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SEPARATION OF BERKELIUM FROM TRIVALENT ACTINIDES BY
CHROMATE OXIDATION AND HDEHP EXTRACTION

ABSTRACT

The extraction of ^{144}Ce by organic phases of varying HDEHP concentrations from nitric acid media of varying concentrations containing varying concentrations of oxidizing agents, i.e., NaBrO_3 and/or CrO_3 , is discussed. The extraction of ^{249}Bk under similar aqueous and organic phase conditions as used for ^{144}Ce extractions is described. Procedures for stripping the extracted ^{144}Ce or ^{249}Bk are discussed. Results of the actual separation of ^{244}Cm from ^{249}Bk are also given. Finally, a process for the separation of ^{249}Bk from the other transplutonium elements is proposed.

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J. B. Knauer and Boyd Weaver

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INTRODUCTION

The following research was undertaken to determine a method for separating berkelium from the other transplutonium elements. Under controlled conditions it has been shown¹ that the tetravalent and hexavalent members of the lanthanide and actinide series may be extracted efficiently from an aqueous nitric acid phase into an opposing phase containing di(2-ethylhexyl)orthophosphoric acid (HDEHP). The trivalent members of these groups, however, remain preferentially in the aqueous phase.

Considerable effort has been put forth in attempting to exploit the tetravalent state of these elements to effect their separation from the other elements in the lanthanide and actinide series.¹⁻⁷ Oxidation to the tetravalent state was accomplished by the use of mineral acid solutions, e.g., HNO_3 , containing bromate. However, some difficulty has arisen with this oxidizing aqueous phase, due to the instability of the bromate⁸ at the high acid concentrations required. A primary objective of this research has, therefore, been to obtain a more stable aqueous phase capable of oxidizing berkelium to the tetravalent state in order that it can be separated from the other transplutonium elements.

The similarity of the chemistry of Bk and the chemistry of Ce has also been demonstrated.⁹ Figures 1 and 6, which give results of the extractions of Bk and Ce from HNO_3 solutions in the present work, illustrate this behavior, although there is some difference at the higher acidities in Fig. 1. Therefore, the distribution of Ce(IV) between an organic phase of HDEHP and an aqueous phase of some oxidizing agent in a nitric acid medium was investigated and used as a model to predict the optimum conditions for the Bk(IV) distribution.

The extraction of Ce by HDEHP at various concentrations was investigated under different conditions of the aqueous phase, i.e., as a function of the acidity, the NaBrO_3 concentration, and the phase contact times. Next, since it was known from previous preliminary tests¹⁰ that the addition of CrO_3 to the NaBrO_3 - HNO_3 aqueous medium would enhance the

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Fig. 1. Extraction of Bk(III) and Ce(III) as a Function of HNO_3 Concentration in the Absence of NaBrO_3 or CrO_3 at Different HDEHP Concentrations.

oxidation of the Ce to the tetravalent state and thereby increase its extraction into the organic phase, it seemed advantageous to explore systematically the use of CrO_3 as an oxidizing agent for Ce. The information gained from the Ce extraction was then applied to testing the Bk distribution. Finally, the actual separation of ^{249}Bk from Cm was investigated as a function of the HDEHP concentration using the best conditions indicated by the preceding tests.

Based on the results obtained, a preliminary chemical flowsheet (Fig. 11) is proposed for the process for separating Bk from Cm and other transplutonium elements.

EXPERIMENTAL

General

HDEHP was obtained from the Virginia-Carolina Chemical Company with a purity of greater than 98%. No further purification of this reagent was carried out. The diluents used were Amsco 125-82, which was obtained from the American Mineral Spirits Company, and reagent grade n-dodecane, which was obtained from Matheson Coleman and Bell. The 314 d beta-active ^{249}Bk , the 470 y ^{241}Am , and the 18 y ^{244}Cm were obtained from the ORNL TRU Facility. The ORNL Isotopes Division provided the ^{144}Ce and ^{152}Eu .

Determination of E_A^O

The distribution coefficient, E_A^O , defined for a given nuclide as the ratio of the concentration of nuclide in the organic phase to the concentration of nuclide in the aqueous phase, was determined by direct counting of the radioactivity of equal volumes of each phase.

The alpha and beta activities of ^{244}Cm and ^{249}Bk , respectively, were counted with a Packard Tri-Carb Liquid Scintillation spectrometer, Model 3003. Counting efficiency was tested by means of standard scintillation quenching curves, which were obtained for each of the systems under consideration. Quenching was found to be negligible in all organic

phases tested, but became significant in the more concentrated aqueous solutions.

Gamma activity was determined with a well-type scintillation counter, which employs a thallium-activated sodium iodide [NaI(Tl)] crystal as the detector. The background counting rate for this instrument was ~ 5 cts/sec.

Extraction and Stripping

Ce(III) and Bk(III) were extracted from HNO_3 solutions of varying concentrations by HDEHP solutions of different concentrations. The tetravalent states of these elements were extracted by HDEHP solutions of varying concentration from a nitric acid medium containing NaBrO_3 and/or CrO_3 , which act as oxidizing agents, of varying concentrations. Equal volumes of aqueous and organic phases were equilibrated in separatory funnels mounted on a rotating contactor, and comparisons were made of contact and oxidation periods, i.e., phase contacts of 5, 20, and 60 minutes, and 20 minutes following a one-hour oxidation period in the aqueous phase.

Tests were made of stripping of Ce and Bk from the organic phase by HCl , HNO_3 , and the same acids containing the reductant H_2O_2 . All extractions and strips were performed at room temperature, 23-27°C.

RESULTS WITH CERIUM

Cerium Extraction

In the absence of any oxidizing agent in the aqueous phase the distribution coefficient for Ce decreases with an increase in HNO_3 concentration. Extraction of Bk(III) is similarly dependent on acid concentration except for an increase above $\sim 4 \text{ N } \text{HNO}_3$ (Fig. 1). However, when the acidity of a $0.05 \text{ M } \text{NaBrO}_3$ - HNO_3 system is increased, the Ce extraction is observed to decrease slightly at low acidities and then to increase rapidly, almost linearly, above $4 \text{ N } \text{HNO}_3$ (Fig. 2). The curves of Figure 2 indicate that the oxidation of Ce(III) to Ce(IV) by $0.05 \text{ M } \text{NaBrO}_3$ is not effective until the higher acidities are reached.

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Fig. 2. ^{144}Ce Extraction as a Function of the HNO_3 Concentrations, Both With and Without 0.05 M NaBrO_3 .

In order to determine the most effective contact period of the two phases, the Ce extraction was studied at various contact times both with and without NaBrO_3 present in the aqueous phase. As can be seen from Figure 3, the length of the contact period gives differences of up to 2.5 times in the extraction of Ce at acid concentrations up to $\sim 5 \text{ N}$. It was also noted that allowing the Ce to stand in the oxidizing aqueous phase for a one-hour period prior to a 20 minute contact with the organic phase improved the Ce extraction by a factor of 2 to 3.

Figure 4 shows the plot of the distribution coefficients for the Ce extraction by 0.5 M HDEHP-Amsco 125-82 from aqueous solutions of 0.01 M CrO_3 -0.05 M NaBrO_3 and varying HNO_3 concentrations at different contact times. Comparing the results in Figure 4 with those shown in Figure 3 shows a significant improvement in the Ce extraction, which results from the addition of this small quantity of CrO_3 (0.01 M) to the aqueous phase. This is especially true at the lower acidities. For example, between 1 N and 4 N HNO_3 the presence of 0.01 M CrO_3 enhances the Ce extraction by factors of 1400 and 460 for 5 and 20 minute contacts, respectively, without the decrease in the Ce extraction observed in Figure 3 for 0.05 M NaBrO_3 alone.

The distribution coefficients for Ce in the presence of both CrO_3 and NaBrO_3 (Fig. 4) are seen to decrease with increased acidity at and above 4 N HNO_3 . It is thought that this decrease at the higher acidities is due to the decomposition of the NaBrO_3 present. This idea is supported by the results obtained for Ce extractions from CrO_3 - HNO_3 systems not containing NaBrO_3 (Fig. 5). It can be seen that in the absence of NaBrO_3 the distribution coefficients of Ce increase with increasing acidity over the entire acid concentration range studied, indicating little or no decomposition of CrO_3 .

Increasing the contact time, between the organic phase and the aqueous phases that contain both CrO_3 and NaBrO_3 , decreases the extraction of Ce (Fig. 4). On the other hand, the Ce extraction from CrO_3 - HNO_3 systems not containing NaBrO_3 , over the same acid concentration range, is seen to be improved only slightly with increased contact periods (Fig. 5). It

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Fig. 3. ^{144}Ce Extraction by 0.5 M HDEHP-Amsco 125-82 as a Function of HNO_3 Concentrations, Both With and Without 0.05 M NaBrO_3 , at Different Contact Times.

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Fig. 4. ^{144}Ce Extraction by 0.5 M HDEHP-Amsco 125-82 from 0.01 M CrO_3 -0.05 M NaBrO_3 as a Function of the HNO_3 Concentration at Different Contact Times.

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Fig. 5. ^{144}Ce Extraction by 0.5 M HDEHP-Dodecane from 0.08 M CrO_3 as a Function of the HNO_3 Concentration at Different Contact Times.

was also observed that a one-hour oxidation period in the $\text{CrO}_3\text{-HNO}_3$ solutions prior to a 20 minute contact with extractant did not improve the Ce extraction. This supports the idea that the oxidation of Ce is faster with CrO_3 than with NaBrO_3 .

A significant improvement in the values of the distribution coefficients for the Ce extraction was obtained when the organic phase diluent was changed from Amsco 125-82 to n-dodecane. For example, E_A^0 values from ~400 to 500 were obtained with n-dodecane as diluent as compared with values of ~100 to 200 with Amsco 125-82 under corresponding conditions.

Laboratory experiments were also carried out on the extraction of Ce as a function of one of the oxidants in the aqueous phase while holding constant the concentrations of the other oxidant and the HNO_3 . The most significant result from these tests was confirmation that, in the concentration range of 0.02 to 0.2 M CrO_3 , the extraction of Ce was at least as efficient from solutions without NaBrO_3 as from solutions which did contain NaBrO_3 over the same CrO_3 concentration range.

During the extraction of Ce by 0.5 M HDEHP from aqueous phases containing CrO_3 a vivid green color was formed in the organic phase, with a corresponding decrease in the intensity of the yellow color of the aqueous phase. It is believed that the green color derives from an extractable chromium compound of unknown composition. No attempt was made in the present work to determine the composition of this chromium compound; however, it was found that the green color produced in the organic increased in intensity with increasing concentrations of HNO_3 , CrO_3 , and extractant. Changing the diluent from Amsco 125-82 to n-dodecane reduced formation of the green color considerably. A further reduction in color was obtained by scrubbing the n-dodecane with concentrated H_2SO_4 prior to its use as a diluent, suggesting that interactions with reactive organic contaminants may be involved. The formation of the green color was determined to be independent of the NO_3^- ion (in contrast to HNO_3) concentration present in the aqueous phase.

Additional experiments concerning the nature of the substance causing the green color are being made at the present time.¹⁰ It has been shown that prolonged contact, i.e., 2 to 3 days, causes the green substance to be reduced. As a result a blue color, which is thought to be due to Cr^{+3} , is formed in the aqueous phase. During this transition Ce was observed to be reduced from Ce(IV) to Ce(III), thus being stripped from the organic back into the aqueous phase. Since phases are never to be in contact for periods of this length in the process under consideration, it is believed that the green color does not have any significant effect on the extraction of Ce.

Cerium Stripping

Stripping of the Ce from HDEHP-dodecane (0.1 to 0.5 M) was studied using aqueous systems of either HCl or HNO_3 . The stripping coefficients, S_O^A , ranged from 2×10^2 to 3.3×10^3 for an aqueous system of 4 N HCl over this HDEHP concentration range. The aqueous phase, however, resulting from the strip with HCl was yellow in color indicating that part of the chromium compound present in the organic was also stripped into the aqueous phase.

Using 10 N HNO_3 as the strippant eliminated the yellow color from the resulting aqueous phase, but yielded S_O^A values which were much lower, i.e., 0.60 to 1.2, than those obtained with HCl. These values were improved greatly when H_2O_2 was added to the 10 N HNO_3 at a concentration of 1 M. The values of S_O^A obtained for the 1 M H_2O_2 -10 N HNO_3 system were $\sim 1.4 \times 10^2$ and the stripping phase remained colorless. These results indicate that the extracted Ce(IV) is completely reduced by HCl or H_2O_2 - HNO_3 , but only partially reduced by HNO_3 alone.

RESULTS WITH BERKELIUM

Berkelium Extraction

In the absence of any oxidizing agent, the extraction of Bk decreases with increasing HNO_3 concentrations below ~ 3 N (Fig. 1), with both 0.1

and 0.5 M HDEHP solutions in *n*-dodecane. This decrease was expected a priori.^{11,12} At ~ 4 N HNO_3 the Bk extraction begins to increase slightly.

Figure 6 shows the results of the extraction of ^{249}Bk as a function of the HNO_3 concentration in the presence of 0.08 M CrO_3 . The high values of E_A° obtained here seem to indicate, when compared with the results shown in Figure 1, that the Bk is nearly completely oxidized to the highly extractable Bk(IV) species in the presence of CrO_3 , whereas in the absence of oxidant (Fig. 1) the species present is most likely Bk(III).

The extractant concentration dependence of the Bk(IV) extraction from 0.08 M CrO_3 -4 N HNO_3 solutions is shown graphically in Figure 7. At a reagent concentration of ~ 0.1 M, the extraction of Bk(IV) appears to become nearly independent of the extractant concentration. It is likely that this observed behavior for Bk results from an analytical limit in the Bk analysis in the raffinate, e.g., a non-extractable radioactive contaminant. The discrepancy between the $E_A^{\circ}(\text{Bk})$ values obtained for the separate Bk extractions (shown by open symbols in Fig. 7) and the $E_A^{\circ}(\text{Bk})$ (Table 2) values obtained in the combined separation of Bk and Cm (shown by closed symbols in Fig. 7) is similarly believed to be the result of the presence of a radioactive contaminant. Since the values of E_A° for the Bk extraction were already so high, further tests to determine whether or not a contaminant was the cause of this behavior were not felt necessary.

Figure 7 also shows the extractant concentration dependence exhibited by $^{152-154}\text{Eu}$, ^{241}Am , and ^{244}Cm . These isotopes all show a direct second power dependence on the extractant concentration and remain in their trivalent states throughout the extraction process.

Separation factors, $SF_{\text{Cm}}^{\text{Bk}} = E_A^{\circ}(\text{Bk})/E_A^{\circ}(\text{Cm})$, calculated from the separate extraction curves of Figure 7, ranged from 5×10^4 to $>10^6$. These are believed to be minimum values, since the $E_A^{\circ}(\text{Bk})$ values are thought to be analytically depressed, as noted above.

Increasing the CrO_3 concentration in an aqueous medium of 4 N HNO_3 with 0.5 M HDEHP-dodecane as the extractant phase yielded the E_A° values

Fig. 6. Comparison of the Extractions of ^{249}Bk and ^{144}Ce by HDEHP Solutions from 0.08 M $\text{CrO}_3\text{-HNO}_3$ as a Function of the Acid Concentration.

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Fig. 7. Comparison of the Extractions of ^{249}Bk , ^{244}Cm , ^{241}Am , and $^{152-154}\text{Eu}$ as a Function of the HDEHP Concentration from 0.08 M CrO_3 - 4 N HNO_3 .

shown in Figure 8. These values are seen to remain high in the more concentrated CrO_3 solutions with a maximum of ~ 1800 at $0.2 \text{ M } \text{CrO}_3$, thus, permitting the use of higher CrO_3 concentrations without significant loss in the Bk extraction efficiency. This could be an important factor, if there is any loss of CrO_3 as a result of radiolysis at the high radiation levels at which the separation process will be employed. Testing at high radiation levels was not permitted in the area where this research was performed; however, tests to determine the radiation effects on the system are being planned.

Over the same increasing CrO_3 concentration range used for the Bk extractions (Fig. 8), the values of E_A^0 for Cm increased from $\sim 3 \times 10^{-2}$ to 2×10^{-2} . It is suspected that this increase in the Cm extraction is the result of a synergistic effect rather than a result of some oxidation of the Cm. Calculation of the separation factor of Bk from Cm at $0.08 \text{ M } \text{CrO}_3$ - $4 \text{ N } \text{HNO}_3$ (Fig. 8) yielded a value of $> 7.5 \times 10^4$, which is in good agreement with values of $\text{SF}_{\text{Cm}}^{\text{Bk}}$ from Figure 7.

From the results obtained on the Bk extraction, as discussed above, it may be concluded that, as with Ce, the Bk extraction from nitric acid solutions is low in the absence of any oxidizing agent but high in the presence of an oxidizing agent, and CrO_3 is a satisfactory oxidizing agent.

Since Li and Zr are likely contaminants in the expected feed solutions, we tested their effects on the Bk extraction from $0.08 \text{ M } \text{CrO}_3$ - $4 \text{ N } \text{HNO}_3$ solutions. Neither impaired the extraction of Bk at concentrations up to $5 \text{ M } \text{LiNO}_3$ or 1 g/l Zr ($0.01 \text{ M } \text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$). Since chloride was present in the solutions containing Zr, it may also be concluded that the presence of up to 0.02 M chloride does not interfere with the extraction of Bk by 0.5 M HDEHP -dodecane from $0.08 \text{ M } \text{CrO}_3$ - $4 \text{ N } \text{HNO}_3$.

Berkelium Stripping

In order to determine whether Bk could be stripped from the organic phase with the same procedure as employed for Ce stripping, both HCl and HNO_3 acid systems were tested. Neither of these acids alone proved satisfactory for stripping Bk from 0.5 M HDEHP -dodecane solutions (Fig. 9).

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Fig. 8. Comparison of the Extraction of ^{249}Bk with That of ^{244}Cm by 0.5 M HDEHP -Dodecane from 4.0 N HNO_3 as a Function of the CrO_3 Concentration.

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Fig. 9. Stripping of ^{249}Bk from 0.5 M HDEHP as a Function of the Acidity.

The maximum stripping attained was 50% with HCl (1.0 N) and 50-70% with HNO_3 (~10 N). As with Ce, the stripping of Bk was improved by the addition of H_2O_2 to the acids at these concentrations, i.e., 78% Bk stripped by 1 M H_2O_2 -1 N HCl and 96% Bk stripped with 1 M H_2O_2 -8 N HNO_3 . Stripping was still further improved by the addition of H_2O_2 to 4 N HCl and 4 N HNO_3 , >99% being stripped by 4 N HCl containing 0.01 to 1.0 M H_2O_2 or 4 N HNO_3 containing 0.5 to 1.0 M H_2O_2 (Table 1 and Figure 10).

Table 1

Bk Stripping as a Function of the H_2O_2 Concentration

H_2O_2 conc., M in acid phase	Percentage of Bk stripped by			
	1 N HCl- H_2O_2	8 N HNO_3 - H_2O_2	4 N HCl- H_2O_2	4 N HNO_3 - H_2O_2
0.01	64	74.	99.69	33.
0.05	81	81.	99.86	50.
0.10	82	83.	99.95	69.
0.50	80	93.4	99.99	99.50
1.00	78	96.2	99.95	99.84

ACTUAL SEPARATION OF Bk AND Cm

The actual separation of Bk and Cm was investigated as a function of the HDEHP concentration with the aqueous phase being 0.08 M CrO_3 -4 N HNO_3 . The results from this series of extractions appear in Table 2 below. These results could not be obtained by direct analysis, because of an overlapping in the spectra such that Cm interfered with the Bk analysis. This was overcome by recontacting the aqueous phase, resulting from the original contact, with fresh organic. The counts detected in the organic of the second contact were taken as the number of counts due

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Fig. 10. Stripping of ²⁴⁹Bk from 0.5 M HDEHP-Dodecane as a Function of the H₂O₂ Concentration.

Table 2

Bk-Cm Separation as a Function of the HDEHP Concentration

HDEHP conc., <u>M</u>	$E_A^O(\text{Bk})$	$E_A^O(\text{Cm})$	Percent Bk Extracted	Percent Cm Extracted	Separation Factor
0.1	62.0	5.6×10^{-4}	98.41	0.056	1.1×10^5
0.2	180	1.5×10^{-3}	99.44	0.15	1.2×10^5
0.3	520	3.7×10^{-3}	99.81	0.37	1.4×10^5
0.4	220	4.2×10^{-3}	99.56	0.42	5.6×10^4
0.5	350	9.4×10^{-3}	99.72	0.94	3.8×10^4

to Bk in the original aqueous phase. This seems permissible, since it has been shown that >99.7% of the Bk is extracted by HDEHP-dodecane solutions in the concentration range under investigation. Berkelium does not interfere with the detection of Cm. By this procedure the Cm interference was decreased by ~300 and the results contained in Table 2 were obtained. As can be seen the separation factors obtained are in good agreement with the values predicted from the individual distributions of Bk and Cm shown in Figure 7.

The results presented herein indicate that it is possible to attain separation factors of at least $\sim 10^5$ for the separation of Bk from Cm by using 0.08 M CrO_3 and N HNO_3 as the oxidizing aqueous phase and HDEHP-dodecane solutions in the range of 0.1 to 0.5 M as the extractant phase. It has been shown that 0.1 M HDEHP-dodecane extracts 98.4 to 99.8% of the Bk from an equal volume portion of 0.08 M CrO_3 and N HNO_3 and only 0.035 to 0.056% of the Cm. It was calculated that 99.9% to 99.99% of the Bk and 0.042 to 0.06% of the Cm could be extracted from this aqueous phase by two half-volume passes of 0.1 M HDEHP-dodecane. Using an equal volume portion of 0.5 M HDEHP-dodecane, 99.8 to 99.93% of the Bk should be extracted; however, at this higher concentration 0.8 to 0.94% of the Cm should be extracted.

PROPOSED SEPARATION PROCESS

The process depicted in the flowsheet of Figure 11 is proposed for the separation of Bk from Cm and other transplutonium elements. The extractant phase should consist of 0.1 M HDEHP with H_2SO_4 -treated dodecane as the diluent. The aqueous phase concentration should be 0.08 M CrO_3 -4 N HNO_3 . This CrO_3 concentration was chosen on the basis of the experimental results obtained at the tracer level for Bk. At higher radiation levels, in which the process is to be used, it might be necessary to increase the CrO_3 concentration if significant decomposition occurs.

First the aqueous feed, which contains Bk, Cm, etc., is converted to a nitrate medium (4 N HNO_3) and adjusted to 0.08 M CrO_3 . It is then contacted with two half-volume passes of the extractant phase (20 minutes each), which should yield a separation factor of $\sim 2 \times 10^6$. The resulting extractant phases are combined, and then scrubbed with a one-tenth volume portion of 0.08 M CrO_3 -4 N HNO_3 . Calculations indicate that $\sim 0.02\%$ of the Bk should be scrubbed from the extractant phase during this one-tenth volume scrub, together with all but 0.0004% of the Cm. This yields a theoretical value of $>10^9$ for the separation of Bk from Cm. The aqueous raffinate and the aqueous phase from the scrub are then combined and sent to the Cm-Am separation.

The Bk in the extractant phase is then stripped by two half-volume passes (20 minutes each) of either 1 M H_2O_2 -4 N HCl or 1 M H_2O_2 -4 N HNO_3 . More than 99.9% of the Bk will be stripped from the extractant phase with either of these strippants. Therefore, a choice between the two should be made on the basis of whether a nitrate or chloride medium is more convenient for further processing or use of the Bk. The two strippant phases are combined and evaporated to dryness to concentrate the Bk and to destroy the H_2O_2 . The Bk product can then be taken up in an aqueous phase of any desired concentration.

RECOMMENDED FUTURE WORK

Several points arose as a result of this research which deserve further investigation. One is to determine the composition of the substance

Fig. 11. Berkelium Isolation by Selective Extraction of Bk(IV).

causing the green color in the extractant phase during contact with aqueous phases containing CrO_3 , and to study the effect its formation has on the actual oxidation and extraction of Bk. Another is to determine the extent that Bk is oxidized in the aqueous phase, i.e., to determine whether the Bk oxidation is complete before contact with the extractant phase, or, if not complete, to determine the dependence of the oxidation on the extraction equilibrium and the amount of Bk present in the aqueous phase during the extraction.

REFERENCES

1. D. F. Peppard, S. W. Moline, and G. W. Mason, J. Inorg. Nucl. Chem., 4, 344 (1957).
2. D. F. Peppard, G. W. Mason, and S. W. Moline, J. Inorg. Nucl. Chem., 5, 141 (1957).
3. J. J. McCown and R. P. Larsen, Anal. Chem., 32, 597 (1960).
4. F. L. Moore and W. T. Mullins, Anal. Chem., 37, 687 (1965).
5. J. M. Chilton and J. J. Fardy, ORNL-CF-68-1-72, Jan. 31, 1968.
6. B. Weaver and F. Kappelmann, USAEC Report ORNL-3559 (1964).
7. F. A. Kappelmann and B. Weaver, U. S. Patent 3,230,036 (1966).
8. D. A. Costanzo, ORNL-CF-67-4-6, April 5, 1967.
9. S. G. Thompson, B. B. Cunningham, and G. T. Seaborg, J.A.C.S., 72, 2798 (1950).
10. Boyd Weaver, unpublished work.
11. F. L. Moore, Anal. Chem., 38, 1872 (1966).
12. D. F. Peppard, G. W. Mason, J. L. Maier, and W. J. Driscoll, J. Inorg. Nucl. Chem., 4, 334 (1957).

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