consideration of conditions suitable for extraction of uranium by both solvents. Neither DBC nor TBP/diluent blends are effective uranium extractants in the absence of a source of nitrate ions. Results of prior tests indicate that nitric acid at low-to-moderate concentration does not produce a salting effect sufficient to obtain efficient uranium extraction by DBC. Prolonged contact of DBC with higher concentrations of the acid results in potentially explosive instability of the solvent. Nitric acid does enhance uranium extraction by TBP/diluent blends only up to moderate concentrations, beyond which the effect is reversed. Therefore, with regard to uranium extraction applications, wide variation of nitric acid concentration is not a practical consideration when evaluating contaminant rejection by DBC and TBP/diluent blends.

Rejection fractions, calculated by dividing contaminant concentrations in the aqueous raffinates by the aqueous feed concentration, are presented in Table 4. Analytically determined feed solution contaminant values were used to calculate these fractions to provide some correction for sample preparation effects. The data in the table indicates that DBC does not generally extract the included contaminants significantly. Exceptions to the general observation occur primarily at conditions of higher aqueous $Al(NO_3)_3$ and nitric acid concentrations, particularly for the elements lanthanum, thorium, arsenic, copper, zinc, cadmium, chromium, and silicon. Considerably more instances of poor selectivity by the 30% TBP solvent (i.e., > 20% uptake of a contaminant by the solvent) are indicated. Particularly poor performance is indicated at high aluminum nitrate concentrations, coupled with low nitric acid and uranium concentrations. This result is not unexpected, as solvent selectivity typically increases when an increased fraction of solvation sites are occupied by extracted acid or $UO_2(NO_3)_2$.

Evaluation of the significance of test variables on outcomes (i.e., rejection fractions) was accomplished by determining the distribution of parameter effects against a normal distribution, according to methods described by Anderson and McLean[6] and by Davies.[7] Summed squares (SS) of the outcomes were calculated by summing outcomes for each effect according to the signs shown in Table 5. The table shown reflects the blocking of the data into two groups, one for each nitric acid concentration level. As an example, the SS value for effect A is $(Y_2 + Y_6 - Y_1 - Y_5)^2/4$, where each Y_i is the yield (or outcome) from a test i and the divisor 4 is the number of outcomes obtained. F-normal distribution values were calculated by dividing the SS for an effect by an estimate of the mean square error. The error estimate was obtained by performing replicate tests under the conditions in Test 2 and Test 3. Significance was tested for at 95% of the distribution by dividing the F-values obtained by 3.84, which is the F-value at the 95th percentile of the normal distribution. Results from tests in each acid condition block are presented in Tables 6 and 7. Values greater than 1 are indicative of parameter effects which significantly affect contaminant rejection at a 95% level of confidence.

Table 5. Effect Versus Treatment Combination Assignments

Effect	Treatment combination			
	Test 1	Test 2	Test 5	Test 6
A = $Al(NO_3)_3$ conc.	-	+	-	+
U = Uranium conc.	-	+	+	-
S = solvent	-	-	+	+
AU	+	+	-	-
AS	+	-	-	+
US	+	-	+	-

It should be noted that significance ratios presented in Tables 6 and 7 for two-factor interaction effects are each equal to a single-effect significance result. These two-factor interactions are considered aliases for the single-factor effects and are not of primary interest in the current study. They are included only for completeness.

Based on the 95% confidence level criteria, aluminum nitrate concentration appears to significantly affect the extractions of thorium and cadmium at both acid concentration conditions applied. At the lower acid concentration, $Al(NO_3)_3$ also affects the extractions of zinc and arsenic. At the higher acid concentration, the extraction of tantalum appears to be affected by aluminum nitrate concentration.

The initial aqueous-phase uranium concentration affects the extraction of zinc at both nitric acid concentrations considered. At the lower acid condition, a significant uranium concentration effect is also indicated in extractions of tungsten, tantalum, and zirconium. At the higher nitric acid level, the extraction of throium, erbium, and magnesium are affected by the aqueous uranium concentration at a 95% confidence level.

At the higher acid concentration, the choice of solvent appears to significantly affect the extractions of thorium, copper, cadmium, zirconium, and silicon. At the lower-acid-concentration value, the choice of solvent was found to significanlty affect extraction of 16 of the 30 elements considered: thorium, vanadium, beryllium, lithium, potassium, zinc, erbium, magnesium,

Table 6. Effect Significance[a] on Contaminant Rejection at 0.4*M* HNO_3

	Effects[b]					
Element	A	U	S	AU	AS	US
As	2.16	0.35	0.08	0.08	0.35	2.16
Ca	0.13	0.52	0.79	0.79	0.52	0.13
La	0.39	0.21	0.97	0.97	0.21	0.39
Mn	0.18	0.40	0.97	0.97	0.40	0.18
Th	4.48	0.06	8.97	8.97	0.06	4.48
Co	0.23	0.43	0.73	0.73	0.43	0.23
Pb	0.10	0.39	0.94	0.94	0.39	0.10
Ni	0.19	0.42	0.91	0.91	0.42	0.19
V	0.02	0.02	2.54	2.54	0.02	0.02
Be	0.08	0.57	1.18	1.18	0.57	0.08
Cu	0.86	0.28	0.58	0.58	0.28	0.86
Li	0.13	0.64	1.13	1.13	0.64	0.13
K	0.04	0.54	1.79	1.79	0.54	0.04
Zn	4.63	4.97	13.46	13.46	4.97	4.63
B	0.55	0.19	0.42	0.42	0.19	0.55
Er	0.13	0.00	4.11	4.11	0.00	0.13
Mg	0.04	0.74	1.34	1.34	0.74	0.04
Sr	0.02	0.61	2.15	2.15	0.61	0.02
Cr	0.61	0.28	0.42	0.42	0.28	0.61
Ba	0.22	0.57	0.86	0.86	0.57	0.22
Cd	1.43	0.13	0.09	0.09	0.13	1.43
Na	0.07	0.39	1.48	1.48	0.39	0.07
W	0.00	2.47	1.72	1.72	2.47	0.00
Fe	0.42	0.35	0.73	0.73	0.35	0.42
Ta	0.57	1.43	1.18	1.18	1.43	0.57
Zr	0.02	4.39	10.28	10.28	4.39	0.02
Mo	0.09	0.58	2.92	2.92	0.58	0.09
Sn	0.02	0.50	1.29	1.29	0.50	0.02
Si	0.37	0.63	0.03	0.03	0.63	0.37
Ti	0.00	0.56	1.92	1.92	0.56	0.00

[a] (Values > 1.0 indicate a > 95% level of confidence that a factor has a significant affect on the rejection or extraction of an element.)

[b] Effects: A = $Al(NO_3)_3$ concentration
U = uranium concentration
S = solvent selection (DBC or TBP/diluent)
AU = aluminum/uranium concentration interaction
AS = aluminum/solvent interaction
US = uranium/solvent interaction

Table 7. Effect Significance[a] on Contaminant Rejection at 1.0*M* HNO_3

	Effects[b]					
Element	A	U	S	AU	AS	US
As	0.42	0.20	0.28	0.28	0.20	0.42
Ca	0.03	0.00	0.03	0.03	0.00	0.03
La	0.00	0.72	0.00	0.00	0.72	0.00
Mn	0.00	0.05	0.02	0.02	0.05	0.00
Th	3.85	3.68	8.36	8.36	3.68	3.85
Co	0.05	0.00	0.04	0.04	0.00	0.05
Pb	0.03	0.00	0.01	0.01	0.00	0.03
Ni	0.33	0.02	0.04	0.04	0.02	0.33
V	0.04	0.06	0.01	0.01	0.06	0.04
Be	0.06	0.22	0.07	0.07	0.22	0.06
Cu	0.20	0.13	1.31	1.31	0.13	0.20
Li	0.03	0.06	0.01	0.01	0.06	0.03
K	0.29	0.13	0.09	0.09	0.13	0.29
Zn	0.59	3.81	0.61	0.61	3.81	0.59
B	0.03	0.02	0.15	0.15	0.02	0.03
Er	0.00	1.68	0.11	0.11	1.68	0.00
Mg	0.03	1.06	0.00	0.00	1.06	0.03
Sr	0.59	0.01	0.57	0.57	0.01	0.59
Cr	0.40	0.06	0.42	0.42	0.06	0.40
Ba	0.03	0.02	0.04	0.04	0.02	0.03
Cd	2.14	0.02	2.25	2.25	0.02	2.14
Na	0.93	0.00	0.74	0.74	0.00	0.93
W	0.17	0.08	1.13	1.13	0.08	0.17
Fe	0.25	0.00	0.09	0.09	0.00	0.25
Ta	1.60	0.49	0.14	0.14	0.49	1.60
Zr	0.77	0.09	9.62	9.62	0.09	0.77
Mo	0.05	0.32	0.40	0.40	0.32	0.05
Sn	0.04	0.01	0.26	0.26	0.01	0.04
Si	0.47	0.01	1.11	1.11	0.01	0.47
Ti	0.23	0.11	0.29	0.29	0.11	0.23

[a] (Values > 1.0 indicate a > 95% level of confidence that a factor has a significant affect on the rejection or extraction of an element.)

[b] Effects: A = $Al(NO_3)_3$ concentration
U = uranium concentration
S = solvent selection (DBC or TBP/diluent)
AU = aluminum/uranium concentration interaction
AS = aluminum/solvent interaction
US = uranium/solvent interaction

strontium, sodium, tungsten, tantalum, zirconium, molybdenum, tin, and titanium. Review of rejection fractions in Table 4 indicates that 30% TBP rejects contaminants less effectively than does DBC for all elements affected by choice of solvent, with the exception of silicon. Comparison of solvent effect results in Tables 6 and 7 indicates that the selectivity of the 30% TBP extractant is improved by increasing the acid concentration in the system. This improvement is likely the result of increased occupation of solvation sites by extracted acid and by slightly increased uranium extraction due to greater nitric acid salting.

Since the results indicate that aluminum nitrate concentration significantly affects contaminant rejection in a very limited number of cases, a third data analysis was performed to determine acid concentration–related effects without regard to $Al(NO_3)_3$ concentration. The results are presented in Table 8. As before, two-factor interaction effects are aliases for single-factor effects and are not be considered. The results indicate that only the extraction of thorium, and to a lesser degree cadmium, are significantly affected by changes in acid concentration alone.

Effects of TOPO Uranium Strip Prior to ICP/AES Analysis

Concentrations of contaminant elements in a aqueous control solution and in samples of the control solution after one and two extractions with 0.1 *M* TOPO in cylcohexane, are presented in Table 9. The solvent-to-feed volume ratio in the extractions was 1.0. As stated previously, the test was performed to determine if removal of uranium from aqueous samples by contact with TOPO also results in the removal of other elements from the samples. The data indicate that a considerable percentage of most contaminants present is removed in a single TOPO strip. Removal percentages for a single TOPO treatment ranged from 11.1% for beryllium to 88.7% for thorium. A second stripping resulted in significant additional removals (>10%) of thorium, erbium, zirconium, and molybdenum. Second strip results for zinc exhibited a significant variation and were therefore inconclusive. Second strip removal percentages for the remaining contaminants ranged from -1.2% for magnesium (the negative value reflecting analytical error) to 7.6% for tantalum.

Table 8. Effect Significance[a] on Contaminant Rejection Without $Al(NO_3)_3$ Consideration

	Effects[b]					
Element	H	U	S	HU	HS	US
As	0.37	0.11	0.41	0.41	0.11	0.37
Ca	0.15	0.02	0.00	0.00	0.02	0.15
La	0.27	0.44	0.02	0.02	0.44	0.27
Mn	0.04	0.13	0.00	0.00	0.13	0.04
Th	10.22	0.78	3.45	3.45	0.78	10.22
Co	0.11	0.05	0.00	0.00	0.05	0.11
Pb	0.09	0.01	0.07	0.07	0.01	0.09
Ni	0.60	0.10	0.00	0.00	0.10	0.60
V	0.08	1.09	0.46	0.46	1.09	0.08
Be	0.00	0.28	0.04	0.04	0.28	0.00
Cu	0.20	0.76	0.41	0.41	0.76	0.20
Li	0.12	0.00	0.10	0.10	0.00	0.12
K	0.00	0.11	0.07	0.07	0.11	0.00
Zn	0.91	4.35	0.42	0.42	4.35	0.91
B	0.11	0.13	0.02	0.02	0.13	0.11
Er	0.00	2.27	0.29	0.29	2.27	0.00
Mg	0.00	0.12	0.41	0.41	0.12	0.00
Sr	0.10	0.00	0.44	0.44	0.00	0.10
Cr	0.34	0.26	0.15	0.15	0.26	0.34
Ba	0.11	0.06	0.01	0.01	0.06	0.11
Cd	1.09	0.42	0.52	0.52	0.42	1.09
Na	0.18	0.01	0.48	0.48	0.01	0.18
W	0.18	0.27	0.07	0.07	0.27	0.18
Fe	0.30	0.08	0.00	0.00	0.08	0.30
Ta	0.93	0.01	0.05	0.05	0.01	0.93
Zr	0.02	1.30	5.08	5.08	1.30	0.02
Mo	0.01	0.19	0.25	0.25	0.19	0.01
Sn	0.00	0.00	0.17	0.17	0.00	0.00
Si	0.08	0.03	0.61	0.61	0.03	0.08
Ti	0.04	0.05	0.18	0.18	0.05	0.04

[a] (Values > 1.0 indicate a > 95% level of confidence that a factor has a significant affect on the rejection or extraction of an element.)

[b] Effects: H = nitric acid concentration
U = uranium concentration
S = solvent selection (DBC or TBP/diluent)
HU = nitric acid/uranium concentration interaction
HS = nitric acid/solvent interaction
US = uranium/solvent interaction

Table 9. Results of TOPO Sample Preparation on Control Contaminant Solutions

Element	Concentrations without TOPO extraction (ppm)		Concentration after 1 TOPO extraction (ppm)		Concentration after 2 TOPO extractions (ppm)		Average percent removed	
	Replicate 1	Replicate 2	Replicate 1	Replicate 2	Replicate 1	Replicate 2	After 1 extraction	After 2 extractions
As	55	58.5	49.3	48.8	47.4	46.4	13.6	4.4
Ca	1110	1190	861	855	858	826	25.4	1.9
La	649	371	269	265	268	255	47.6	2.1
Mn	55.8	59	45.8	45.2	45.6	43.7	20.7	1.9
Th	57.9	61.4	7.05	6.44	2.09	2.27	88.7	67.7
Co	56.2	59.5	43.9	43.4	44	41.8	24.5	1.7
Pb	55	58.8	37	37.2	38.1	36.1	34.8	0.0
Ni	111	118	83.2	82.4	83.8	78.8	27.7	1.8
V	55.4	58.6	44.6	44.1	43.7	42.8	22.2	2.5
Be	53.9	57.1	49.7	49	48.3	47	11.1	3.4
Cu	1260	1350	951	941	957	920	27.5	0.8
Li	58.3	62.4	41	40.1	40.8	39.4	32.8	1.1
K	112	119	89.5	88.1	88.5	85	23.1	2.3
Zn	119	127	84.6	101	159	85.4	24.6	-31.7
B	120	133	93.1	91.8	91.9	87.2	26.9	3.1
Er	151	160	118	116	103	101	24.8	12.8
Mg	111	117	65.6	65.6	68.3	64.5	42.5	-1.2
Sr	52.9	56	40.4	39.6	40.1	37.8	26.5	2.6
Cr	603	642	493	490	494	481	21.0	0.8
Ba	53	56	41.6	41.4	41.8	39.8	23.9	1.7
Cd	1320	1380	1010	1000	1010	964	25.6	1.8
Na	962	1020	771	759	782	762	22.8	-0.9
W	47.8	52.4	23	21.6	21.2	20.4	55.5	6.7
Fe	1150	1220	894	855	888	854	26.2	0.4
Ta	48.8	52.2	33.1	31.3	29.9	29.6	36.2	7.6
Zr	101	107	48.9	47.7	31.6	32.3	53.6	33.9
Mo	50.3	53.3	38.5	37.8	33	32.7	26.4	13.9
Sn	49.7	54.1	39.7	39.5	39.5	38.6	23.7	1.4
Si	240	260	167	165	168	161	33.6	0.9
Ti	50.8	53.5	42.4	41.8	41.3	40.1	19.3	3.3

It is important to note that reductions in extraction removal percentages between the first and second TOPO treatments were accompanied by a change in the aqueous-solution nitric acid concentration. The nitric acid concentration in the control solution before stripping was 0.34 *M*. The first TOPO treatment resulted in reducing the aqueous-phase acid concentration to 0.15 *M*. The aqueous raffinate after the second treatment contained nitric acid at a concentration of 0.14 *M*. The loss of acid available for salting is a likely factor in the reduction in extraction efficiency between the first and second TOPO treatment steps.

CONCLUSIONS

Dibutyl carbitol and tri-*n*-butyl phosphate exhibit significant differences with regard to their abilities to reject common contaminant elements, rejection by DBC being superior to that of TBP over a range of nitric acid, aluminum nitrate, and uranium concentration conditions. Based on the results of the current study, it appears that control of the nitric acid concentration system may improve TBP selectivity for uranium. This result likely occurs because of the occupation of a larger fraction of solvation sites by extracted acid, making these sites unavailable to other constituents. Blocking of the data obtained to evaluate a uranium/TBP selectivity effect may show the same result for the same reason. Uranium concentrations in production operations are generally dictated by throughput considerations and equipment limitations and cannot be changed as easily as acid levels.

The stripping of uranium from aqueous samples using TOPO solutions prior to ICP/AES or other emission-type analyses may have a significant effect on the analytical results due to removal of analytes. In the study reported, the extent to which analytes are removed appeared to be a function of nitric acid concentration in the sample. Since the TOPO extraction mechanism is similar to that of TBP, it is expected that the presence of any significant source of nitrate ions in aqueous samples will result in some alteration of samples by TOPO stripping to remove uranium. When possible, it is desirable to correct for sample preparation effects by normalizing results.

This has been done in the reported work by expressing mass transfer results in terms of removal fractions, rather than as absolute concentrations.

NOMENCLATURE

A	aluminum nitrate concentration effect on contaminant rejection
AS	aluminum nitrate/solvent interaction effect on contaminant rejection
AU	aluminum nitrate/uranium concentration interaction effect on contaminant rejection
DBC	dibutyl carbitol (diethylene glycol dibutyl ether)
ICP/AES	Inductively Coupled Plasma/Atomic Emission Spectroscopy
ppm	parts per million, calculated on the basis of mass/volume
PUREX	Plutonium URanium Extraction process developed for processing of spent nuclear reactor fuel
S	solvent effect on contaminant rejection
SS	squared sum
TBP	tri-*n*-butyl phosphate
TOPO	trioctyl phosphine oxide
U	uranium concentration effect on contaminant rejection
US	uranium concentration/solvent interaction effect on contaminant rejection

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