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V. K. Manchanda[a]; P. K. Mohapatra[a]
[a] RADIOCHEMISTRY DIVISION BHABHA ATOMIC RESEARCH CENTRE, BOMBAY, INDIA

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1-Phenyl-3-methyl-4-benzoyl-pyrazolone-5: A Promising Extractant for Plutonium

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V. K. MANCHANDA and P. K. MOHAPATRA
RADIOCHEMISTRY DIVISION
BHABHA ATOMIC RESEARCH CENTRE
BOMBAY 400085, INDIA

ABSTRACT

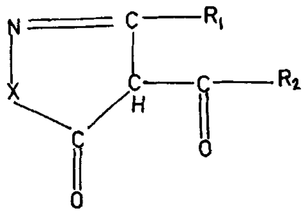
Pyrazolones and isoxazolones have been found to be promising extractants for metal ions, particularly from strong acidic media and in the presence of complexing anions. Extraction constants (log k_{ex}) in toluene medium at 25°C for PuX_4 species, where X = 1-phenyl-3-methyl-4-acetyl-pyrazolone-5 (HPMAP), 1-phenyl-3-methyl-4-benzoyl-pyrazolone-5 (HPMBP), or 1-phenyl-3-methyl-4-(3:5-dinitrobenzoyl)pyrazolone-5 (HPMDP), are determined as 11.35 ± 0.04, 12.89 ± 0.03, and 12.73 ± 0.02, respectively. These values are comparable to the corresponding value for 3-phenyl-4-benzoyl-5-isoxazolone (HPBI) and several order of magnitude larger than that for 2-thenoyltrifluoroacetone (HTTA). A systematic study is carried out to investigate the extraction behavior of these β-diketones toward plutonium present in the analytical waste solution obtained during the determination of uranium in a (U, Pu) fuel sample by the Davies Gray method. Whereas 0.3 M HPMBP extracts >85% of the plutonium present in a single step, maximum extraction observed with other reagents is ≤0.1% HTTA, 0.3% HPMAP, and 2.5% HPBI. The extraction of plutonium increases with different diluents in the order n-dodecane < n-hexane < $CHCl_3$ < CCl_4 < toluene. Extracted plutonium is quantitatively stripped with either 10 M HNO_3 or 1:1 HCl + 0.1 M hydroquinone.

INTRODUCTION

β-Diketones are a versatile class of chelating agents employed for the analytical separation of actinide ions. Systematic study of the extraction of U(VI) with several β-diketones by Batzar et al. (1) demonstrated that the proton affinity constants (pK_a) of these ligands play a vital role in determining their extraction abilities. An excellent inverse relationship between the extraction constants and the pK_a of several β-diketones was observed. Simple β-diketones like thenoyltrifluoroacetone (HTTA) and benzoyltrifluoroacetone (HBTFA) with their pK_a close to 6.2 were found quite promising to extract metal ions from weakly acidic solutions. On the other hand, they were incapable of extraction from strongly acidic media, particularly when complexing anions are present. Due to their lower pK_a values (2.0–4.2), pyrazolones have proved to be better extractants of the actinide ions compared to the simple β-diketones (2). Unfortunately, most of the work on the actinides with pyrazolones as the extractants has been confined to divalent uranium(VI) and the tervalent ions (2–4). The literature on Pu(IV) is scarce (5, 6).

Figure 1 shows the structures of pyrazolones and the isoxazolone employed in the present study. The presence of the heterocyclic ring (pyrazole/isoxazole) facilitates the delocalization of the negative charge and thereby decreases the pK_a values of these ligands as compared to β-diketones like acetylacetone and thenoyltrifluoroacetone.

In this communication we report the extraction behavior of 1-phenyl-3-methyl-4-acetyl-pyrazolone-5 (HPMAP), 1-phenyl-3-methyl-4-benzoyl-pyrazolone-5 (HPMBP), 1-phenyl-3-methyl-4-trifluoroacetyl-pyrazolone-5 (HPMTFP), and 1-phenyl-3-methyl-4-(3:5-dinitrobenzoyl)-pyrazolone-5 (HPMDP) with Pu(IV). An attempt was also made to employ HPMBP for the extraction of plutonium from the analytical waste (a.w.) solution generated during the electrochemical determination of uranium in plutonium-based nuclear fuel samples (7). The recovery of plutonium from this solution is difficult due to the presence of large concentrations of phosphoric acid and sulfuric acid apart from several other metal ions.



X = O; R_1, R_2 = Ph: PBI
X = N - Ph; R_1 = Me; R_2 = Ph: PMBP
X = N - Ph; R_1, R_2 = Me : PMAP
X = N - Ph; R_1 = Me; R_2 = CF_3: PMTFP

FIG. 1 Structure of the ligands used as extractants.

The experimental conditions necessary for the quantitative stripping and recycling of the extractant are also reported.

EXPERIMENTAL

Reagents

Thenoyltrifluoroacetone was procured from Eastman Kodak Co. The pyrazolones HPMBP, HPMDP, HPMAP, and HPMTFP, as well as the isoxazolone HPBI (3-phenyl-4-benzoyl-5-isoxazolone), were synthesized in this laboratory by reported procedures (8, 9). The extractants were purified by recrystallization prior to their use. Table 1 lists the physical and analytical data of these ligands. Hydroquinone was obtained from Agfa-Gevaert (India) Ltd. All the other reagents used in this work were of A.R. Grade.

Preparation of the Pu(IV) Extract

The plutonium was adjusted to Pu(IV) in 4 M HNO_3 by adding a few drops of 30% H_2O_2, the excess of which was destroyed by heating. The desired aliquot of plutonium from this stock was spiked into a 1 M HNO_3 solution containing 5×10^{-4} M $KBrO_3$ as the holding oxidant. Extraction was carried out with a suitable concentration of the pyrazolone in toluene as the organic phase. This Pu(IV)-loaded organic phase was used for all the subsequent experiments.

Distribution Studies

The distribution experiments were carried out by attaining equilibrium from the reverse direction wherein the Pu(IV) extract was employed after appropriate dilution. The aqueous phase used was a HNO_3 solution of the desired concentration containing 5×10^{-4} M $KBrO_3$. The ionic

TABLE 1
Physical and Analytical Data for Pyrazolones and Isoxazolones

Compound	Medium of recrystalization	Color	mp (°C)	Elemental analysis %C	%H	%N
HPMBP	Dioxane–water	Bright yellow	92.0	73.1 (73.4)	5.2 (5.0)	10.0 (10.1)
HPMAP	*n*-Hexane	Dull yellow	58.2	66.1 (66.6)	5.6 (5.6)	12.9 (13.0)
HPMTFP	Ethanol–water	Light pink	144.0	52.9 (53.3)	3.7 (3.4)	10.3 (10.2)
HDMPP	*n*-Hexane	Yellow	255.5	55.6 (55.4)	3.1 (3.4)	15.0 (15.2)
HPBI	*n*-Hexane	Pale brown	146.3	72.7 (72.5)	4.1 (4.1)	—

strength was maintained at 1.0 M (unless otherwise stated) using sodium nitrate. The volume of each phase was 1.0 mL. The equilibrations were carried out for 1 hour in a thermostated water bath at 25°C. Thereafter, the phases were separated and assayed radiometrically using an α-liquid scintillation counter. The aliquot size for the radiometric assay was restricted to 10 μL for the aqueous phase to avoid quenching. The distribution ratio values were reproducible within ±5%.

Work on the Analytical Waste Solution

Distribution experiments with the analytical waste solution were carried out by attaining extraction equilibrium in the forward direction. The holding oxidant ($KBrO_3$) was not used in this work. Dilution of the analytical waste solution was carried out with 0.1 M HNO_3 in some cases, and the volume ratio (aqueous:organic) was maintained at 2:1.

The stripping experiments were carried out by equilibrating the activity-loaded organic phase with the desired strippant solution.

The mass balance was found to be within ±5%.

CALCULATIONS

The extraction of Pu(IV) by a pyrazolone (HA) is represented by

$$\mathrm{Pu} + 4\mathrm{HA}_{(o)} \rightleftharpoons \mathrm{PuA}_{4(o)} + 4\mathrm{H} \tag{1}$$

The subscript "o" refers to the species in the organic phase. The charges have been omitted for the sake of convenience. From Eq. (1), k_{ex} can be defined as

$$k_{ex} = \frac{[\mathrm{PuA_4}]_o\{\mathrm{H}\}^4}{[\mathrm{Pu}][\mathrm{HA}]_o^4} \tag{2}$$

The brackets denote concentrations and the braces denote the activity of the respective species. Concentration terms are used for PuA_4, Pu, and HA because very dilute solutions of these are involved.

The distribution ratio (D), defined as the ratio of the counts per unit time per unit volume of the organic phase to that of the aqueous phase, is given as

$$D = \frac{[\mathrm{PuA_4}]_o}{[\mathrm{Pu}] + \sum_i[\mathrm{PuX}_i]} \tag{3}$$

The second term in the denominator refers to the total concentration of the complexes of plutonium with X in the aqueous phase (where X represents the NO_3^- ion) at equilibrium. The concentrations of the complexes of Pu(IV) with A in the aqueous phase have been neglected. The expanded form of $\sum_i [PuX_i]$ is

$$\sum_i [PuX_i] = [Pu](\beta_1[X] + \beta_2[X]^2 + \cdots) \tag{4}$$

where β_1, β_2, . . . are the overall stepwise complexation constants.

From Eqs. (2), (3), and (4) we obtain

$$k_{ex} = \frac{D[H]^4\gamma_H^4 F}{[HA]_o^4} \tag{5}$$

where $F = 1 + \sum_i \beta_i[X]^i$.

The apparent extraction constant k_{ex}^a is related to k_{ex} by

$$k_{ex} = k_{ex}^a F \gamma_H^4 \tag{6}$$

γ_H, the activity coefficient of H, is obtained from Reference 10. F, the aqueous complexation factor, is obtained from References 11 and 12.

The percentage extraction (%E) is expressed as:

$$\%E = 100D/(D + V_a/V_o) \tag{7}$$

where V_a refers to the aqueous-phase volume and V_o to the organic-phase volume.

RESULTS AND DISCUSSION

Distribution Studies of Pu(IV) with HPMBP, HPMAP, and HPMDP

Table 2 shows the distribution data of Pu(IV) between 1 M HNO_3 and various concentrations of different pyrazolones (HA) in a toluene medium.

TABLE 2
Distribution Ratio Data of Pu(IV) between 1 M HNO_3 and Varying Concentrations of Different Pyrazolones

[HPMBP] × 10^3 (M)	D	[HPMAP] × 10^3 (M)	D	[HPMDP] × 10^4 (M)	D
1.297	5.532	1.321	0.163	5.402	0.123
1.513	9.985	1.542	0.305	6.302	0.225
1.729	16.266	1.762	0.503	7.202	0.404
1.945	23.527	1.982	0.708	8.102	0.623
2.161	39.968	2.202	1.206	9.003	0.980

Plots of log D vs log [HA] yielded a slope of 4.01 ± 0.1 in each case, suggesting the presence of four pyrazolone moieties in the extracted species. Similarly, Table 3 shows the distribution data of Pu(IV) at a fixed concentration of pyrazolone but at various concentrations of HNO_3 while keeping the ionic strength constant throughout at 1.0 M. Linear plots of log D vs log a_{H}^{+} yielded negative slopes of 4.0 ± 0.15 in each case, indicating the liberation of four H^+ ions during the extraction of Pu(IV) by the pyrazolones. The overall two-phase equilibrium is represented by Eq. (1). The two-phase extraction constants (k_{ex}) obtained in this work are listed in Table 4. There is excellent agreement in the values obtained independently by the ligand variation and the acid variation experiments. As seen in Table 4, pyrazolones examined in the present study have pK_a values varying from 2.0 to 4.1. The limited data available do not permit extrapolation of the inverse relationship of pK_a and log k_{ex} reported earlier (1). It may be mentioned that steric factors probably play a prominent role in the coordination of pyrazolones and isoxazolones with tetravalent plutonium (13). Table 4 further shows that the extraction constants with the pyrazolones are larger by ~6 log units compared to the corresponding value with HTTA (14). On the other hand, the former values are comparable to the corresponding value with HPBI (15).

The apparent extraction constants (k_{ex}^{a}) obtained by neglecting the nitrate complexation of Pu(IV) as well as the activity coefficient of H^+ in the aqueous phase and by assuming the complete ionization of HNO_3 are smaller than the corresponding thermodynamic values. In the present work, log k_{ex}^{a} values for the Pu(IV)–HPMBP system at 1.0 and 2.0 M HNO_3 are found to be 11.73 ± 0.03 and 11.36 ± 0.02, respectively. They

TABLE 3
Distribution Ratio Data of Pu(IV) with Varying HNO_3 Concentrations for Different Pyrazolones
(ionic strength = 1.0 M[a])

$[HNO_3]$ (M)	D_{HPMBP}[b]	D_{HPMAP}[c]	D_{HPMDP}[d]
0.5	—	0.447	—
0.6	112.4	0.237	13.0
0.7	56.8	0.128	6.87
0.8	36.4	0.078	4.01
0.9	22.6	0.036	2.56
1.0	14.4	—	1.61

[a] Ionic strength is adjusted by using 1.0 M $NaNO_3$ solution.
[b] [HPMBP] = 1.653×10^{-3} M.
[c] [HPMAP] = 8.469×10^{-4} M.
[d] [HPMDP] = 1.086×10^{-3} M.

TABLE 4
Extraction Constants[a] of Pu(IV) with Different Pyrazolones at 25°C

HA	pK_a	log K_{ex}[b]	log K_{ex}[c]
HPMBP	4.09[d]	12.88 ± 0.02	12.90 ± 0.03
HPMAP	3.78[d]	11.33 ± 0.02	11.38 ± 0.04
HPMDP	2.00[e]	12.78 ± 0.02	12.69 ± 0.01
HPBI	1.12[f]	12.30 ± 0.06[g]	12.32 ± 0.09[g]
HTTA	6.23[f]	6.622[h]	—

[a] Mean of five values along with deviation (2σ).
[b] Values obtained from the ligand variation experiments.
[c] Values obtained from the H^+ variation experiments.
[d] Reference 2.
[e] Reference 17.
[f] Reference 19.
[g] Values quoted from Ref. 15 after activity correction.
[h] Values quoted from Ref. 14 after activity correction.

are expected to decrease further with an increase of HNO_3 concentration. However, the k_{ex}^{a} value at 5.0 M HNO_3 is sufficiently high to result in quantitative extraction of Pu(IV) even with 0.05 M HPMBP. Figure 2 shows the extraction behavior of Pu(IV) with 0.05 M HPMBP as well as with 0.05 M HTTA from nitric acid media. The significantly better extraction property of the pyrazolone is well illustrated.

Time of Equilibration

Figure 3 depicts the attainment of equilibrium of Pu(IV) extraction in the forward direction for both HPMBP and HTTA systems. It takes about 20 minutes for the HPMBP system to attain equilibrium whereas 30 minutes are required for the HTTA system. Similar experiments carried out with preequilibrated extractant solutions (equilibrated for 24 hours with 1.0 M $HClO_4$) show that equilibrium is attained in 10 and 15 minutes, respectively.

Distribution Studies of Pu(IV) with HPMTFP

On the basis of its pK_a value (2.73), HPMTFP appears to be a promising extractant, but the ligand dependency as well as the [H^+] dependency observed for the Pu(IV)–HPMTFP system is 3.1 and −3.1, respectively, after the usual 1 hour equilibration time. Further examination reveals that this system does not attain equilibrium even after 3 days, and the distribution ratio decreases by a factor greater than 10 during this period. On the other hand, UV/Visible spectral studies of the HPMTFP solution in tolu-

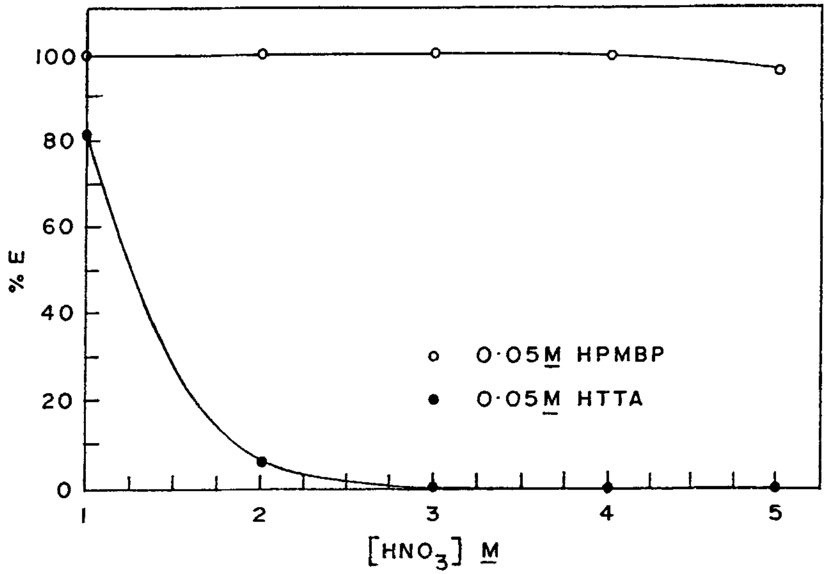


FIG. 2 Percent extraction of plutonium with 0.05 M HPMBP and 0.05 M HTTA from various concentrations of HNO_3.

ene show a continuous increase of absorbance (λ_{max} = 286 nm as well as λ_{max} = 418 nm). It appears that HPMTFP undergoes continuous chemical degradation and/or structural modification during the extraction process. The slow kinetics of the keto–enol transition for fluorinated β-diketones has been reported (16).

Extraction of Plutonium from the Analytical Waste Solution

The determination of U in Pu-based fuels is carried out routinely by the Davies Gray method in nuclear quality control laboratories. The composition of a typical analytical waste solution generated by this method and used in the present work is: Pu, 0.1 mg/mL; U, 0.17 mg/mL; Fe, 1.3 mg/mL; V, 0.5 mg/mL; Cr, 0.02 mg/mL; HNO_3, 0.5 M; H_2SO_4, 1.0 M; H_3PO_4, 2.5 M. Table 5 shows that HPMBP is the most suitable reagent for the extraction of plutonium from the analytical waste solution when employing 0.1 M of different β-diketones. It is not possible to prepare a 0.1 M solution of HPMDP due to its poor solubility. Consequently, further work was pursued with HPMBP; for comparison, HTTA was used in a few experiments.

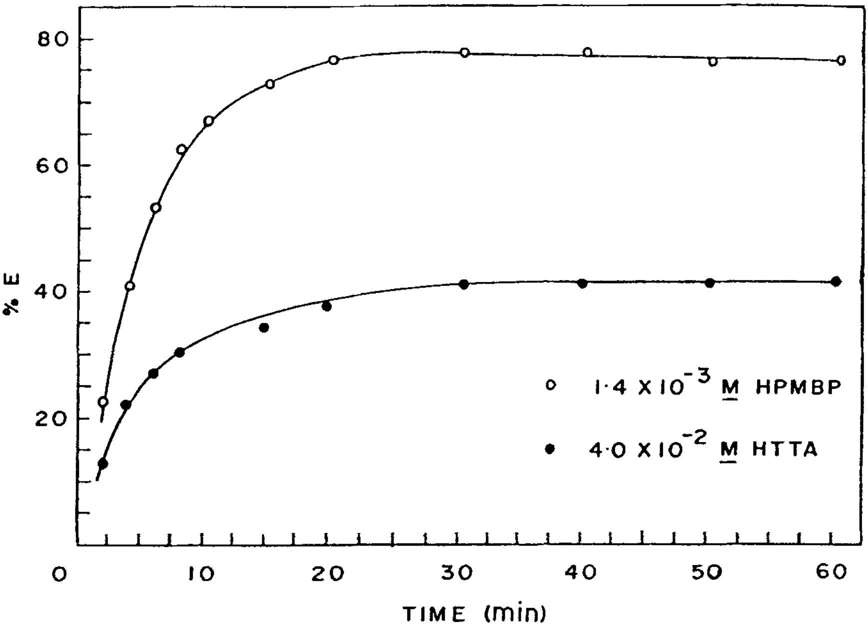


FIG. 3 Percent extraction of plutonium as a function of time (minutes) using 1.4×10^{-3} M HPMBP and 4.0×10^{-2} M HTTA.

Figure 4 shows the percent extraction of plutonium from the analytical waste solution as a function of HPMBP concentration. Curve (a) indicates a plateau region beyond 0.3 M HPMBP. Curve (b) refers to the distribution experiments carried out on the analytical waste solution diluted (1 : 1) with 0.1 M HNO_3. It is interesting to observe that for 0.1 M HPMBP, dilution of the aqueous phase causes enhancement of the distribution coefficient

TABLE 5
Percent Extraction of Plutonium from Analytical Waste Solution Using Different Extractants

Extractant (0.1 M)	% Extraction
HTTA	≪0.1[a]
HPBI	2.5
HPMAP	0.3
HPMBP	15.4

[a] Negligible extraction.

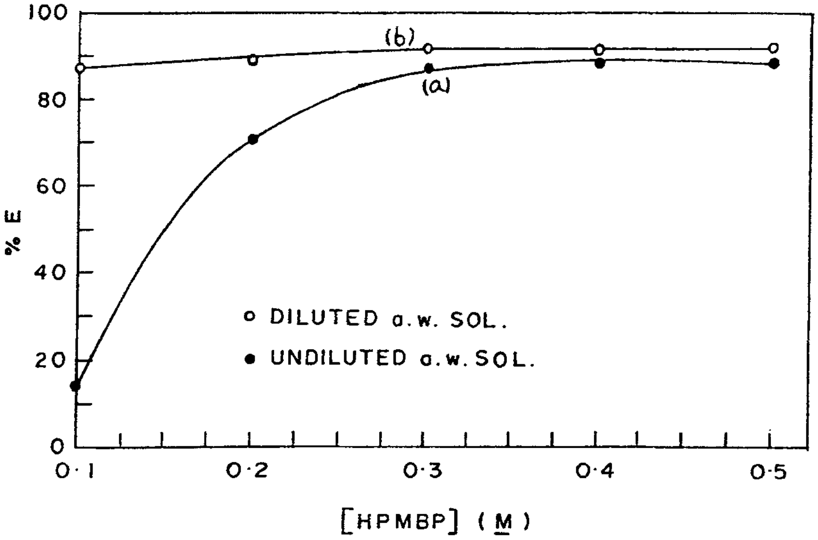


FIG. 4 Percent extraction of plutonium from the analytical waste solution with various concentrations of HPMBP.

from 0.2 to 15.0. On increasing the HPMBP concentration further (up to 0.5 M), the extraction of plutonium did not increase beyond 93%.

A strong oxodonor like tri-*n*-octyl phosphine oxide (TOPO) is known to enhance Pu(IV) extraction by HPMBP synergistically (13). The presence of 0.2 M TOPO increases the extraction of plutonium from the diluted analytical waste solution by 0.2 M HPMBP only marginally from 93 to 95%. No enhancement was observed with oxodonors like tri-*n*-butyl phosphate (TBP) and di-*n*-octyl sulfoxide (DOSO).

Table 6 shows the effect of diluent on the %*E* of plutonium employing 0.2 M HPMBP. Toluene is the most appropriate among the five diluents investigated. Aliphatic diluents like *n*-hexane and *n*-dodecane are found to be of limited use due to the poor solubility of the ligand as well as the formation of a third phase during the extraction process.

Stripping Behavior

Table 7 shows the stripping behavior of plutonium with increasing HNO_3 concentration. Column 2 refers to the results of back-extraction experiments performed with the organic phase obtained after 0.3 M HPMBP is contacted with the analytical waste solution. Column 3 refers to results with the extract obtained using 0.1 M HPMBP and diluted (1 : 1)

TABLE 6
Effect of Diluent on the Percent Extraction of Plutonium from Analytical Waste Solution Using 0.2 M HPMBP

Diluent	% Extraction
Carbon tetrachloride	64.2
Chloroform	33.7
n-Hexane	18.4[a]
n-Dodecane	13.2[a]
Toluene	66.2

[a] A third phase was observed.

analytical waste solution. It is seen that in both the cases 10 M HNO_3 is adequate to strip plutonium quantitatively. No extraction of plutonium is observed if the HPMBP solution recovered after stripping with 10 M HNO_3 is employed in the distribution experiments. This is attributed to the chemical degradation of HPMBP by the NO_2^- ion which is also likely to be present in the HNO_3 solution used as a strippant. This is in accordance with our recent observation (17) that the presence of 10 to 15 mg $NaNO_2$ in the aqueous phase (used as a redox reagent) resulted in a dramatic decrease in the extraction of plutonium ($\%E \leqslant 0.1$) present in the analytical waste solution. In the absence of any redox reagent or in the presence of 0.01 M H_2O_2, the $\%E$ under identical conditions is 88.0. Thus, stripping by 10 M HNO_3 suffers from a serious drawback, viz., the reagent (HPMBP) cannot be recovered and recycled.

TABLE 7
Percent Stripping of Plutonium from the Loaded Organic Phase Containing HPMBP

$[HNO_3]$ (M)	% Stripping[a]	% Stripping[b]
7	15.2	19.6
8	45.0	56.5
9	50.4	85.8
10	>99	>99

[a] A loaded organic phase was obtained by equilibrating 0.3 M HPMBP with the analytical waste solution.

[b] A loaded organic phase was obtained by equilibrating 0.1 M HPMBP with the (1:1) diluted analytical waste solution.

TABLE 8
Percent Stripping of Plutonium Using HCl and Hydroquinone (0.1 M) Mixture under Different Experimental Conditions

Molarity of HCl	Volume ratio ($V_a:V_o$)	% Stripping
4.0	1:1	27.0
6.0	1:1	92.0
6.0	2:1	97.1
6.0	4:1	>99
6.0	10:1	>99

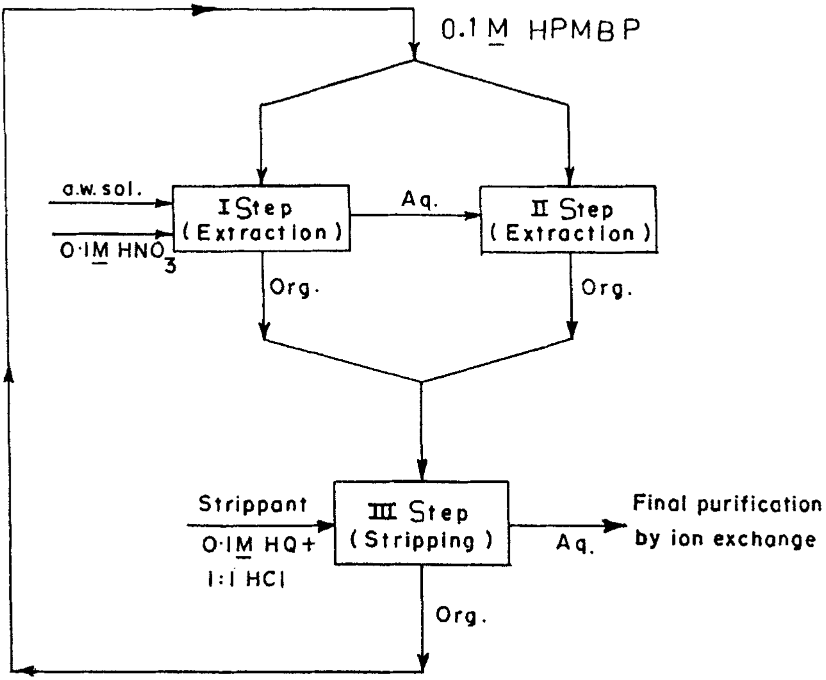


FIG. 5 Schematic procedure for the recovery of plutonium from the analytical waste solution.

An attempt was made to find an alternative stripping agent which could permit the recycling of the extractant. In our recent work (15) a mixture of 4 M HCl and 0.1 M hydroquinone was found to be the most effective among various stripping agents employed for the back-extraction of plutonium from an organic phase comprising 0.05 M HPBI in toluene. Table 8 summarizes the results obtained in the present work by using a mixture of HCl and hydroquinone for the stripping of plutonium from an organic phase comprising 0.1 M HPMBP in toluene. A mixture of 0.1 M hydroquinone and 1:1 HCl was found to be effective for quantitative stripping.

Recycling of the Extractant

The organic phase recovered after the stripping experiments (strippant: 0.1 M hydroquinone in 1:1 HCl) was recycled as the extractant for a fresh lot of 1:1 diluted analytical waste solution, and 91% of the plutonium present was found to be transferred to the organic phase. Thus, the method developed during the present work appears quite promising for application on a routine basis. Figure 5 shows schematically the procedure for the recovery of plutonium from the analytical waste solution. It is obvious that the bulk uranium and the transplutonium elements (if present) remain in the aqueous phase of the first extraction step. The final purification of plutonium from the aqueous stream leaving the third stage could be carried out by an ion-exchange method (18).

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REFERENCES

1. K. Batzar, D. E. Goldberg, and L. Newman, *J. Inorg. Nucl. Chem.*, *29*, 1511 (1967).
2. W. Bacher and C. Keller, *Ibid.*, *35*, 2945 (1973).
3. S. K. Mundra, S. A. Pai, and M. S. Subramanian, *Lanth. Act. Res.*, *2*, 323 (1988).
4. J. N. Mathur and P. K. Khopkar, *Sep. Sci. Technol.*, *17*, 985 (1982).
5. Yu. A. Zolotov, M. K. Chmutova, and P. N. Palei, *Zh. Anal. Khim.*, *21*, 1217 (1966).
6. B. F. Myasoedov, N. E. Kochetkova, and M. K. Chmutova, *Ibid.*, *28*, 1723 (1973).
7. A. R. Eberle, M. W. Lerner, C. G. Goldbeck, and C. J. Rodden, *Report*, *NBL-251* (1970).
8. B. S. Jensen, *Acta Chem. Scand.*, *13*, 1668 (1959).
9. F. Korte and K. Storiko, *Chem. Ber.*, *4*, 1961 (1956).
10. R. Parsons, *Handbook of Electrochemical Constants*, Butterworths, London, 1959.

11. S. K. Patil, V. V. Ramakrishna, P. K. S. Kartha, and N. M. Gudi, *Sep. Sci. Technol.*, *15*, 1459 (1980).
12. S. V. Bagawde, V. V. Ramakrishna, and S. K. Patil, *J. Inorg. Nucl. Chem.*, *38*, 1339 (1976).
13. V. K. Manchanda and P. K. Mohapatra, *Radiochim. Acta*, In Press.
14. K. L. Nash and J. M. Cleveland, *Ibid.*, *33*, 1050 (1983).
15. V. K. Manchanda and P. K. Mohapatra, *Transuranium Elements* (M. Brown, Ed.), ACS Books, 1992.
16. D. G. Schultz and E. M. Larson, *J. Am. Chem. Soc.*, *71*, 3250 (1949).
17. V. K. Manchanda and P. K. Mohapatra, Unpublished Work.
18. J. M. Cleveland, in *Plutonium Handbook*, Vol. I (O. J. Wick, Ed.), American Nuclear Society, Illinois, 1980, p. 459.
19. A. Jyothi and G. N. Rao, *Chem. Scripta*, *27*, 367 (1987).

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