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Extraction of Trivalent Actinides and Lanthanides from Californium Campaign Rework Solution Using TODGA-based Solvent Extraction System

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Nuclear Security & Isotope Technology Division

EXTRACTION OF TRIVALENT ACTINIDES AND LANTHANIDES FROM CALIFORNIUM CAMPAIGN REWORK SOLUTION USING TODGA-BASED SOLVENT EXTRACTION SYSTEM

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ABSTRACT

This report presents the studies carried out to demonstrate the possibility of quantitatively extracting trivalent actinides and lanthanides from highly acidic solutions using a neutral ligand-based solvent extraction system. These studies stemmed from the perceived advantage of such systems over cation-exchange-based solvent extraction systems that require an extensive feed adjustment to make a low-acid feed. The targeted feed solutions are highly acidic aqueous phases obtained after the dissolution of curium targets during a californium (Cf) campaign. Results obtained with actual Cf campaign solutions, but highly diluted to be manageable in a glove box, are presented, followed by results of tests run in the hot cells with Cf campaign rework solutions. It was demonstrated that a solvent extraction system based on the tetraoctyl diglycolamide molecule is capable of quantitatively extracting trivalent actinides from highly acidic solutions. This system was validated using actual feeds from a Cf campaign.

1. INTRODUCTION

The production, recovery, and purification of the transuranium (TRU) actinide elements has been a mission of Oak Ridge National Laboratory (ORNL) since the early-1960s with the construction and operation of the High Flux Isotope Reactor and the associated Transuranium Processing Facility hot cell processing facilities (now called the Radiochemical Engineering Development Center, REDC). This production capability has supplied radioisotopes for research worldwide, providing materials for basic chemical and nuclear property studies, including target isotope material for new element discoveries, and also to commercial facilities for a wide variety of applications.

Among the various radioisotopes, Cf-252 is currently being produced by irradiating curium (Cm) targets. Californium is separated from the irradiated targets and purified. The first processing step after dissolution of the irradiated Cm targets is the coextraction of trivalent actinides and lanthanides using the cation exchanger bis-diethyl hexyl phosphoric acid (HDEHP) at 1 *M* in the diluent, Exxsol D60. This step is done to purify the actinide and lanthanide elements and to convert them from nitrates to chlorides. For the extraction to be successful, the nitric acid (HNO_3) that is present in high concentration (6–8 *M*) to ensure complete dissolution of the actinide oxides must be reduced to less than 0.1 *M* to enable extraction in the cation exchanger, HDEHP. Use of a neutral ligand capable of extracting trivalent actinides and lanthanides from the concentrated HNO_3 would be an alternative worth considering. The neutral ligand would require a high concentration of anion (nitrate in this case through HNO_3) to extract the cations of interest. The ligand tetra octyl diglycolamide (TODGA) is proposed, since it has been used in studies pertaining to the nuclear fuel cycle worldwide and has been proven a superior extractant for minor actinides and lanthanides (AnLn) [1–4]. Studies conducted in hot cells in France at the Atalante facility and in the gamma radiolysis test loop at Idaho National Laboratory have shown that TODGA is resistant to radiation damage and is, overall, very robust in harsh chemical or radiolytic conditions [5–6]. Therefore, this extractant should be adequate for the extraction of trivalent actinides and lanthanides at high acidity. The goal of this study is to demonstrate the capability to extract actinides and lanthanides and to define the optimum extraction conditions (acidity, extractant concentration), followed by scrubbing and stripping in hydrochloric acid (HCl) solutions. Testing was first carried out in a glove box setting using a feed corresponding to the dissolution of the irradiated Cm targets diluted to low activity; these conditions were then validated with hot cell tests at full activity. As part of these experiments, conditions for quantitatively stripping the AnLn and co-extracted species were defined, as it is critical to be able to recycle and reuse the TODGA solvent to minimize the generation of organic waste liquids. The composition of the feed was varied to assess the extraction capabilities of the ligand, where the presence of major contaminants (such as aluminum) could impair the ability of TODGA to quantitatively extract the species of interest.

2. EXPERIMENTAL SECTION

2.1 MATERIALS

The aqueous solutions handled in the glove box consisted of hot cell solutions diluted 250 times using HNO_3. Concentrated HNO_3 and HCl (ACS grade) were obtained from EMD Millipore Corp. and used as received. Distilled, deionized water was obtained from a Millipore Milli-Q filtering system (resistivity at least 18.0 MΩ-cm) and used to prepare all the dilutions in volumetric flasks. The organic phases consisted of TODGA (obtained from Marshallton Research Laboratories, Inc., and used as received) at various concentrations diluted in Exxsol D60 (technical grade, Exxon Mobil, provided by Univar, Inc.).

2.2 FEED COMPOSITIONS

2.2.1 Glove Box Solutions from the Dissolution of Irradiated Targets

Two similar feed solutions were used for the glove box tests. Both solutions originated from the dissolution products of TRU Campaign 76, and each was diluted 250-fold with HNO_3 at their respective acidities, i.e., 6 *N* and 8 *N*. Such dilutions were required to enable tests to be made in glove boxes due to the significant neutron radiation field generated by these Cm and Cf solutions. These samples were taken immediately post-dissolution (samples DSDP-560 and 561, cf. Appendices) and therefore did not contain any of the Campaign 75 rework solutions. The total amount of lanthanides plus yttrium present in the dissolution step is about 1 g from the irradiation. The aluminum (Al) content was not measured. Compositions are presented in Tables 1 and 2.

Table 1. Composition of the 6 *N* dissolution solution from C76

Species	6 *N* original solution (mg/L)	6 *N* 250-fold dilution (mg/L)	6 *N* 250-fold dilution (m*M*)
Ln + Y	34.8	0.14	0.001
Al	unknown	unknown	unknown
Cm-244	340	1.34	0.005
Total Cm	1020	4.10	0.017
Total An[a]	1250	5	0.02

[a] This total is estimated based on isotopics and Cm/Am ratios found for subsequent rework solutions.

Table 2. Composition of the 8 *N* dissolution solution from C76

Species	8 *N* original solution (mg/L)	8 *N* 250-fold dilution (mg/L)	8 *N* 250-fold dilution (m*M*)
Ln + Y	64.9	0.26	0.002
Al	unknown	unknown	unknown
Cm-244	619	2.48	0.010
Total Cm	1890	7.57	0.031
Total An[a]	2000	8	0.033

[a] This total is estimated based on isotopics and Cm/Am ratios found for subsequent rework solutions.

Since the organic-to-aqueous phase ratio (O/A) will be 1 for all glove box tests, as long as the concentration of the solvent is greater than 1 m*M*, the presence of extracted species in the organic phase will not impact the concentration of the ligand at equilibrium, thereby ensuring that the distribution ratio calculated for these systems will be under dilute conditions.

2.2.2 Hot-Cell Rework Solutions

All rework solutions from Campaign 76 were contacted with 1 *M* HDEHP in Exxsol D60 to recover trivalent and tetravalent cations. The organic extractant was then stripped with highly concentrated HNO_3 to recover the trivalent cations. This stripping solution was then analyzed, and a 680 mL sample was diverted for the solvent extraction tests (Table 3). The rest of the solution was treated with oxalic acid to precipitate the trivalent actinides and lanthanides. This precipitation step will not be described in this report, but a portion of the filtrate was tested (Section 2.2.3). The original analytical reports are presented in the appendices. A complete analysis (CLCP-435 A&B) was carried out about 3 months before the test was run. Another analysis was done just before the test, and the alpha analysis showed identical results (MSA-133). The acidity was also measured and determined to be adequate for the solvent extraction test.

Table 3. Composition of C76 rework solution

Species	Concentration, g/L	Concentration, m*M*
Cm-244	0.086	0.353
Total Cm	0.310	1.258
Cf-252	0.001	0.004
Total Cf	0.002	0.008
Am-241	0.011	0.046
Total Am	0.062	0.255
La	0.050	0.360
Ce	0.130	0.922
Nd	0.111	0.076
Sm	0.015	0.099
Eu	0.005	0.038
Gd	0.020	0.132
Total Ln	0.332	2.310
Ca	0.084	2.113
Al	1.100	40.741
Zn	0.260	3.980

The aqueous feed was titrated and showed a free acidity of 5 *M* and subsequent cation titration of 0.26 *M*. If one assumes that all cations in solutions are titrated at the same time and that the number of hydroxides consumed corresponds to the charge of the cation in acidic media [except for Al and zinc (Zn) for which the number is 4], the theoretical bound acidity is calculated as 0.194 *M*, indicating that the concentrations of the different species defining the composition of the solution are in the right order of magnitude.

2.2.3 Hot-Cell Rework Solution Containing Oxalic Acid

A portion of the raffinate of the oxalate precipitation process was saved for a solvent extraction test to determine whether the organic ligand is strong enough to compete with oxalic acid and can provide a quantitative extraction of trivalent actinides and lanthanides. It is reasonable to assume that the trivalent actinides and lanthanides precipitated out of the solution in roughly the same proportions. It is expected that Al, Zn, and other cations remained in the raffinate of the oxalate precipitation. However, for comparison with the previous rework solution, only Cm and Cf will be followed by radiochemistry.

The free acidity of the raffinate of the oxalate precipitation was measured at 0.9 *M*. Since 900 mL of the solution was available, it was decided to split the amount of feed in half and add 200 mL of concentrated (68%) HNO_3 to each bottle.

Table 4. Composition of C76 rework solution post-oxalate precipitation

	Bottle #1		Bottle #2	
	Estimated	**Measured**	**Estimated**	**Measured**
Volume (mL)	650	560	650	740
Acidity (*M*)	5.4	5.9	5.4	5.1
Cm-244, mg	15.5	5.1	15.5	2.1
Cf-252, µg	105	29	105	3.7
Al, mg	1.81	Not available	1.81	1.55

There is a significant discrepancy between the anticipated values and those measured. In all likelihood, more precipitation may have occurred after the raffinate was originally analyzed and before the 900 mL sample of the raffinate was taken. More troubling is the difference in Cm and Cf between the two bottles that had received the nominal equal split of the sample. The bottle containing the feed before it was split and reacidified exhibited a film of precipitate, which would therefore have a greater activity since the precipitate would have gone back in solution upon acidification. As Al is minimally impacted by the presence of oxalate, its concentration should remain consistent throughout the test, which was observed (Table 4). Subsequent results obtained for the solvent extraction test will shed some light on the reasons for these discrepancies (Section 2.3).

2.3 EXTRACTION PROCEDURES

Glove box extraction tests were carried out in capped polypropylene 2 mL micro-tubes. These tubes were placed in a foam holder with holes of a slightly smaller diameter than the tubes. The holder was then rocked back and forth by hand to ensure complete dispersion of organic and aqueous phases. Tests were run at the glove box temperature, nominally 23 °C, for 5 minutes. After the contacting period, the tubes were centrifuged for 1 minute at 2000 RPM in a VWR microcentrifuge. The organic and aqueous phases were then subsampled for analysis.

Hot cell tests were done in a similar fashion, but their larger scale led to some changes. The solvent consisting of 0.2 *M* TODGA in Exxsol D60 with a phase ratio O/A =3 was added to the glass bottle containing the feed. The mixing procedure was a vigorous end-over-end shaking for 30 s, then settling for 30 s. This was repeated five times. The temperature of the hot cell cubicle was 33°C ± 2°C. The phases were allowed to settle for a minimum of 15 minutes, after which full phase disengagement was noted. A ¼ in. polyethylene line connected to a high-flow pump [Fluid Metering, Inc. (FMI) CeramPump®] was then inserted through the organic phase into the aqueous phase to pump the aqueous phase to a separate container. Great care was taken to remove all of the aqueous phase (level monitored using binoculars through the hot cell window) as any significant remainder could negatively impact the following stage. The aqueous phase corresponding to the next step was then added to the original glass bottle. The steps consisted of one or two extractions, one scrub with 3 *M* HCl, and three strips with 50 m*M* HCl. Both the organic and the aqueous phases were sampled at each step and submitted for analysis. Californium distribution ratios were calculated using the alpha activity detected at 6.11 MeV in the organic and aqueous phases. These distribution ratios could therefore be underestimated: the activity at this energy also corresponds to Cm-242, and TODGA extracts Cf inherently better than Cm (or generally heavier f elements over lighter f elements).

3. RESULTS AND DISCUSSION

3.1 GLOVE BOX TESTS

Preliminary experiments were conducted using both the 6 *N* and 8 *N* feed solutions diluted 250 times with HNO_3 at their corresponding concentrations. Extraction tests were performed with equal volumes of organic and aqueous phases. Three different concentrations of TODGA were used (0.1, 0.2, and 0.5 *M*). In all cases, the extraction of trivalent actinides appears to be essentially quantitative: it became obvious that the handling of the aqueous-phase post-extraction required great care to avoid cross-contamination with the organic phase. Hardly any alpha activity is left in the aqueous phase after a single batch contact. Little improvement in the distribution ratios is obtained by using a higher ligand concentration. A TODGA concentration of 0.2 *M* is chosen for subsequent experiments; the lower concentration should still have enough capacity for complete extraction. As for the other elements present in the solution, zirconium (Zr) and plutonium (Pu), as expected, are quantitatively extracted. They are also mostly stripped, with about 5% of the original amount remaining in the organic phase after the third strip. About 20% of ruthenium (Ru) is extracted and then seems to be evenly split between the organic and the aqueous phase upon scrubbing and stripping. Finally, trying to strip with low HCl concentration directly after the extraction strip leads to very high distribution ratios in the first strip. A scrub stage was added with a 3/1 O/A ratio with 3*M* HCl, which should be a high enough concentration to maintain most of the trivalent cations in the organic phase. While the work presented in this report did not address the potential for forming aqua regia in-tank, should the heel of the extraction be mixed with the scrub solution, follow-on studies included a first scrub using 1*M* HNO_3, followed by the HCl scrub. Such a preliminary scrub would alleviate all issue since the final concentration of HNO_3 in the second scrub would be less than 0.5 *M*, the threshold for corrosion issues.

Detailed results for Cm, Cf, and fission products are presented in Table 5. Distribution ratios of the fission products were calculated using the activities of Ce-144, Zr-95, and Ru-106. It is important to note that the 250-fold dilution for the feed coupled to the subsequent dilutions required for analysis led to relatively low gamma activities. The errors on the distribution ratios obtained for the fission products are relatively large.

Table 5. Distribution ratios obtained with the 6 *N* solution[a] and TODGA at 0.2 *M*

Stage	O/A ratio	D_{Cm}	D_{Cf}	D_{Ce}	D_{Zr}	D_{Ru}
Extraction	1-2	10^5	1.2×10^5	1100	> 130	0.21
Scrub #1	3-1	120	140	83	> 7.8	> 8.7
Scrub #2	3-1	450	490	32	> 2.6	12
Strip #1	3-1	1.2	1.5	0.41	0.56	1.3
Strip #2	3-1	1.5×10^{-4}	3.3×10^{-4}	3.5×10^{-3}	0.14	> 1.7
Strip #3	3-1	1.4×10^{-3}	5.6×10^{-4}	< 0.2	0.3	8.8

[a] Table 1, diluted 250-fold

Based on these results, we chose to focus our efforts on a solvent extraction system using 0.2 *M* TODGA in Exxsol D60 for the organic phase, 3 *M* HCl for the scrub stage, and 50 m*M* for the strip stages. As for the extraction, the acidity of the feed was varied: we used either the 6 *N* feed as presented previously or the 8 *N* solution diluted with an equal volume of 0.01 *M* HNO_3 (final acidity around 4 *M*). Results are presented in Tables 6 and 7.

Table 6. Solvent extraction cycle using diluted feed at 4 *N* HNO_3[a]

Stage	O/A ratio	D_{Cm}	% ext/strip	D_{Cf}	% ext/strip
Extraction	1-1	4.73×10^{4}	99.9979%	7.18×10^{4}	99.9986%
Scrub	3-1	1.45×10^{3}	99.93%	1.78×10^{3}	99.94%
Strip #1	1-1	4.26×10^{-1}	70.12%	6.07×10^{-1}	62.22%
Strip #2	1-1	2.46×10^{-5}	99.9975%	3.08×10^{-5}	99.9969%
Strip #3	1-1	2.52×10^{-2}	97.5424%	1.51×10^{-2}	98.5087%

[a] Organic phase: TODGA 0.2 *M* in Exxsol D60
Aqueous phase: DSDP-560 diluted 250-fold in 8 *N* HNO_3 (Table 2) then diluted two-fold with 0.01 *M* HNO_3 (final acidity about 4 *M*)
Note: the percentages presented are noncumulative (valid only for the given stage).

Table 7. Solvent extraction cycle using diluted feed at 6 *N* HNO_3

Stage	O/A ratio	D_{Cm}	$\%_{Cm}$ ext/strip	D_{Cf}	$\%_{Cf}$ ext/strip
Extraction	1-1	3.35×10^{5}	99.9997%	2.39×10^{5}	99.9996%
Scrub	3-1	5.74×10^{3}	99.983%	7.75×10^{3}	99.987%
Strip #1	1-1	9.71×10^{-1}	50.75%	1.21	45.17%
Strip #2	1-1	3.48×10^{-5}	99.997%	7.96×10^{-5}	99.992%
Strip #3	1-1	1.10×10^{-1}	90.082%	0	100%

Organic phase: TODGA 0.2 *M* in Exxsol D60
Aqueous phase: DSDP-561 diluted 250-fold in 6 *N* HNO_3 (Table 1)
Note: the percentages presented are noncumulative (valid only for the given stage).

It appears that the 6 *N* HNO_3-based system leads to slightly better extraction results, but the range of acidity can remain broad and still yield a quantitative extraction of Cm and Cf. The distribution ratios obtained for the 6 *N* feed can be explained by the fact that more HNO_3 is coextracted in the extraction stage and then released in the scrub stage, hence larger distribution ratios for the scrub step and the first strip. Distribution ratios in the second and third strips are for information only as the amount of alpha activity detected in both the organic and aqueous phases was very low. It is important to note that the concentrations of neither the scrub solution nor the strip solutions have been optimized. Preliminary tests have shown that HCl is the only mineral acid option for the hot cell environment, since stripping with HNO_3 will not provide a quantitative release of the cations into the aqueous phase. However, the impact of the concentration of the acid and the organic/aqueous phase ratios has not been investigated, and there may be potential for improvement. For example, less Cf and Cm would be released into the scrub solution if 4–5 *M* HCl were to be used.

3.2 HOT CELL TESTS

The hot cell solution chosen to validate the glove box results is a rework solution from a previous Cf campaign and contained a significant molar concentration of Al that was similar to dissolved target solutions.

3.2.1 Rework Solutions

No feed adjustment was made to the rework solution as the only parameter that could have been changed was the acidity, and the analyzed 5 *M* was satisfactory based on the results from the glove box tests. While samples were collected for all aqueous phases, only selected organic phases were sampled to minimize the number of analyses. The corresponding distribution ratios are presented in Table 8.

Table 8. Solvent extraction cycle using C76 rework solution

Stage	Org volume (mL)	Aq volume (mL)	D_{Am}	D_{Cm}	D_{Cf}	D_{Ce}
Extraction	250	680	> 230	10,500	40,000	404
Scrub	250	100	94	131	459	7.9
Strip #3	250	220	10^{-3}	3×10^{-4}	4×10^{-4}	$< 2\times10^{-3}$

Based on the isotopics and the concentrations of the corresponding isotopes, the recovery/mass balances were calculated (Table 9).

Table 9. Recovery of trivalent actinides

Stage	Am, mg	Cm, mg	Cf, μg
Feed	39.0	196	1070
Strip #1	11.9	53.8	91.9
Strip #2	25.4	133	801
Strip #3	1.07	5.71	95.5
Mass Balance	98.3%	98.1%	92.6%

Several conclusions can be drawn from this experiment. First, the extraction of trivalent actinides and lanthanides is quantitative, with distribution ratios similar to those obtained for the glove box tests. Aluminum analyses in the aqueous phases at each stage (Table 10) confirm the fact that Al is not extracted by TODGA [1].

Table 10. Aluminum content in each stage of the extraction test (aqueous phase)

Stage	Feed	Extraction	Scrub	Strip #1	Strip #2	Strip #3
[Al], mg/L	1960	2010	25.7	< 26.3	< 26.3	< 10.1

The results from this test validate the extraction/stripping performances demonstrated during the glove box tests. The ligand TODGA could become a candidate for efficient extraction of trivalent actinides and lanthanides from high HNO_3 or HCl solutions. Further studies are required to ensure that fission products, such as Zr, Ru, Pd, and Mo, are adequately rejected (lack of extraction, selective complexation in the feed, or suitable scrubbing) from the final product.

3.2.2 Rework Solutions Containing Oxalic Acid

Another validation experiment was added to the series of tests performed in the hot cells. Oxalate precipitation is commonly used to purify Cm solutions from other metals in trace quantities. Raffinate and tank heels from this process may contain up to 5–10% of the starting quantity of Cm (cf. Appendices, sample code OXFL-623), a quantity that could be removed by contacting it with a TODGA-based solvent. Such raffinate was available and was treated with the stripped solvent from the previous tests. This experiment could demonstrate both the recyclability of the solvent along with its ability to quantitatively extract trivalent actinides and lanthanides in the presence of a strong complexant, i.e., oxalate.

The feed for this test was split in half and acidified to a nominal 5.5 *M*. It turned out that more acid was added to the second half of the feed. The recycled TODGA solvent was contacted with the first half of the feed. The aqueous phase was then removed and replaced with the second half. The solvent was used as it was left after the third strip of the previous experiment, without any additional washes or reconditioning.

The first extraction exhibited low distribution ratios, while the second one behaved essentially as expected. The differences in acidity cannot explain this, and while some impact for the oxalic acid was expected, it should have been consistent for both extraction steps. Based on what was seen in the glove box in the original experiments where phases were not centrifuged before subsampling, some entrainment of the organic phase in the aqueous phase could explain these low distribution ratios. The fact that the distribution ratios for Cf are lower than those for Cm may indicate that the Cf is better complexed and therefore better retained in the aqueous phase by the oxalate. Qualitatively, the raffinate from the second extraction shows a level of activity at the background level of the hot cells (Table 11).

Table 11. Distribution ratios from solvent extraction system containing oxalate

Stage	Org volume (mL)	Aq volume (mL)	D_{Am}	D_{Cm}	D_{Cf}	D_{Ce}
Extraction#1	250	560	39	28	1.1	290
Extraction #2	250	740	48	7300	1900	480
Scrub	250	220	140	150	13	15

The organic phase after the second extraction also shows more cations (in mass) than analyzed in the feeds, which casts some doubt on the original feed composition. However, and maybe more importantly, the recovery from the solvent is excellent, as shown in Table 12. It was confirmed that the Al was not extracted under these conditions, as expected. Results are presented in Table 13.

Table 12. Recovery of trivalent actinides from TODGA extractant

	Extr. #2, org	Strip #1, aq	Strip #2, aq	Strip #3, aq	% recovered
Cm-244, mg	8.6	5.0	3.4	0.1	98.8
Cf-252, μg	64	21	38	2.9	96.7
Am-241, mg	1.2	0.55	0.41	0.01	80

Table 13. Aluminum content at each stage of the extraction test with oxalic acid (aqueous phase)

Stage	Bottle #2	Extr. #1	Extr. #2	Scrub	Strip #1	Strip #2	Strip #3
[Al], mg/L	2100	2150	2010	N/A	< 105	< 105	< 4.04

3.2.3 Solution Recovery from Cubicle Sump

A solution containing Cm and low levels of Cf was being purified via oxalate precipitation when an equipment malfunction led to the loss of that solution into the sump of the hot cell cubicle. The solution was subsequently retrieved from the sump followed by several rinses to total about 2.5 L. Based on the analyses, 125 mg of Cm-244 could be recovered. One analysis was questioned as being high but was not repeated. It was decided to assess the efficacy of the solvent extraction system by checking how much Cm was left in the raffinate after each extraction.

The total amount of solution recovered from the sump was split evenly in six different fractions adjusted to about 5 *M* HNO_3 by adding concentrated (68%) HNO_3. The volume of each fraction was 600 mL. Each fraction was contacted with 200 mL of 0.2 *M* TODGA in Exxsol D60. The same organic phase was therefore contacted six times without any scrubbing or stripping in between; 200 mL of solvent was used to treat all 3.6 L of solution. The solvent was then scrubbed once with 100 mL of 3 *M* HCl and then stripped three times with 200 mL of 50 m*M* HCl (Table 14).

Table 14. Curium-244 remaining in the aqueous phases post extraction

	Extr. #1	Extr. #2	Extr. #3	Extr. #4	Extr. #5	Extr. #6
Cm-244, µg/L	0.93	1.3	3.3	6.8	15	17
Cm-244, µg	0.56	0.79	2	4.1	8.7	10
Accumulated loss, µg	0.56	1.3	3.3	7.4	16	26

Out of over 100 mg of Cm-244, only 26 µg was lost to the raffinate, or 0.026%. The reuse of the organic phase for each fresh batch of feed worked according to expectation: since the conditions were essentially the same for each extraction and since the extraction of trivalent actinides and lanthanides is expected to be quantitative, each contact should double the amount of Cm in the organic phase while the distribution ratios remain the same. This is well demonstrated by the continuous increase of the Cm-244 concentration in the raffinate solutions.

In the scrub stage, 81 µg of Cm-244 was lost, representing about 0.1% of the original amount.

Table 15. Curium-244 remaining in the aqueous strips

	Strip #1	Strip #2	Strip #3	Org. Strip #3
Cm-244, mg/L	270	230	24	0.15
Cm-244, mg	54	46	4.7	0.03
Recovered amount, mg	54	100	104.7	

The stripping of the organic phase, just like for the previous tests, appears to be quantitative, with an overall recovery of Cm-244 greater than 100 mg. Based on the uncertainty on the original amount present in the sump and the fact that the various raffinate solutions were essentially free of significant amounts of Cm, it is reasonable to think that the solvent extraction system was very effective for the recovery of Cm under these conditions (Table 15).

4. CONCLUSIONS

A solvent extraction system capable of quantitatively extracting trivalent actinides from highly acidic solutions has been designed and validated using actual feeds from a Cf campaign. While the scrubbing and stripping steps or the removal of Zr and Ru fission products have not been optimized, it still exhibited remarkable performance. The reuse of the solvent was also demonstrated, along with its ability to compete with strong aqueous complexants such as oxalate. This system presents a viable alternative to the current process that requires adjustment to low acidity for quantitative extraction of trivalent actinides.

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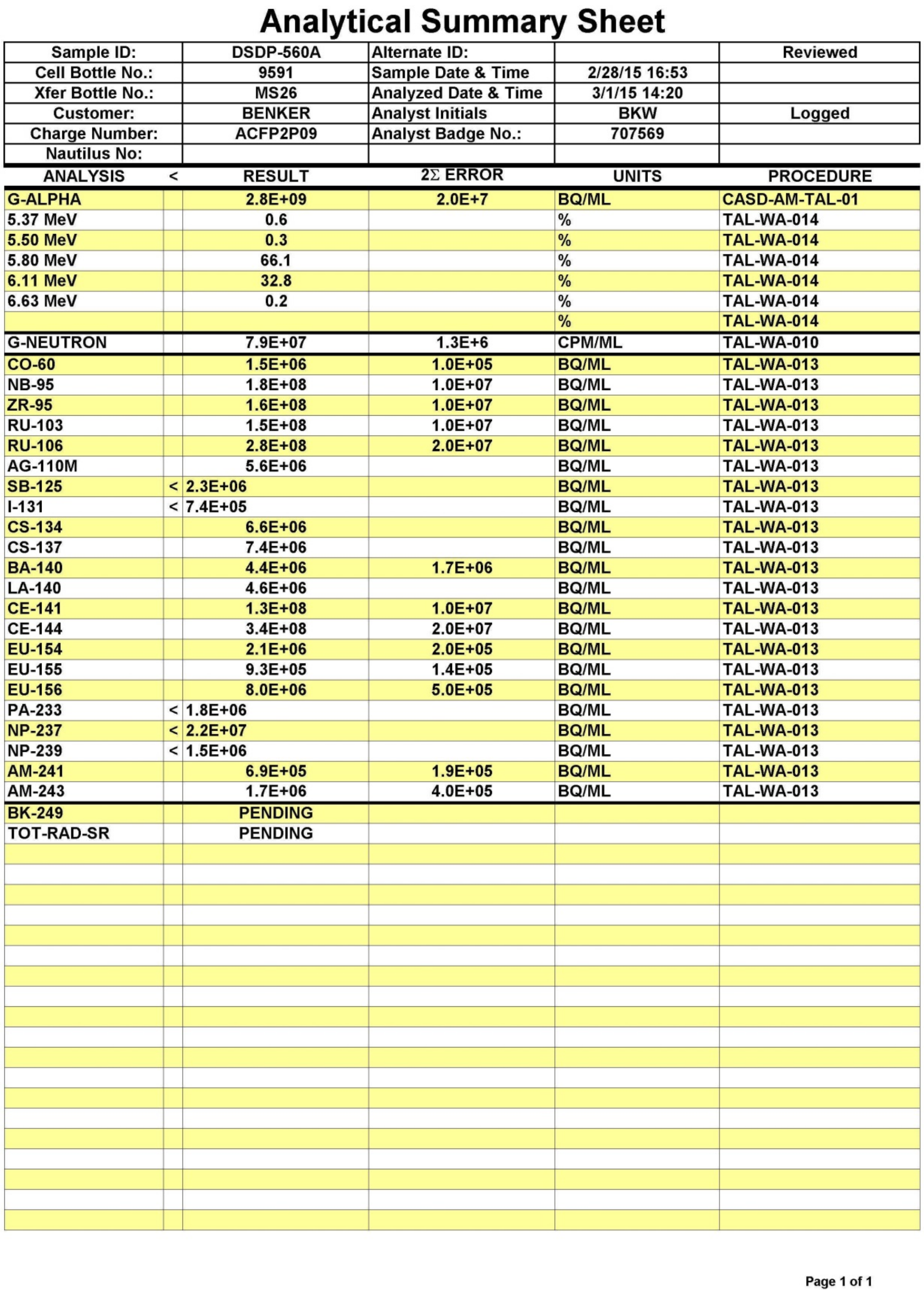
APPENDIX A. ORIGINAL ANALYTICAL DATA SHEETS

Original Analytical Data Sheets for feed solutions are included for reference purposes.



Analytical Summary Sheet

Sample ID:	DSDP-560A	Alternate ID:		Reviewed
Cell Bottle No.:	9591	Sample Date & Time	2/28/15 16:53	
Xfer Bottle No.:	MS26	Analyzed Date & Time	3/1/15 14:20	
Customer:	BENKER	Analyst Initials	BKW	Logged
Charge Number:	ACFP2P09	Analyst Badge No.:	707569	
Nautilus No:				

ANALYSIS	<	RESULT	2Σ ERROR	UNITS	PROCEDURE
G-ALPHA		2.8E+09	2.0E+7	BQ/ML	CASD-AM-TAL-01
5.37 MeV		0.6		%	TAL-WA-014
5.50 MeV		0.3		%	TAL-WA-014
5.80 MeV		66.1		%	TAL-WA-014
6.11 MeV		32.8		%	TAL-WA-014
6.63 MeV		0.2		%	TAL-WA-014
				%	TAL-WA-014
G-NEUTRON		7.9E+07	1.3E+6	CPM/ML	TAL-WA-010
CO-60		1.5E+06	1.0E+05	BQ/ML	TAL-WA-013
NB-95		1.8E+08	1.0E+07	BQ/ML	TAL-WA-013
ZR-95		1.6E+08	1.0E+07	BQ/ML	TAL-WA-013
RU-103		1.5E+08	1.0E+07	BQ/ML	TAL-WA-013
RU-106		2.8E+08	2.0E+07	BQ/ML	TAL-WA-013
AG-110M		5.6E+06		BQ/ML	TAL-WA-013
SB-125	<	2.3E+06		BQ/ML	TAL-WA-013
I-131	<	7.4E+05		BQ/ML	TAL-WA-013
CS-134		6.6E+06		BQ/ML	TAL-WA-013
CS-137		7.4E+06		BQ/ML	TAL-WA-013
BA-140		4.4E+06	1.7E+06	BQ/ML	TAL-WA-013
LA-140		4.6E+06		BQ/ML	TAL-WA-013
CE-141		1.3E+08	1.0E+07	BQ/ML	TAL-WA-013
CE-144		3.4E+08	2.0E+07	BQ/ML	TAL-WA-013
EU-154		2.1E+06	2.0E+05	BQ/ML	TAL-WA-013
EU-155		9.3E+05	1.4E+05	BQ/ML	TAL-WA-013
EU-156		8.0E+06	5.0E+05	BQ/ML	TAL-WA-013
PA-233	<	1.8E+06		BQ/ML	TAL-WA-013
NP-237	<	2.2E+07		BQ/ML	TAL-WA-013
NP-239	<	1.5E+06		BQ/ML	TAL-WA-013
AM-241		6.9E+05	1.9E+05	BQ/ML	TAL-WA-013
AM-243		1.7E+06	4.0E+05	BQ/ML	TAL-WA-013
BK-249		PENDING			
TOT-RAD-SR		PENDING			

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Analytical Summary Sheet

Sample ID:	DSDP-561B	Alternate ID:		Reviewed
Cell Bottle No.:	9830	Sample Date & Time	3/2/15 16:00	
Xfer Bottle No.:	272	Analyzed Date & Time	3/4/15 13:37	
Customer:	BENKER	Analyst Initials	RDC	Logged
Charge Number:	ACFP2P09	Analyst Badge No.:	35993	
Nautilus No:				

ANALYSIS	<	RESULT	2Σ ERROR	UNITS	PROCEDURE
G-ALPHA		1.4E+09	1.4E+7	BQ/ML	CASD-AM-TAL-01
5.37 MeV		0.6		%	TAL-WA-014
5.50 MeV		0.3		%	TAL-WA-014
5.80 MeV		66.4		%	TAL-WA-014
6.11 MeV		32.5		%	TAL-WA-014
6.63 MeV		0.2		%	TAL-WA-014
				%	TAL-WA-014
G-NEUTRON		4.1E+07	2.1E+6	CPM/ML	TAL-WA-010
CO-60	<	6.6E+05		BQ/ML	TAL-WA-013
NB-95		7.1E+07		BQ/ML	TAL-WA-013
ZR-95		6.8E+07		BQ/ML	TAL-WA-013
RU-103		9.8E+07	6.0E+06	BQ/ML	TAL-WA-013
RU-106		1.4E+08	1.0E+07	BQ/ML	TAL-WA-013
AG-110M		2.7E+06	3.0E+05	BQ/ML	TAL-WA-013
SB-125	<	2.9E+06		BQ/ML	TAL-WA-013
I-131	<	9.2E+05		BQ/ML	TAL-WA-013
CS-134		3.5E+06	3.0E+05	BQ/ML	TAL-WA-013
CS-137		3.7E+06	4.0E+05	BQ/ML	TAL-WA-013
BA-140	<	4.0E+06		BQ/ML	TAL-WA-013
LA-140		2.1E+06	4.0E+05	BQ/ML	TAL-WA-013
CE-141		6.7E+07		BQ/ML	TAL-WA-013
CE-144		1.5E+08	1.0E+07	BQ/ML	TAL-WA-013
EU-154		1.1E+06	6.0E+05	BQ/ML	TAL-WA-013
EU-155	<	1.4E+06		BQ/ML	TAL-WA-013
EU-156	<	4.5E+06		BQ/ML	TAL-WA-013
PA-233	<	2.2E+06		BQ/ML	TAL-WA-013
NP-237	<	3.0E+07		BQ/ML	TAL-WA-013
NP-239	<	2.1E+06		BQ/ML	TAL-WA-013
AM-241	<	1.2E+06		BQ/ML	TAL-WA-013
AM-243		6.3E+05	3.7E+05	BQ/ML	TAL-WA-013

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Analytical Summary Sheet

Sample ID:	CLCP-435B	Alternate ID:	
Cell Bottle No.:	1360	Sample Date & Time	9/28/16 0:00
Xfer Bottle No.:	MS21	Analyzed Date & Time	10/3/16 9:53
Customer:	NNFD	Analyst Initials	VJG
Charge Number:	ACFP2P09	Analyst Badge No.:	34610
		REVISION	

ANALYSIS	<	RESULT	2Σ ERROR	UNITS
G-ALPHA		2.8E+08	3.5E+6	BQ/ML
5.37 MeV		0.9		%
5.50 MeV		0.5		%
5.80 MeV		92.2		%
6.11 MeV		6.4		%
				%
				%
G-NEUTRON		8.3E+06	2.4E+5	CPM/ML
CO-60	<	4.6E+04		BQ/ML
NB-95	<	4.8E+04		BQ/ML
ZR-95		6.5E+04	3.3E+04	BQ/ML
RU-103	<	4.7E+04		BQ/ML
RU-106	<	5.1E+05		BQ/ML
AG-110M	<	5.0E+04		BQ/ML
SB-125	<	1.3E+05		BQ/ML
I-131	<	4.2E+04		BQ/ML
CS-134	<	4.7E+04		BQ/ML
CS-137	<	5.6E+04		BQ/ML
BA-140	<	1.8E+05		BQ/ML
LA-140	<	6.3E+04		BQ/ML
CE-141	<	4.8E+04		BQ/ML
CE-144		5.7E+06	7.0E+05	BQ/ML
EU-154		8.1E+05	5.0E+04	BQ/ML
EU-155		1.6E+05	6.0E+04	BQ/ML
EU-156	<	3.8E+05		BQ/ML
PA-233	<	8.5E+04		BQ/ML
NP-237	<	1.9E+06		BQ/ML
NP-239		2.5E+05	8.0E+04	BQ/ML
AM-241		1.4E+06	2.0E+05	BQ/ML
AM-243		3.6E+05	6.0E+04	BQ/ML
PU(TOTAL)		2.1E+05	1.4E+4	BQ/ML
PU 5.15 MeV		18.6		%
PU 5.50 MeV		78.8		%
PU 5.80 MeV		2.6		%
		ICP-MS Impurities		Analysis Date:
Na		2.67E+01	2.67E+00	PPM
Mg		2.36E+00	2.36E-01	PPM
Al		1.10E+03	1.10E+02	PPM
Ca		8.45E+01	8.45E+00	PPM
Cr		1.98E+00	1.98E-01	PPM
Fe		3.26E+01	3.26E+00	PPM
Ni		1.17E+00	1.17E-01	PPM
Zn		2.60E+02	2.60E+01	PPM
Sr	<	6.50E-02	#VALUE!	PPM
Y		4.34E+01	4.34E+00	PPM
Zr		7.49E-01	7.49E-02	PPM
Mo		1.23E-01	1.23E-02	PPM

Analytical Summary Sheet

Sample ID:		**CLCP-435B**	**Alternate ID:**	
Cell Bottle No.:		**1360**	**Sample Date & Time**	**9/28/16 0:00**
Ru		1.41E-01	1.41E-02	PPM
Pd		3.42E+00	3.42E-01	PPM
Sn		1.55E+00	1.55E-01	PPM
Ba		4.81E-02	4.81E-03	PPM
La		5.01E+01	5.01E+00	PPM
Ce		1.30E+02	1.30E+01	PPM
Nd		1.11E+02	1.11E+01	PPM
Sm		1.51E+01	1.51E+00	PPM
Eu		5.80E+00	5.80E-01	PPM
Gd		2.03E+01	2.03E+00	PPM
		Comments:	Reported Lanthanides as fission based on HFIR All others reported as natural.	
		ICP-MS ACTINIDES		**Analysis Date:**
Cm244		8.51E+01	8.51E+00	PPM
		ICP-MS Pu (ISO)		**Analysis Date:**
Pu-238 (ISO)		5.82	1.16	ATOM%
Pu-239 (ISO)		0.74	0.15	ATOM%
Pu-240 (ISO)		92.41	0.92	ATOM%
Pu-241 (ISO)		0.10	0.01	ATOM%
Pu-242 (ISO)		0.93	0.19	ATOM%
Pu-244 (ISO)	<	0.01	NA	ATOM%
		ICP-MS Am (ISO)		**Analysis Date:**
Am-241 (ISO)		17.83	0.18	ATOM%
Am-242m (ISO)		0.02	0.01	ATOM%
Am-243 (ISO)		82.14	0.82	ATOM%
		ICP-MS Cm (ISO)		**Analysis Date:**
Cm-242 (ISO)		0.01	0.01	ATOM%
Cm-243 (ISO)		0.02	0.01	ATOM%
Cm-244 (ISO)		27.89	0.28	ATOM%
Cm-245 (ISO)		1.03	0.02	ATOM%
Cm-246 (ISO)		56.79	0.57	ATOM%
Cm-247 (ISO)		1.58	0.03	ATOM%
Cm-248 (ISO)		12.68	0.13	ATOM%
Cm-249 (ISO)	<	0.01	NA	ATOM%
		ICP-MS CF (ISO)		**Analysis Date:**
Cf-249 (ISO)		27.65	0.55	ATOM%
Cf-250 (ISO)		18.76	0.38	ATOM%
Cf-251 (ISO)		6.42	0.13	ATOM%
Cf-252 (ISO)		47.17	0.94	ATOM%
Cf-253 (ISO)	<	0.01	NA	ATOM%
Cf-254 (ISO)	<	0.01	NA	ATOM%

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Analytical Summary Sheet

Sample ID:	MSA-133	Alternate ID:		Reviewed
Cell Bottle No.:	1541	Sample Date & Time	12/14/16 0:00	
Xfer Bottle No.:	B58	Analyzed Date & Time	12/14/16 13:59	
Customer:	NNFD	Analyst Initials	HAM	Logged
Charge Number:	X2DEMCSD	Analyst Badge No.:	3036186	
		REVISED: H+ ADDED		

ANALYSIS	<	RESULT	2Σ ERROR	UNITS	PROCEDURE
G-ALPHA		2.6E+08	2.6E+6	BQ/ML	CASD-AM-TAL-01
5.27 MeV		0.2		%	TAL-WA-014
5.37 MeV		0.7		%	TAL-WA-014
5.50 MeV		1.1		%	TAL-WA-014
5.80 MeV		92.5		%	TAL-WA-014
6.11 MeV		5.5		%	TAL-WA-014
				%	TAL-WA-014
G-NEUTRON		7.9E+06	2.8E+5	CPM/ML	TAL-WA-010
CO-60				BQ/ML	TAL-WA-013
NB-95				BQ/ML	TAL-WA-013
ZR-95				BQ/ML	TAL-WA-013
RU-103				BQ/ML	TAL-WA-013
RU-106				BQ/ML	TAL-WA-013
AG-110M				BQ/ML	TAL-WA-013
SB-125				BQ/ML	TAL-WA-013
I-131				BQ/ML	TAL-WA-013
CS-134				BQ/ML	TAL-WA-013
CS-137				BQ/ML	TAL-WA-013
BA-140				BQ/ML	TAL-WA-013
LA-140				BQ/ML	TAL-WA-013
CE-141				BQ/ML	TAL-WA-013
CE-144				BQ/ML	TAL-WA-013
EU-154				BQ/ML	TAL-WA-013
EU-155				BQ/ML	TAL-WA-013
EU-156				BQ/ML	TAL-WA-013
PA-233				BQ/ML	TAL-WA-013
NP-237				BQ/ML	TAL-WA-013
NP-239				BQ/ML	TAL-WA-013
AM-241				BQ/ML	TAL-WA-013
AM-243				BQ/ML	TAL-WA-013
H+		5.00			
HI		0.26			

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Analytical Summary Sheet

Sample ID:	OXFL-623	Alternate ID:		Reviewed
Cell Bottle No.:	5154	Sample Date & Time	12/21/16 1:50	
Xfer Bottle No.:	W91	Analyzed Date & Time	12/21/16 16:17	
Customer:	NNFD	Analyst Initials	JSD	Logged
Charge Number:	C76RWK	Analyst Badge No.:	30028	
		REVISED: H+ UPDATE BDR		12/27/16

ANALYSIS	<	RESULT	2Σ ERROR	UNITS	PROCEDURE
G-ALPHA		1.1E+08	9.0E+5	BQ/ML	CASD-AM-TAL-01
5.15 MeV		0.0		%	TAL-WA-014
5.27 MeV		0.1		%	TAL-WA-014
5.37 MeV		0.8		%	TAL-WA-014
5.50 MeV		1.1		%	TAL-WA-014
5.80 MeV		93.9		%	TAL-WA-014
6.11 MeV		4.1		%	TAL-WA-014
G-NEUTRON		2.2E+06	1.5E+4	CPM/ML	TAL-WA-010
CO-60	<	2.9E+03		BQ/ML	TAL-WA-013
NB-95		5.0E+03	2.0E+03	BQ/ML	TAL-WA-013
ZR-95		2.5E+04	3.0E+03	BQ/ML	TAL-WA-013
RU-103		2.3E+04	3.0E+03	BQ/ML	TAL-WA-013
RU-106		3.0E+05	3.0E+04	BQ/ML	TAL-WA-013
AG-110M		1.2E+03	7.0E+02	BQ/ML	TAL-WA-013
SB-125		1.7E+04	3.0E+03	BQ/ML	TAL-WA-013
I-131	<	3.1E+03		BQ/ML	TAL-WA-013
CS-134		1.1E+04	2.0E+03	BQ/ML	TAL-WA-013
CS-137		2.6E+04	2.0E+03	BQ/ML	TAL-WA-013
BA-140		3.3E+04	9.0E+03	BQ/ML	TAL-WA-013
LA-140		2.3E+04	2.0E+03	BQ/ML	TAL-WA-013
CE-141		1.1E+04	2.0E+03	BQ/ML	TAL-WA-013
CE-144		3.8E+06	3.0E+05	BQ/ML	TAL-WA-013
EU-154		3.3E+05		BQ/ML	TAL-WA-013
EU-155		6.8E+04	8.0E+03	BQ/ML	TAL-WA-013
EU-156	<	2.5E+04		BQ/ML	TAL-WA-013
PA-233		6.9E+03	2.2E+03	BQ/ML	TAL-WA-013
NP-237	<	1.7E+05		BQ/ML	TAL-WA-013
NP-239		2.9E+05	2.0E+04	BQ/ML	TAL-WA-013
AM-241		5.4E+05	3.0E+04	BQ/ML	TAL-WA-013
AM-243		1.6E+05	1.0E+04	BQ/ML	TAL-WA-013
H+		0.86		N	
HI		0.07		N	
HI2		0.26		N	