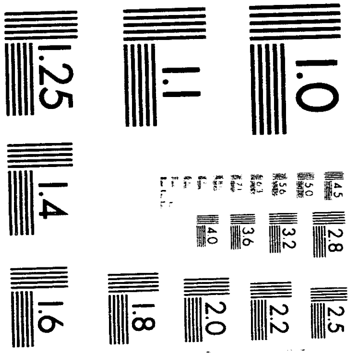
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5.0
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CMPO PURITY TESTS IN THE TRUEX SOLVENT USING AMERICIUM-241

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Summary

The Transuranic Extraction (TRUEX) Process was developed by E. P. Horwitz and coworkers at Argonne National Laboratory (ANL) to separate the +4, +6, and +3 actinides from acidic aqueous solutions of nuclear wastes. Octyl(phenyl)-N-N-diisobutyl-carbamoylmethylphosphine oxide (CMPO) is the active actinide complexant used in the TRUEX solvent. CMPO is combined with tributyl phosphate (TBP) in an organic diluent, typically n-dodecane, to form the TRUEX solvent. Small quantities of impurities in the CMPO resulting from: 1) synthesis, 2) acid hydrolysis, or 3) radiolysis can result in actinide stripping problems from the solvent. The impurity, octylphenylphosphinic acid (POPPA), is a powerful extractant at low acid concentrations which may be formed during CMPO synthesis. Consequently, commercial CMPO may contain sufficient quantities of POPPA to significantly impact the stripping of actinides from the TRUEX solvent. Sodium carbonate washing of the solvent is ineffective for POPPA removal. The americium distribution coefficient from 0.01M to 0.05M HNO_3 solutions is particularly sensitive to small quantities of POPPA in the CMPO.

The purpose of these tests was to 1) determine if commercially available CMPO is sufficiently pure to alleviate actinide stripping problems from the TRUEX process and 2) to determine if solvent cleanup methods are sufficient to purify the commercially

purchased CMPO. Extraction and solvent cleanup methodologies used by Horwitz and coworkers at ANL were used to determine CMPO purity with ^{241}Am.

A sample of purified CMPO (>99%) was obtained from ANL. A "reference" TRUEX solvent was prepared from this material and used as a standard or control in this work. Commercially available solvent extraction grade CMPO was purchased at a specified purity of >97% and was used to prepare the "commercial" TRUEX solvent. The commercially purchased CMPO was sent to ANL for further purification and was used to prepare the "further purified" TRUEX solvent. The ^{241}Am distribution coefficients (D_{Am}) from 0.01$\underline{M}$ HNO_3 obtained with the reference, commercial, and further purified solvents were then compared to establish CMPO purity. These tests indicate D_{Am}= 0.01 from 0.01$\underline{M}$ HNO_3 for the reference solvent. This agrees with the published value of D_{Am} = 0.011. However, the observed D_{Am} = 0.14 with the commercial solvent from 0.01$\underline{M}$ HNO_3 indicates this material contains enough manufacturing impurities to inhibit americium stripping. After further purification of the commercially purchased CMPO, the D_{Am} decreased to 0.03 in 0.01$\underline{M}$ HNO_3.

The commercial TRUEX solvent was further tested after washing with sodium carbonate prior to ^{241}Am extraction in an attempt to remove the impurities. The D_{Am} = 0.31 obtained from 0.01$\underline{M}$ HNO_3 indicates sodium carbonate was ineffective for removal of the

manufacturing impurities. Consequently, the commercial material is believed to contain significant quantities of the impurity POPPA. However, the improvement of the americium distribution coefficient in dilute nitric acid resulting from further purifying this CMPO is not significant enough to warrant additional CMPO purifying steps. The commercially purchased CMPO is found to be acceptable to use, as received, in a full-scale TRUEX process.

Table Of Contents

Lists Of Tables

Lists of Figures

Introduction

The Transuranic Extraction (TRUEX) Process, developed by E. P. Horwitz and coworkers at Argonne National Laboratory (ANL) [1], is currently being evaluated for actinide separations from various waste streams at the Idaho Chemical Processing Plant (ICPP). To evaluate the TRUEX process, the purity of the primary actinide extractant in the TRUEX solvent, octyl(phenyl)-N-N-diisobutyl-carbamoylmethylphosphine oxide (CMPO), must be determined. Small concentrations of impurities in the CMPO can dramatically effect actinide stripping from the TRUEX solvent [2]. The distribution ratio of americium at low acid concentrations is particularly sensitive to any impurities in CMPO.

Octylphenylphosphinic acid (POPPA) is a powerful extractant at low acid concentrations which may be formed during synthesis of CMPO [2]. Commercially available CMPO has a reported minimum purity of 97%. The quantity of POPPA in the 3% impurity is not known. Consequently, commercial CMPO may contain sufficient quantities of POPPA to significantly impact actinide stripping from the TRUEX solvent. Sodium carbonate washing the solvent is ineffective for POPPA removal [2]. It is uncertain if recent improvements in the CMPO manufacturing process have reduced the amount of POPPA in the currently available material. Therefore, extraction tests were conducted with ^{241}Am with the TRUEX solvent made from the commercial CMPO to establish its purity.

Purified CMPO from Argonne National Laboratory (ANL) was also obtained for these tests. ANL purified this CMPO by performing a double crystallization from hexane and it is reported to be >99% pure and contain 0.02% of the impurity, POPPA [2]. ANL reported a ^{241}Am distribution coefficient of D_{Am} = 0.011 using the TRUEX solvent made from this CMPO in a 0.01<u>M</u> HNO_3 feed solution (O/A = 1). The low D_{Am} achieved with the purified CMPO obtained from ANL allowed it to be used for control purposes in this work.

It is reported [3] that D_{Am} is extremely sensitive to acidic impurities at 0.01$\underline{M}$ to 0.04$\underline{M}$ HNO_3. For 2$\underline{M}$ nitric acid solutions, D_{Am} is strongly dependant on the concentration of CMPO in the TRUEX solvent [3]. Therefore, an examination of D_{Am} from 0.01$\underline{M}$ to 2$\underline{M}$ HNO_3 can be used to insure CMPO purity and concentration in the TRUEX solvent.

This work may be directly applied to the development of quality control methods for the TRUEX solvent at the ICPP. Furthermore, techniques for TRUEX experiments can be validated by comparing the results of the experiments with literature reports.

Experimental

Chemicals

CMPO (>99%) obtained from ANL was purified in their laboratory by recrystallizing twice from hexane. The CMPO was vacuum desiccated (to remove entrained water) at the ICPP for three days prior to preparation of the TRUEX solvent. The composition of the solvent, prepared by the ICPP Quality Control (QC) Laboratory, was 0.2<u>M</u> CMPO and 1.4<u>M</u> TBP (≈99%, Fluka AG) in n-dodecane (purified grade, Fisher), as specified for the TRUEX process [3]. The organic solution prepared with the ANL purified material will be denoted as the "reference" TRUEX solvent in this report.

Commercial CMPO (97% min., Elf Atochem) was also desiccated for three days prior to solvent preparation. The QC lab prepared a TRUEX solvent from this CMPO at the same concentrations as specified above for the reference solvent. The solvent prepared from the commercial CMPO will be referred to as the "commercial" solvent in this report.

A NIST traceable ^{241}Am standard (Amersham) in 1 vol% HNO_3 with an activity of 340.8 dps/ml was used to spike solutions of nitric acid (reagent grade, Baker) for the aqueous feeds. The HNO_3 in the ^{241}Am standard was taken into account during the preparation of the spiked nitric acid feed solutions. Feed acid concentrations and ^{241}Am activities are shown in Table 1.

Table 1: Feed Acid Concentrations And ^{241}Am Activities

[HNO_3]	^{241}Am Activity d/s/ml
0.01	21.25
0.04	85
0.20	340
0.50	340
1.80	226
2.00	283
2.25	283

Solvent Pre-equilibration With HNO_3

Prior to each extraction, the TRUEX solvent was pre-equilibrated with a HNO_3 solution of the same concentration as the feed to be tested. Pre-equilibration of the solvent was performed by contacting 5 mls of the TRUEX solvent with five mls of the acid solution and vigorously hand shaking the two phases for two minutes. The phases were separated by centrifuging for 5 minutes at 3000 rpm. After phase separation, the aqueous phase was removed using a disposable glass pipet. Each solvent was contacted three times in this manner with fresh acid to ensure acid equilibration in the solvent. Acid pre-equilibration of the solvent insures that the organic phase is loaded with nitric acid and water. Thus, the only species transferred between phases is the one of interest, ^{241}Am in this case. Pre-equilibration is also necessary since TBP in the solvent extracts large amounts of nitric acid and water which could result in HNO_3 concentration changes between phases.

^{241}Am Extractions

Feed solutions containing ^{241}Am were prepared with HNO_3 concentrations of 0.01, 0.04, 0.2, 1.8, 2.0, and 2.25M. Americium activities in the feeds varied depending on the volume of concentrated (≈16M) HNO_3 added to the standard for the desired acid concentration (Table 1). Four mls of the ^{241}Am + HNO_3 feed was contacted with four mls of the pre-equilibrated solvent. Phase contacts and separations were performed according to the method already stated in the previous section.

Following phase separation, 1 ml of the loaded organic and 1 ml of the aqueous raffinate were placed in vials for ^{241}Am counting. Sample analysis was performed by γ-spectroscopy. The phases were removed from the tube with a disposable glass pipet. Care was taken in removing the bottom (aqueous) phase to prevent contamination by the loaded organic phase. The balance of the aqueous phase was retained for acid analysis.

Solvent Pretreatment By Carbonate Washing

The commercial solvent was also tested after washing twice with a 0.25M sodium carbonate (Na_2CO_3) solution. Twenty-five mls of the TRUEX solvent was contacted with 5 mls of the sodium carbonate soluti for two minutes on a vortex mixer [3]. Phase separation was effected by centrifuging for five minutes at 3000 rpm. The carbonate washed solvent will simply be designated "washed" solvent in this report.

Further Purification Of The Commercial CMPO By Argonne

The commercially purchased CMPO was sent to Argonne National Laboratory for further purification using their double recrystallization method. The QC Laboratory prepared a TRUEX solvent using this CMPO to the same concentrations as the reference and commercial solvents. The TRUEX solvent made from this CMPO was washed with 0.25M sodium carbonate prior to testing.

Testing with this solvent allowed for a comparison of americium distribution coefficients between the reference, commercial, and carbonate washed commercial solvents.

Equilibrium Acid Titrations

Equilibrium acid concentrations in the aqueous raffinates were determined after each extraction. An aliquot of each aqueous raffinate was titrated with a standardized 0.1002M NaOH solution to a phenolphthalein end point.

^{241}Am Analysis

Both aqueous and organic samples were analyzed for ^{241}Am by placing 1 ml of the contacted phase in a 5 dram vial having a calibrated geometry. Organic samples were placed in a glass vial and aqueous samples were placed in a polyethylene vial. The vials were centered against a High Purity Germanium detector having a relative efficiency of 73%. The ^{241}Am primary photopeak at 59.5 Kev was used to determine americium activities in each phase.

Results and Discussion

D_{Am-241} For The Reference Solvent

The experimentally determined ^{241}Am distribution coefficients with the reference solvent were compared with published ANL results [3]. These distribution coefficients are listed in Table 2 and represented graphically in Figure 1. Note that there was a slight difference between the TRUEX solvents in these two studies (ANL used 1.2$\underline{M}$ TBP where the ICPP solvent used 1.4$\underline{M}$ TBP); however, this difference is expected to have negligible effects on D_{Am} since the solvent was pre-equilibrated prior to extractions.

It is apparent from Figure 1 that the D_{Am}'s reported in the literature and those obtained experimentally in this work are in good agreement.

Table 2. D_{Am} For The Reference Solution

$[HNO_3]$	ANL D_{Am}	ICPP D_{Am}
0.01	0.011 (Ref. 3)	0.01
0.04	0.13 (Ref. 3)	0.084
0.52	*	10.66
1.8	*	25.77
2.0	25.0 (Ref. 3)	22.47
2.25	*	22.61

* Data is available in Figure 1, p. 912 of Ref. 3.

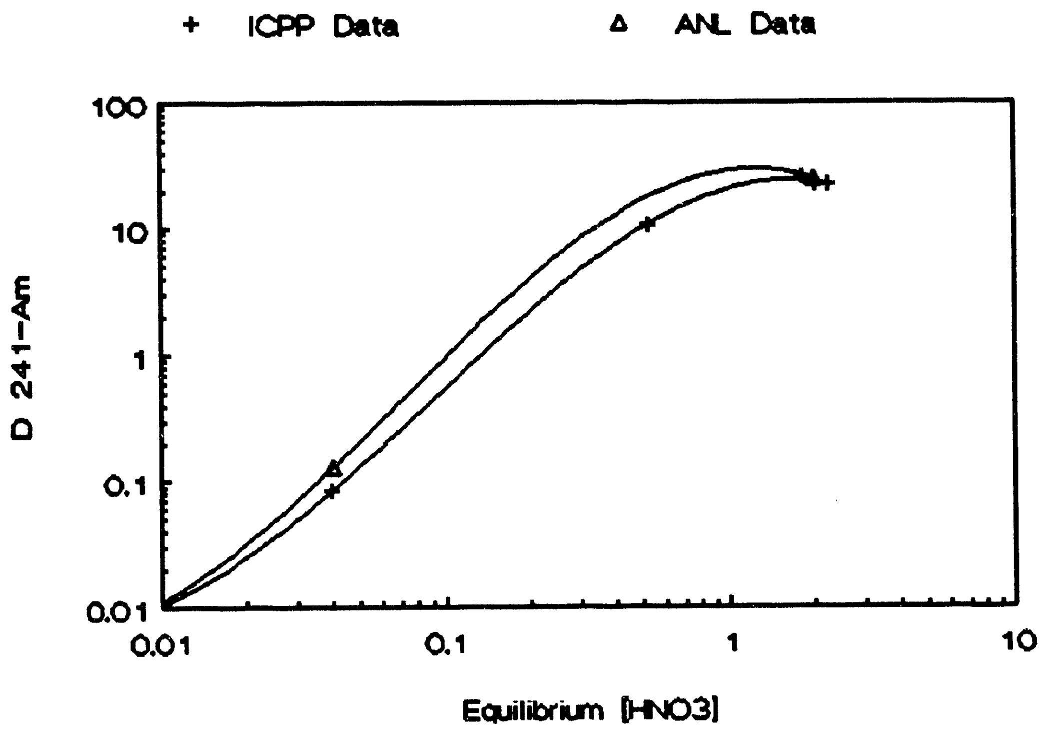

Figure 1: D_{Am} In TRUEX Solvent Made From Purified CMPO

D_{Am-241} For The Commercial Solvent

Americium distribution coefficients were determined as a function of nitric acid concentration for the commercial solvent. These results are listed in Table 3. The values of D_{Am} obtained with the reference solvent are also listed for comparison. The data in Table 3 is presented graphically in Figure 2. It is apparent from Figure 2 that enough impurities remain in the commercial CMPO to affect D_{Am} at lower acid concentrations. D_{Am} in the 0.01<u>M</u> HNO_3 feed solution is an order of magnitude higher with the commercial solvent than with the reference material. This indicates that stripping may be less efficient if the commercial CMPO is used without further purification. As anticipated, the effects of impurities in the CMPO are unnoticed at higher acid concentrations.

Horwitz reports that $D_{Am} = 0.4$ from a 0.01<u>M</u> HNO_3 strip solution using TRUEX solvent made from 85-90% pure CMPO [2]. POPPA is also reported to be the primary reason for this high D_{Am}. Comparing the $D_{Am} = 0.14$ observed with the commercial solvent (>97% pure CMPO) at the same acid concentration indicates a slight improvement in the ability to strip americium from the commercial solvent and therefore, less POPPA contamination in the CMPO.

Table 3. D_{Am} At Different Acid Concentrations With The Commercial And Reference Solvents

[HNO_3]	D_{Am} Commercial Solvent	D_{Am} Reference Solvent
0.01	0.14	0.01
0.04	0.17	0.084
0.16	1.92	*
0.52	*	10.66
1.8	20.9	25.77
2.0	19.68	22.47
2.2	20.16	22.61

* Extraction not performed at this acid concentration

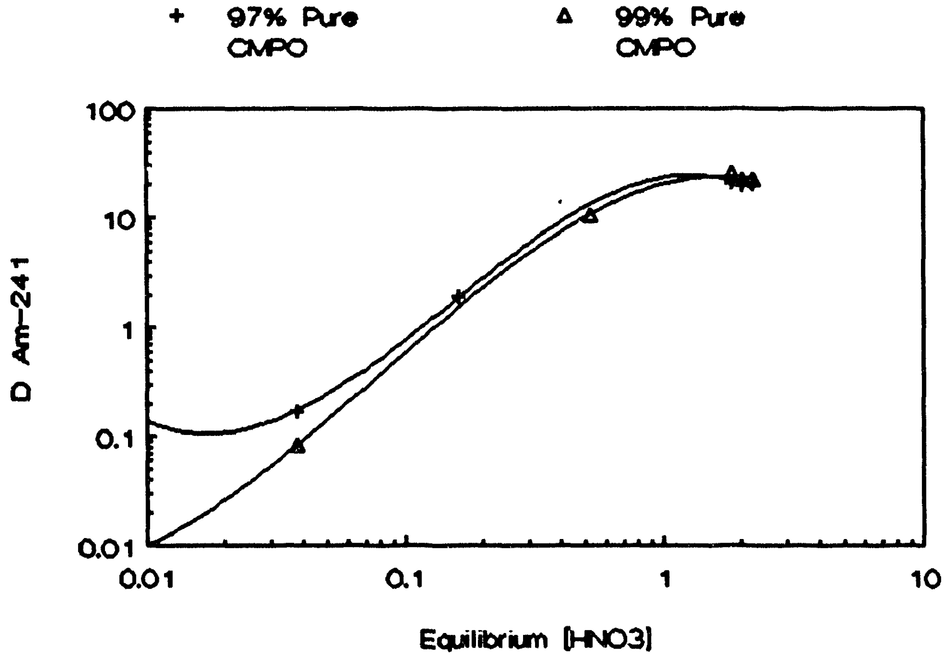

Figure 2: D_{Am} Using 97% And 99% Pure CMPO

D_{Am-241} For The Carbonate Washed Solvent

In an attempt to purify the CMPO, the commercial solvent was washed with sodium carbonate. Sodium carbonate effectively removes many degradation products from the solvent resulting from acid hydrolysis and radiolysis [3]. However, the manufacturing impurity, POPPA, is reported not to be removed by carbonate scrubs [3].

Distribution coefficients for the washed solvent are listed in Table 4. A D_{Am} of 0.31 was obtained from 0.01$\underline{M}$ HNO_3, as compared to the desired D_{Am} of 0.01 obtained with the reference solvent. This is apparently due to significant quantities of POPPA remaining in the CMPO from the manufacturing process. Note that $D_{Am} = 0.31$ for the carbonate washed solvent is slightly higher than that ($D_{Am} = 0.14$) obtained with the unwashed solvent. It is postulated this difference is due to experimental error (temperature changes) rather than an actual increase as a result of carbonate washing. A comparison of D_{Am} for the carbonate washed CMPO and the purified CMPO material is shown in Figure 3.

Table 4. D_{Am} Results For The Carbonate Washed TRUEX Solvent

[HNO_3]	D_{Am} Reference	D_{Am} Washed
0.01	0.01	0.31
0.04	0.084	0.34
0.22	10.66	2.97
2.13	25.77	36.48
2.25	22.47	38.43
2.46	22.61	36.84

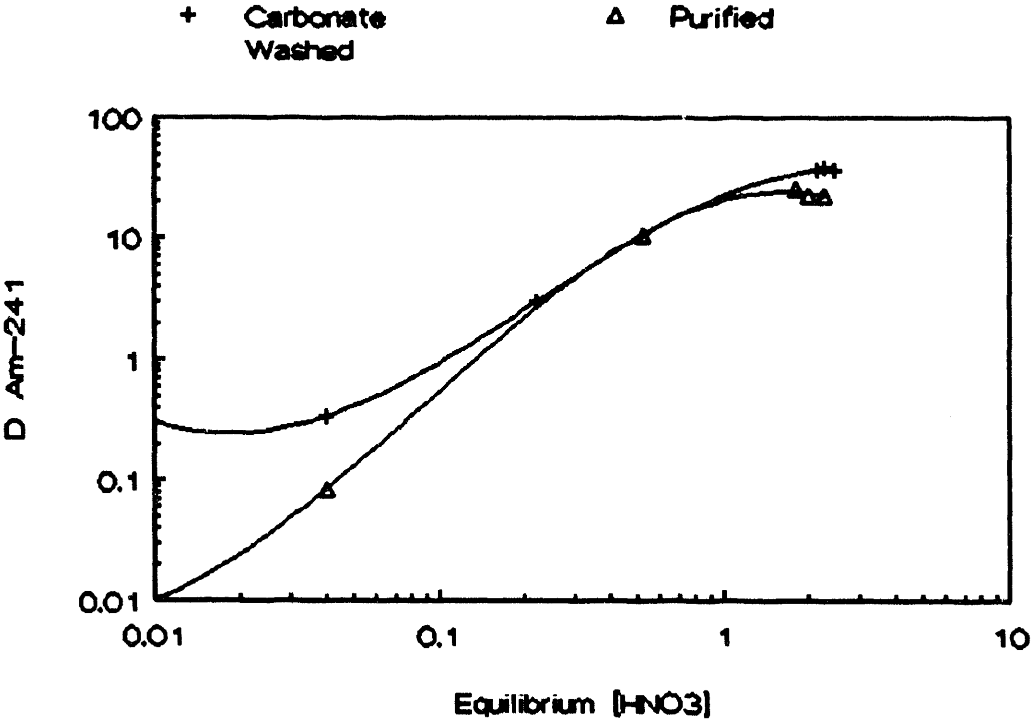

Figure 3: D_{Am} Using Carbonate Washed And Purified CMPO

D_{Am-241} For The Further CMPO Purified Commercial Solvent

In an attempt to achieve a lower D_{Am} at the lower acid concentrations and to better identify the impurity present in the commercially purchased CMPO, this CMPO was sent to ANL for further purification. ANL performed the purification process using the double recrystallization method already mentioned. This purification process removes the POPPA impurity that hinders americium from being stripped from the TRUEX solvent.

Distribution coefficients for this further purified CMPO solvent are listed in Table 5. For comparison purposes, distribution coefficients for the reference and commercial solvents are also listed. As seen from this table, an improvement in D_{Am} was achieved at the lower acid concentrations when compared to the commercial solvent (used as received). Distribution coefficients from the further purified CMPO solvent compare nicely with those obtained with the reference solvent. Results from this test indicate that some of the manufacturing impurities (POPPA) were removed by further purifying the commercially purchased CMPO. A comparison of D_{Am} for the commercial TRUEX solvent and the TRUEX solvent made from the further purified CMPO is shown in Figure 4.

Table 5. D_{Am} Results For The TRUEX Solvent Made From The Further Purified CMPO Compared With Commercially Purchased And ANL Purified CMPO TRUEX Solvents

[HNO_3]	D_{Am} Further Purified Solvent	D_{Am} Commercial Solvent	D_{Am} Reference Solvent
0.01	0.03	0.14	0.01
0.04	0.09	0.17	0.084
0.16	1.08	1.92	*
0.52	*	*	10.66
1.8	16.42	20.9	25.77
2.0	17.80	19.68	22.47
2.2	16.85	20.16	22.61

* Extraction not performed at this acid concentration

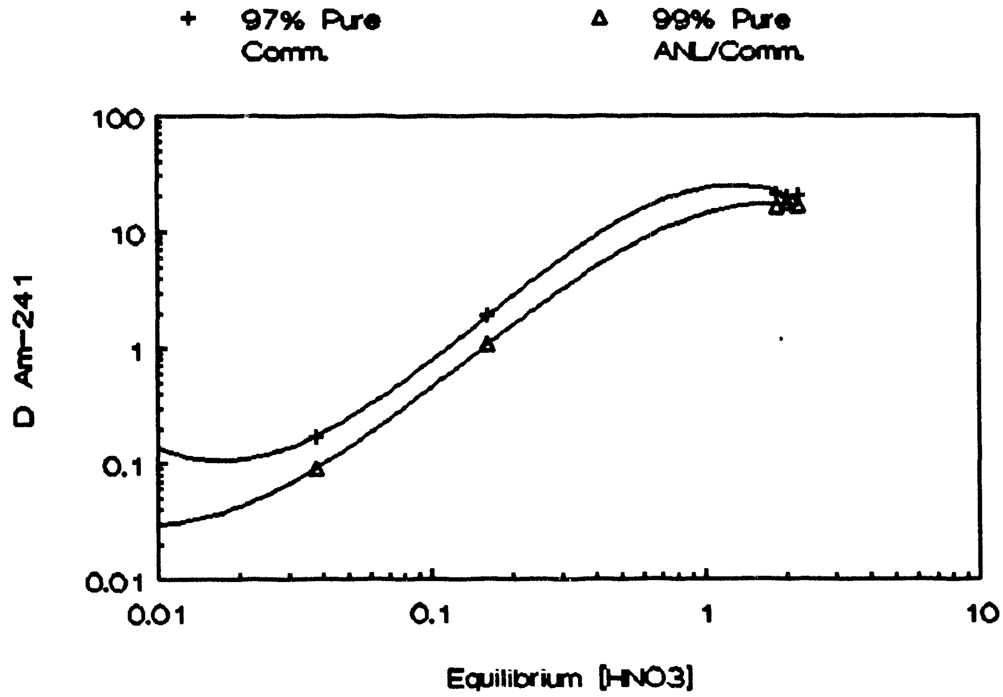

Figure 4: D_{Am} Using Further Purified CMPO

Conclusions

The experimentally determined americium distribution coefficients using the ANL purified CMPO in the TRUEX solvent agree with those reported in the literature. This indicates consistency between the experimental techniques used at ANL and the ICPP. The CMPO, when purified in accord with the ANL procedure, can be used as a "control" or standard to evaluate the TRUEX solvent in pilot plant and experimental tests at the ICPP.

Americium distribution coefficients obtained from 0.01 and 0.04M HNO_3 feed solutions are up to an order of magnitude higher for the commercial solvent as opposed to the reference solution. These high D_{Am}'s indicate that americium stripping may be difficult in the TRUEX Process if the commercially purchased CMPO is not further purified. However, the stripping difficulties may be alleviated by additional stripping stages in the TRUEX process. Another option for using the commercially purchased CMPO, is to allow the americium complexed by the CMPO impurities to remain in the solvent. Even though the D_{Am} is higher with the commercial solvent in 0.01 M HNO_3, the amount of ^{241}Am extracted by the CMPO impurities is small compared to that extracted by the CMPO.

Additional purification of the commercially purchased CMPO does result in D_{Am} similar to that of the ANL reference solution. The slight improvement of the stripping D_{Am} seen in the further purified commercially purchased CMPO is not drastic enough to warrant additional CMPO purification for a full-scale process. This purification is not only time consuming, but may add to the operational cost without contributing significantly to americium stripping efficiency. Therefore, the > 97% pure commercially purchased CMPO is suitable for use as received in a full-scale process.

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2. E. P. Horwitz, et. al., "Behavior Of Americium In The Strip Stages Of The TRUEX Process", Solvent Extraction And Ion Exchange, Vol. 6, pp. 93-110, (1988).

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Appendix

Analytical Data From ^{241}Am Extractions In The TRUEX Solvent Made From The ANL Purified CMPO (O/A = 1)

$[HNO_3]$	^{241}Am Feed Activity d/s/ml	Aqueous Raffinate ^{241}Am Activity d/s/ml	Organic Feed ^{241}Am Activity d/s/ml
0.01	21.25	21.83 ± 1.1	ND
0.04	85	78.38 ± 3.1	ND
0.52	340	28.32 ± 1.6	302 ± 12.0
1.82	226	7.92 ± 0.43	204 ± 7.2
2.02	283	11.51 ± 0.57	259 ± 8.9
2.25	283	11.58 ± 0.57	262 ± 9.9

ND = None Detected

Analytical Data From ^{241}Am Extractions In The TRUEX Solvent Made From The Commercially Purchased CMPO (O/A = 1)

$[HNO_3]$	^{241}Am Feed Activity d/s/ml	Aqueous Raffinate ^{241}Am Activity d/s/ml	Organic Feed ^{241}Am Activity d/s/ml
0.01	21.25	18.5 ± 0.95	2.58 ± 0.22
0.04	85	73.8 ± 2.93	12.9 ± 0.62
0.20	340	113.0 ± 4.21	217.0 ± 7.54
1.82	226	10.1 ± 0.51	211.0 ± 7.73
2.02	283	12.5 ± 0.60	246.0 ± 8.91
2.25	283	12.6 ± 0.73	254.0 ± 8.71

Analytical Data From ^{241}Am Extractions In The Carbonate Washed TRUEX Solvent Made From The Commercially Purchased CMPO (O/A = 1)

[HNO_3]	^{241}Am Feed Activity d/s/ml	Aqueous Raffinate ^{241}Am Activity d/s/ml	Organic Feed ^{241}Am Activity d/s/ml
0.01	21.25	12.2 ± 0.80	3.7 ± 0.33
0.04	85	47.9 ± 3.7	16.1 ± 2.7
0.22	340	73.4 ± 4.4	218.0 ± 9.1
2.13	226	5.4 ± 0.55	197.0 ± 8.7
2.25	283	6.6 ± 0.53	254.0 ± 12.0
2.46	283	6.7 ± 0.53	246.0 ± 10.0

Analytical Data From ^{241}Am Extractions In The TRUEX Solvent Made From The Further Purified Commercially Purchased CMPO (O/A = 1)

[HNO_3]	^{241}Am Feed Activity d/s/ml	Aqueous Raffinate ^{241}Am Activity d/s/ml	Organic Feed ^{241}Am Activity d/s/ml
0.01	21.25	19.3 ± 0.16	0.63 ± 0.065
0.04	85	77.5 ± 0.30	6.65 ± 0.11
0.16	340	160 ± 0.43	172 ± 0.44
1.8	226	12.6 ± 0.13	207 ± 0.48
2.0	283	14.7 ± 0.14	261 ± 0.54
2.2	283	15.5 ± 0.14	261 ± 0.54

These samples were counted by liquid scintillation

Note: Mass balance errors associated with these tables are attributed to experimental and analytical counting uncertainties.

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