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Separation of Uranium and Dibutyl Phosphate Contained in 30 Vol % Tributyl Phosphate Solvents

J. C. Mailen
O. K. Tallent

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ORNL/TM-9837

Chemical Technology Division

SEPARATION OF URANIUM AND DIBUTYL PHOSPHATE CONTAINED IN 30 VOL % TRIBUTYL PHOSPHATE SOLVENTS

J. C. Mailen
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NOTICE This document contains information of a preliminary nature. It is subject to revision or correction and therefore does not represent a final report.

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CONTENTS

Page

ABSTRACT 1

1. INTRODUCTION 1

2. EXPERIMENTAL 2

2.1 EXPECTED REACTIONS. 2
2.2 SCOUTING TESTS. 2
2.3 ANALYSIS OF SOLVENTS FOR URANIUM AND DBP. 6
2.4 SMALL-COLUMN TESTS. 9

2.4.1 Loading 20–50 Mesh Bio-Rad AG MP-50. 9
2.4.2 Eluting 20–50 Mesh Bio-Rad AG MP-50. 13

2.4.3 Loading 60–120 Mesh Alcoa F-1 Activated Alumina. . . 13

2.4.4 Eluting 60–120 Mesh Alcoa F-1 Activated Alumina. . . 21

2.4.5 Loading a Column Containing DTPA on 3-mm Glass Beads. 21

2.4.6 Loading Dowex 21K (Hydroxide Form) 21

2.4.7 Miscellaneous Tests. 21

3. SOLVENT CLEANUP MATHEMATICAL DEVELOPMENT 28

4. CONCLUSIONS. 30

5. ACKNOWLEDGMENTS. 31

6. REFERENCES 31

SEPARATION OF URANIUM AND DIBUTYL PHOSPHATE CONTAINED IN 30 VOL % TRIBUTYL PHOSPHATE SOLVENTS

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ABSTRACT

A number of solid sorbents were tested for the removal of uranium and dibutyl phosphate (DBP) from 30 vol % tributyl phosphate (TBP) solvent. The removal was required to result in separation of the uranium from the DBP with a clean uranium product. The preferred mode of operation was to remove the DBP, leaving the uranium in the cleaned solvent for recycle.

A method for removal of DBP from the solvent while allowing the uranium to remain in the solvent was not found. Both cation resins and diethylene triamine pentaacetic acid (DTPA) deposited on glass beads preferentially removed the uranium, leaving the DBP in the solvent. The DBP could then be readily removed by a number of simple treatments, and the uranium could be recovered by elution with acidified TBP. Both hydroxide-form, anion-exchange resins and activated alumina (used with dry solvent) removed uranium and DBP. It is possible that the DBP and uranium could be separately eluted from these sorbents, but it was not successfully tested.

1. INTRODUCTION

Solvent cleanup practice in Purex plants is to scrub the contaminated tributyl phosphate (TBP) solvent with a sodium carbonate solution before recycle to the solvent extraction system. This procedure removes the acidic solvent degradation products, including dibutyl phosphoric acid (HDBP) and monobutyl phosphoric acid, and transfers the metallic contaminants to the aqueous phase as carbonate complexes.

Purex solvent at the Oak Ridge Y-12 Plant is not cleaned on a routine basis. The solvent is discarded at about 1-month intervals because of the buildup of DBP which causes operational difficulties. Recycle solvent always contains about 20 g uranium/L and has ~0.01 M DBP at discard. The use of sodium carbonate scrubbing after difficulties have been encountered is unsatisfactory because serious emulsions between the organic and sodium

carbonate phases are formed. Continuous cleanup using sodium carbonate would be feasible but would require recovery of significant quantities of enriched uranium from the sodium carbonate—uranium—DBP aqueous scrub solution. In the absence of some solvent cleanup technique, the process requires much operator attention, significant cleanup of equipment on monthly intervals, and probably produces an inferior product. The desired treatment method would (1) use a solid sorbent that would preferentially remove the DBP, leaving the uranium in the solvent; or (2) use a method that would separately remove both the DBP and uranium, yielding a clean uranium product. We prepared a series of solid sorbents which have potential for this separation, performed scouting tests to determine which sorbents provided separate removal of DBP, and conducted tests in small packed columns using the promising sorbents.

2. EXPERIMENTAL

2.1 EXPECTED REACTIONS

It is expected that, before reaction with a damp solid, the components of the organic phase will first have to distribute to the aqueous layer on the solid sorbent. Thereafter, the reactions with the sorbent will be the ones expected for the same components in the aqueous phase. In addition, if a component such as uranyl nitrate should react to form an inextractable compound, the uranium would be trapped in the aqueous layer of the sorbent. An example would be reactions that replace the nitrates with other anions; the resulting compounds would likely not be extractable. Sorbents that are active in the dry state (the principal example is activated alumina) may remove components directly from the solvent.

2.2 SCOUTING TESTS

The ability of a number of solid sorbents to remove uranium and DBP from 30% TBP in normal paraffin hydrocarbon (NPH) was investigated in small-batch equilibrations. A ~0.01 M DBP solution was prepared by

adding HDBP containing about 3.3 mol % monobutyl phosphoric acid to 30% TBP-NPH. This solution was then contacted with a uranyl nitrate solution containing 5 g of uranium/L (0.02 M uranium) in H_2O (pH = 3) to prepare a uranium-DBP test solution containing ~0.01 M DBP and ~0.01 M uranium. These concentrations (rather than the process concentrations with ~10 times as much uranium) were used to simplify the analytical procedures. Preferential removal of DBP would have been followed by tests using a higher uranium:DBP ratio. One-half of the uranium-DBP solution was dried by sparging with 1 volume of dry air per min per volume of solution for ~5 h at ~60°C. This procedure has been shown to result in quite dry solvent (removal of ≥97% of the water from water-saturated solvent).[1] It is expected that some solid sorbents, especially activated alumina, will have higher capacities if water is excluded. Most of the solid sorbents were tested by two methods: dried with dry solvent and damp with wet solvent. The dry sorbents were dried at ~100°C, except for activated alumina that were dried at ~200°C. The damp sorbents were stored in a "desiccator" with a layer of water in the bottom for several days before use. Complete saturation of sorbents with a high capacity for water may not have been achieved; later tests with activated alumina exposed for longer periods gave poorer results than those from these scouting tests. Some sorbents required preparation; these procedures are as follows. Sucrose was deposited on 12–28 mesh silica gel by dissolving 100 mg of sucrose in 3 mL of H_2O, soaking the silica gel in the solution, draining the solution, and drying the solid. Diethylene triamine pentaacetic acid (DTPA) (0.216 g) was dissolved in 10 mL of H_2O by increasing the pH to ~7 to increase the solubility; 1 mL of dried Dowex 21K anion resin in the hydroxyl form was then added, soaked overnight, and then drained. The pH of the solution increased to 7.70 after contact with the resin. Zirconium oxynitrate (0.5 g), dissolved in 5 mL of H_2O, was contacted with 2 g of Norton Z-900 molecular sieve over the weekend; the sieve was drained, and then rinsed with 5 mL of H_2O. The anion-exchange resins were obtained in the chloride form. They were converted to the hydroxide form by passing 1 M NaOH through a packed column of the resin

until a negative chloride result was obtained with a silver nitrate test. The resin was then rinsed with water until the effluent water was near neutral. The nitrate form was produced by passing 1 M $NaNO_3$ through a bed of hydroxide-form resin, followed by rinsing with water.

Either 1 g (most solids) or 1 mL (ion-exchange resins) of solid was contacted with 10 mL of the appropriate solvent (dry solvent with dry sorbent, wet solvent with damp sorbent) by shaking for 1 min three times over a 10-min period. The transfer of uranium color from the organic phase was noted. A portion of the organic phase was stripped with water; if the DBP had been removed leaving the uranium in the organic phase, the uranium would strip with water. In those cases where the uranium was quantitatively removed by contact with the solid sorbent, the colorless solvent was contacted with a uranyl nitrate solution in water. The presence of HDBP in the solvent causes extraction of uranium. The qualitative observations of uranium removal by the solids and presence or absence of HDBP in treated solvent were as follows (Table 1).

The only solids that showed promise for the removal of uranium and/or DBP were cation-exchange resins, anion-exchange resins in the hydroxyl form, and activated alumina. The ion-exchange resins must be used damp. The anion-exchange resins removed both uranium and DBP, but the cation resin removed only the uranium. Note that removal of the DBP after removal of the uranium and recovery of the uranium from the cation resin should be relatively easy. The scouting tests indicated that activated alumina could be used either dry or damp, but later column tests showed that the capacity for both uranium and DBP are reduced by the presence of water.

The promising solid sorbents were then tested in small packed columns.

Table 1. Qualitative results of shake-out tests

Solid sorbent	Uranium removal		DBP removal	
	W[a]	D[b]	W[a]	D[b]
Dowex 1-X4[c]; anion; Cl^-	No	No	No	No
Norton Z-900[d]; Na^+	No	No	No	No
Sucrose on silica gel[e]	No	No	No	No
Dowex 50W-X4[c]; H^+	Yes	No	No	No
Florex[f] (attapulgite clay)	No	No	No	No
Hydrous Zr oxide[g]	No	No	No	No
Dowex 21K[c] + DTPA[h]	No	No	No	No
Dowex 21K[c]; anion; OH^-	Yes	No	Yes	No
Activated alumina[i]	Yes	Yes	Partial	Partial
Silica gel[e]	No	No	No	No
BIORAD AG MP-1[j]; anion; OH^-	Yes	No	Yes	No
Amberlyst A-26[k]; anion; OH^-	Yes	No	Yes	No
Zr + molecular sieve[d]	Slight	No	No	No
Amberlyst A-26[k]; anion; Cl^-	ND[ℓ]	No	ND	No
Dowex 21K[c]; anion; Cl^-	No	ND	No	ND
BioRad AG MP-1; anion; NO_3^-	No	ND	No	ND

[a]Damp solid and damp solvent used in test.

[b]Dry solid and dry solvent used in test.

[c]50–100 mesh (Bio-Rad Laboratories, Richmond, Calif.).

[d]0.16 cm diam x ~0.6 cm long; pore size ~7 Å (Norton Co., Worcester, Mass.).

[e]12–28 mesh, Grade 408 (Fisher Scientific Co., Fairlawn, N.J.).

[f]Florex AA-LVM, 45–60 mesh (Floridin Co., Pittsburgh, Penn.).

[g]100–200 mesh (formerly available from Bio-Rad Laboratories, Richmond, Calif.).

[h]Prepared by and obtained from D. O. Campbell and S. R. Buxton, Oak Ridge National Laboratory.

[i]Alcoa F-1 type, 60–120 mesh (Aluminum Co. of America, Pittsburgh, Penn.).

[j]20–50 mesh (Bio-Rad Laboratories, Richmond, Calif.).

[k]14–50 mesh (Rohm and Haas Co., Philadelphia, Penn.).

[ℓ]Not determined.

2.3 ANALYSIS OF SOLVENTS FOR URANIUM AND DBP

Uranium in the solvent was analyzed by stripping the uranium (plus any DBP and nitric acid) from the solvent with an equal or greater volume of 0.5 M ammonium carbonate. This stripping produced the uranyl carbonate complex (Fig. 1) in the aqueous phase, which is determined spectrophotometrically using the absorbance at 450.4 nm. The absorbance was found to be linear for concentrations up to 0.01 M uranium. The molar concentration in the aqueous phase is given by the absorbance (1-cm path length) divided by 25.1. The molar absorptivity was determined from uranium standards in the same spectrophotometer used for the analyses (Model 200, Hitachi Co., Tokyo, Japan). Under most conditions, uranium forms a 1:1 complex with DBP in TBP solutions.[2] The fact that a 0.01 M HDBP solution extracted only about 0.01 M uranium in the current tests is in agreement with the results of Hahn and Vander Wall. Extraction of uranium by TBP and DBP-TBP solutions was investigated to develop a simple method for analyzing solvents for DBP. A 0.02 M aqueous uranyl nitrate solution (pH ~3) was contacted with an equal volume of clean 30% TBP. The uranium distribution coefficient was 0.0526. Uranium distribution coefficients were then determined for organic phases containing 0.001, 0.0025, 0.005, and 0.01 M DBP. Assuming the uranium-DBP complex was 1:1, the free DBP was calculated for each case. Figure 2 shows a plot of the distribution of uranium to the DBP complex (extracted uranium corrected for extraction by TBP; distribution coefficient of 0.0526) vs the free DBP concentration. The plot is approximately linear, with a slope of 314. An unknown solvent can be contacted with a standard uranyl nitrate solution, and the extracted uranium can be determined. The correlation given in Fig. 2, plus the extraction of uranium by TBP, allows the calculation of the DBP content. When the organic phase itself initially contains uranium, its concentration must be determined to know the total uranium in the system. To determine both the uranium and DBP in a 30% TBP sample, the solution is divided into two parts. The uranium in one portion is measured by stripping with ammonium carbonate solution and determining the absorbance. The other portion is contacted with an equal volume of the standard 0.02 M uranyl

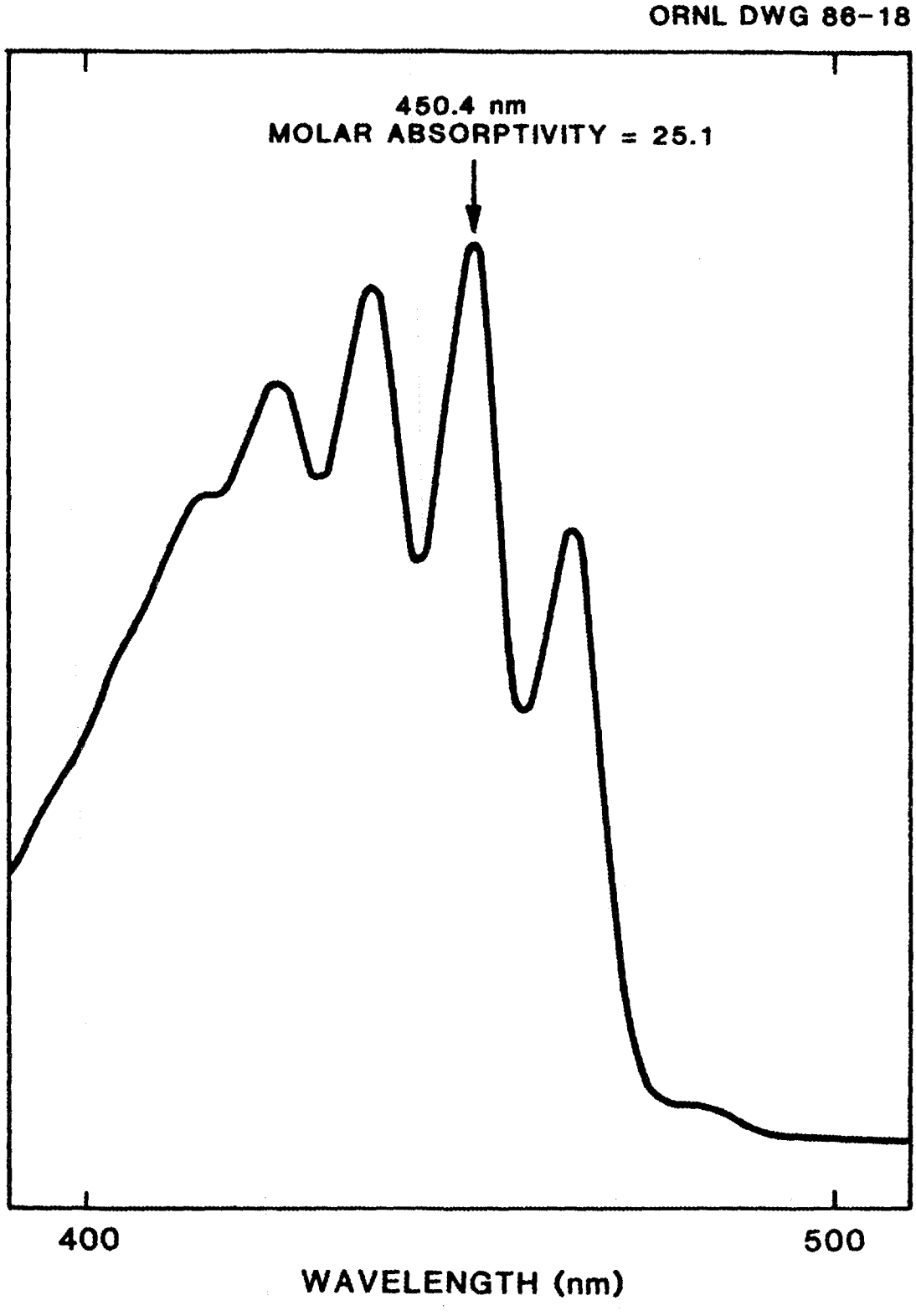

Fig. 1. Absorption spectrum of uranyl carbonate.

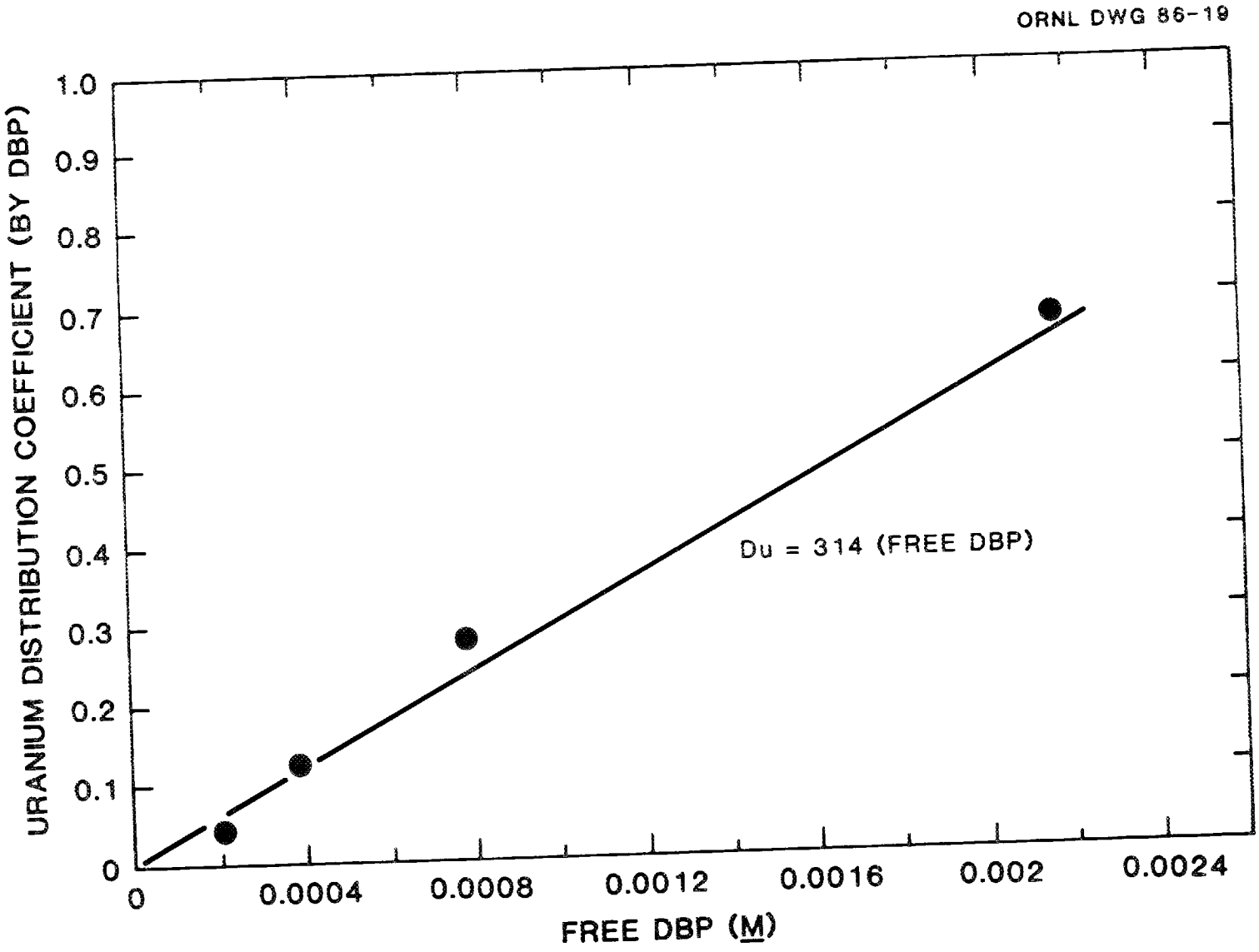

Fig. 2. Uranium extraction by HDBP. The quantity of uranium extracted was corrected by subtraction of uranium extracted by TBP. Free DBP is DBP not complexed with uranium.

nitrate solution. This solution is stripped with ammonium carbonate, and the uranium is determined by absorbance. The DBP concentration is then determined by the following BASIC program:

```
10  INPUT "WHAT IS THE ABSORBANCE OF THE FIRST CARBONATE
    STRIP";A1

20  INPUT "WHAT IS THE ABSORBANCE OF THE CARBONATE STRIP AFTER
    URANIUM EQUILIBRATION";A2

30  UT=0.0526*(0.02+A1/25.1)

40  CD=(A2/25.1-UT)/(0.02+A1/25.1-A2/25.1)/314-UT+A2/25.1

50  PRINT "THE DBP CONC. IS ";CD;" MOLAR"

60  PRINT:PRINT:

70  GOTO 10
```

Note that this analytical method may only be used when the nitric acid and nitrates other than uranyl nitrate are near zero.

2.4 SMALL-COLUMN TESTS

The column used in the tests is shown in Fig. 3. The bed was contained in an 8-mm-OD, 6-mm-ID glass tube with a jack-leg and could be immersed in a beaker of heated water for elevated temperature tests. In all cases the solvent passed through the beds was intended to be ~0.01 M in both uranium and DBP (in one test the DBP concentration was found to be ~0.015 M in the feed) and was prepared as described in Sect. 2.1.

2.4.1 Loading 20–50 Mesh Bio-Rad AG MP-50

Small-column tests used 1 mL of 20–50 mesh BIO-RAD AG MP-50 macroporous cation resin (H^+ form) to treat ~1 ml per min of solvent containing ~0.01 M uranium and DBP. Tests were conducted at 22° (duplicates) and 52°C. Figure 4 shows effluent concentrations of the two loading tests at 22°C. Significant removal of uranium and no detectable removal of DBP were found. Figure 5 shows the uranium and DBP concentrations in the column effluent in the test at 52°C; again, uranium loaded on the sorbent without the loading of DBP. Uranium removal half-times were ~20 s at

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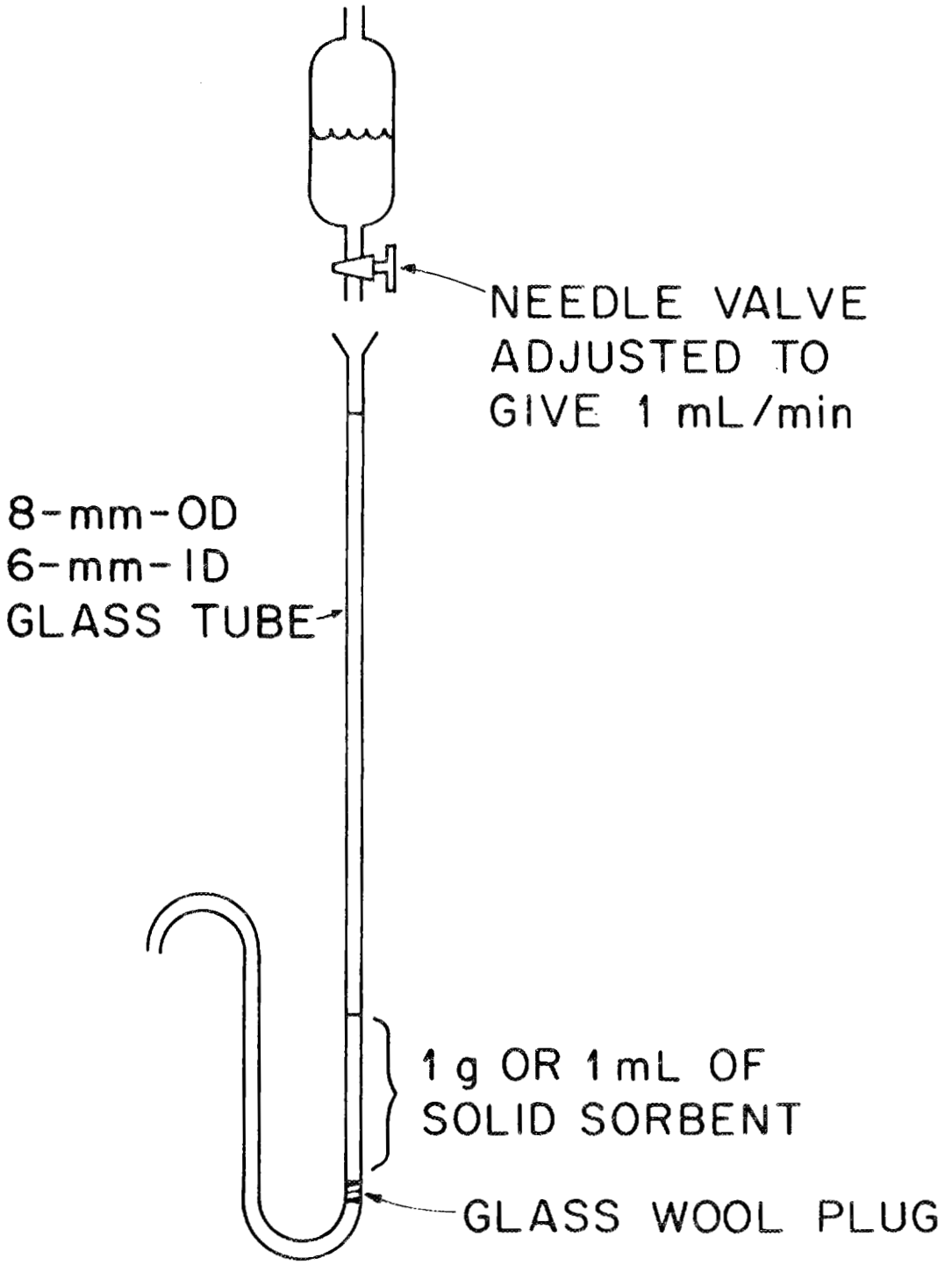

Fig. 3. Apparatus used in small-bed tests.

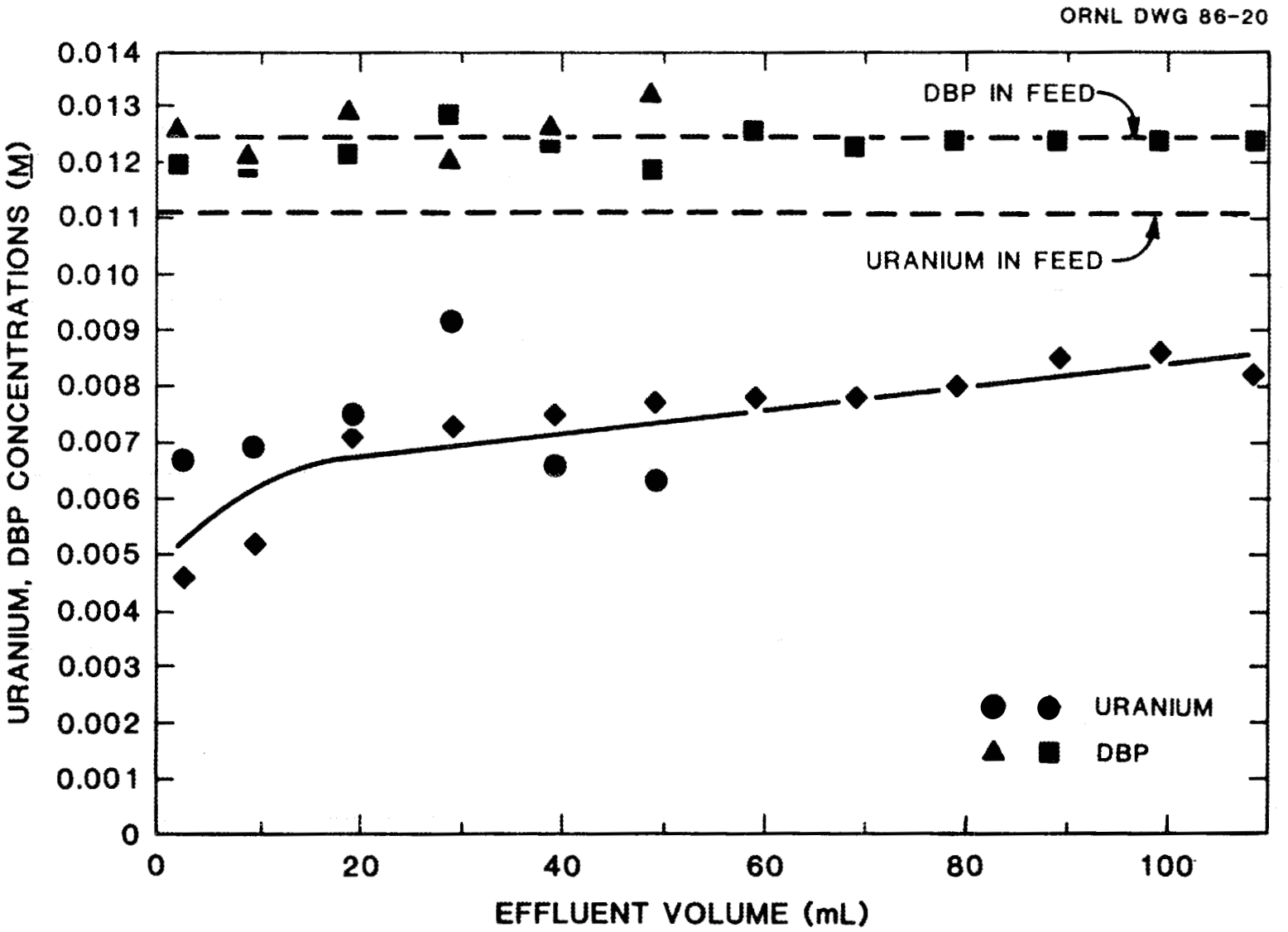

Fig. 4. Effluent uranium and DBP concentrations from duplicate test loadings of 1 mL of Dowex 50W-X4 cation-exchange resin (H^+ form) at 22°C. The flow rates of the solvent were 1 mL/min.

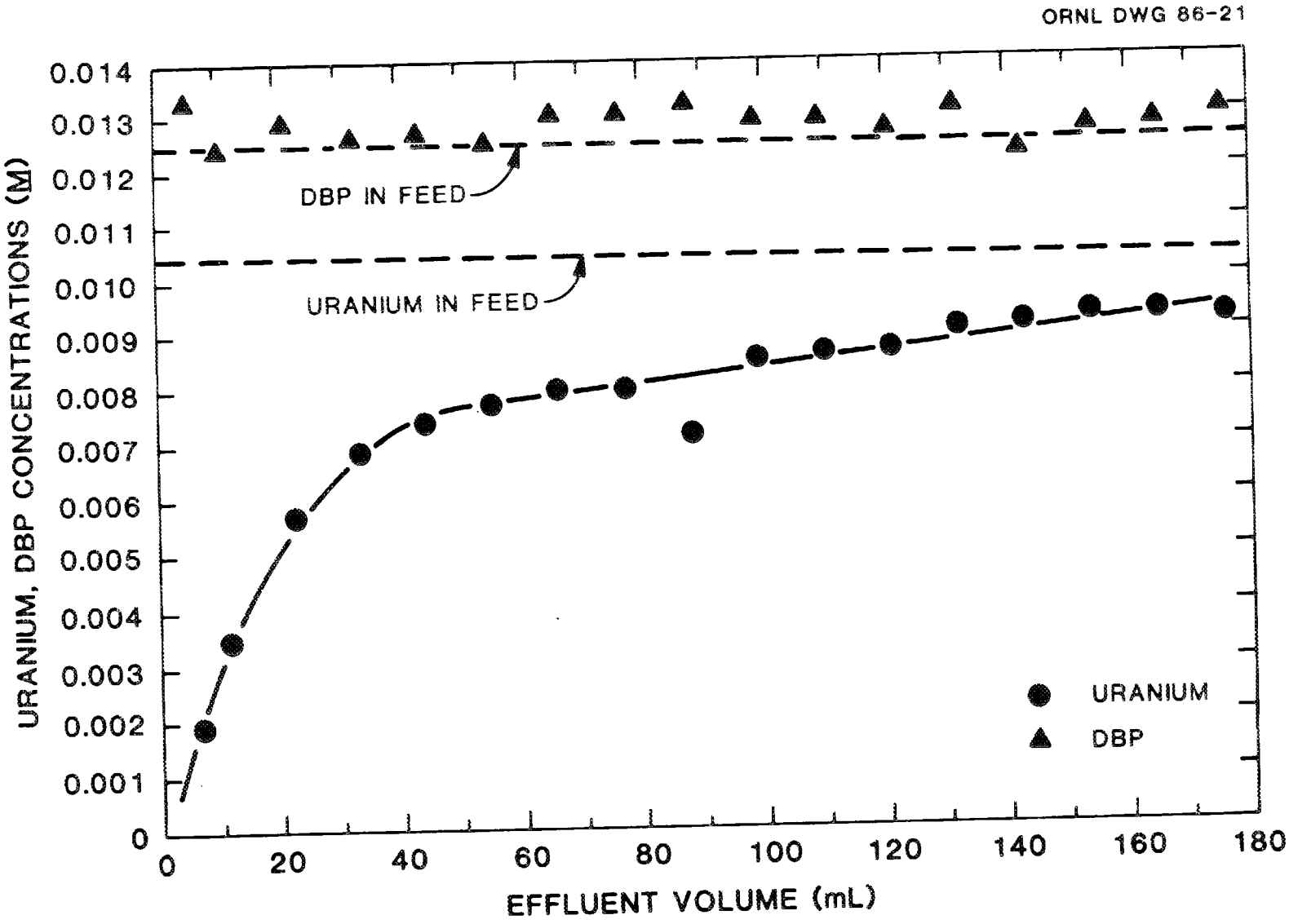

Fig. 5. Effluent uranium and DBP concentrations from a test loading of 1 mL of Dowex 50W-X4 cation-exchange resin (H^+ form) at 52°C. The flow rate of the solvent was 1 mL/min.

52°C and ~40 s at 22°C. The apparent capacity of the resin was ~0.35 mmol uranium per mL of resin at 22°C and 0.56 mmol uranium per mL of resin at 52°C (stated capacity is 1.86 meq/mL). A later test repeated the loading of the cation-exchange resin at 50°C (Figs. 6 and 7). In this case the volume of sorbent was decreased to 0.75 mL, and the flow rate was decreased to 0.5 mL/min — an increase of 50% in the residence time of the solvent in the sorbent bed. DBP was not removed. The efficiency of uranium removal was significantly improved over that in the earlier tests, with the half-time reduced to ~10 s and the apparent capacity of the bed increased to ~1 mmol uranium per mL of resin; this value represents approximately the theoretical capacity of the resin. In a larger bed, where the residence times are larger relative to the half-times for removal, the sensitivity to flow rate may be less.

2.4.2 Eluting 20–50 Mesh Bio-Rad AG MP-50

Elution of the uranium loaded in the 52°C test was approximately 50% complete by passage of 80 mL of 30% TBP containing 0.06 M HNO_3 at a flow rate of 1 mL/min at 22°C (Figs. 8 and 9). Uranium elution at 22°C from loaded cation resin was tested in duplicate using 30% TBP which had been equilibrated with 2 M HNO_3 (0.36 M HNO_3 in the 30% TBP) (Fig. 10). Essentially all the mobile uranium had been removed with the passage of 80 mL of solvent. The increased acidity of the solvent significantly increased the removal rate; a further increase by operating at elevated temperatures should also be possible.

2.4.3 Loading 60–120 Mesh Alcoa F-1 Activated Alumina

Columns containing 1 mL of damp (equilibrated with water-saturated air for about 6 weeks) and 1 mL of dry 60–120 mesh Alcoa F-1 activated alumina were tested at 22°C for the removal of uranium and DBP from damp and dry solvent (dried by sparging with air at 60°C), respectively. Figure 11 shows the cumulative loading of uranium and DBP vs effluent volume for the damp sorbent and solvent test. Uranium was found to load preferentially, with essentially no loading of DBP. The total capacity for uranium was <0.1 mmol/g. Figure 12 shows the cumulative loadings of uranium and DBP for the dry sorbent and solvent tests. Both uranium and

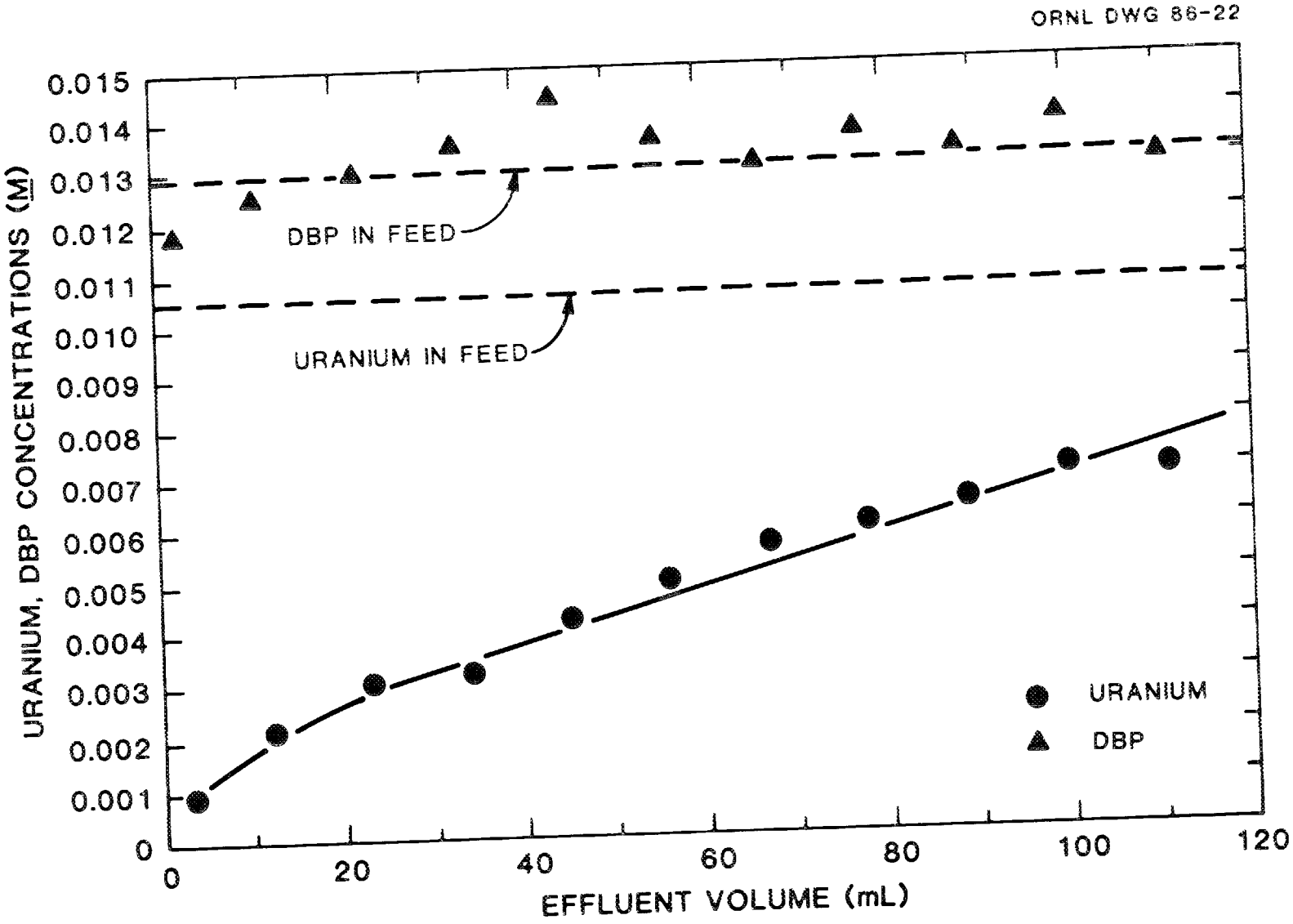

Fig. 6. Effluent uranium and DBP concentrations from a test loading of 0.75 mL of Dowex 50W-X4 cation-exchange resin (H^+ form) at 50°C. The flow rate of the solvent was 0.5 mL/min.

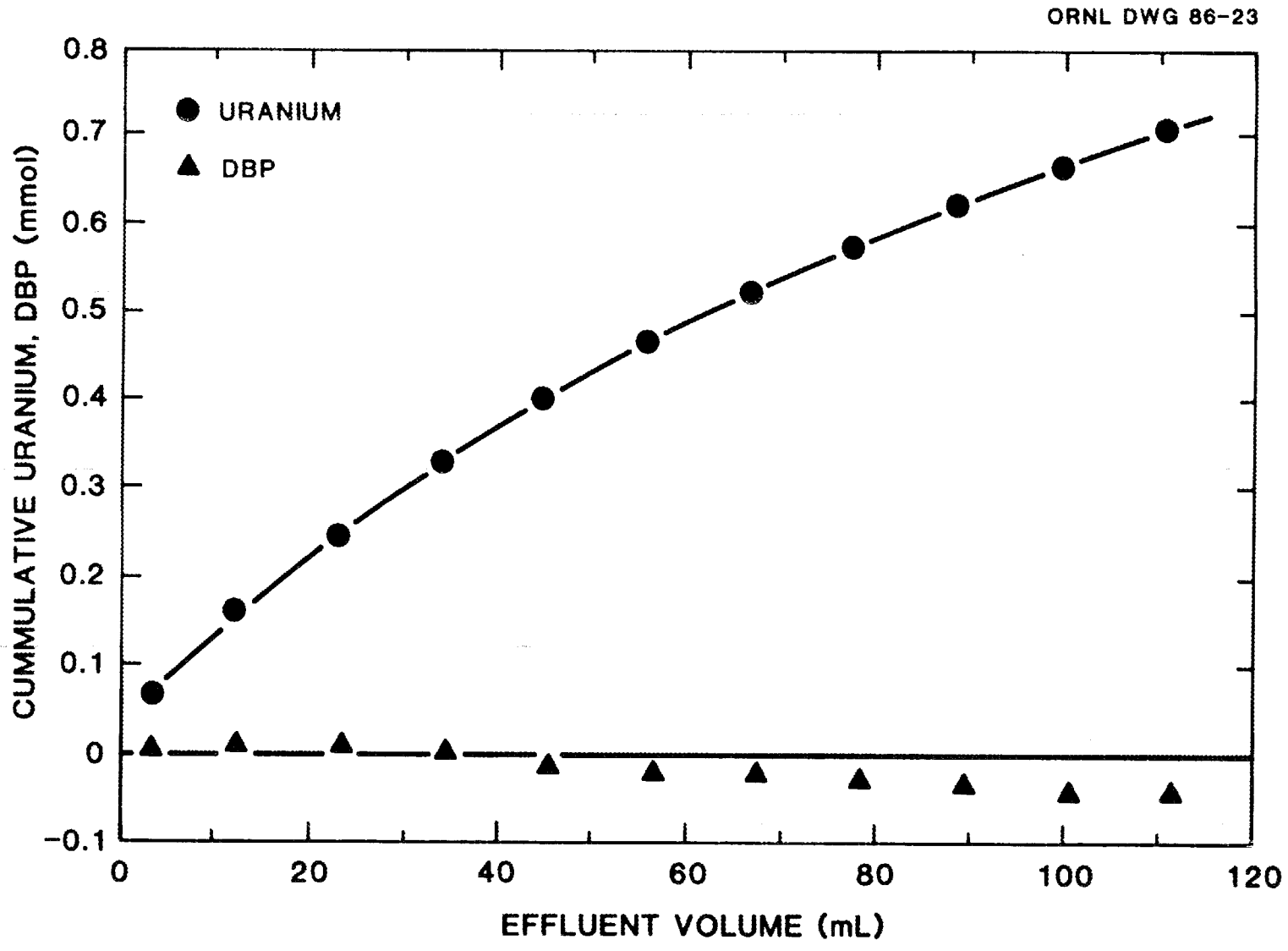

Fig. 7. Uranium and DBP loaded on the resin of the test using 0.75 mL of Dowex 50W-X4 cation-exchange resin (H^+ form) at 50°C. The flow rate of the solvent was 0.5 mL/min.

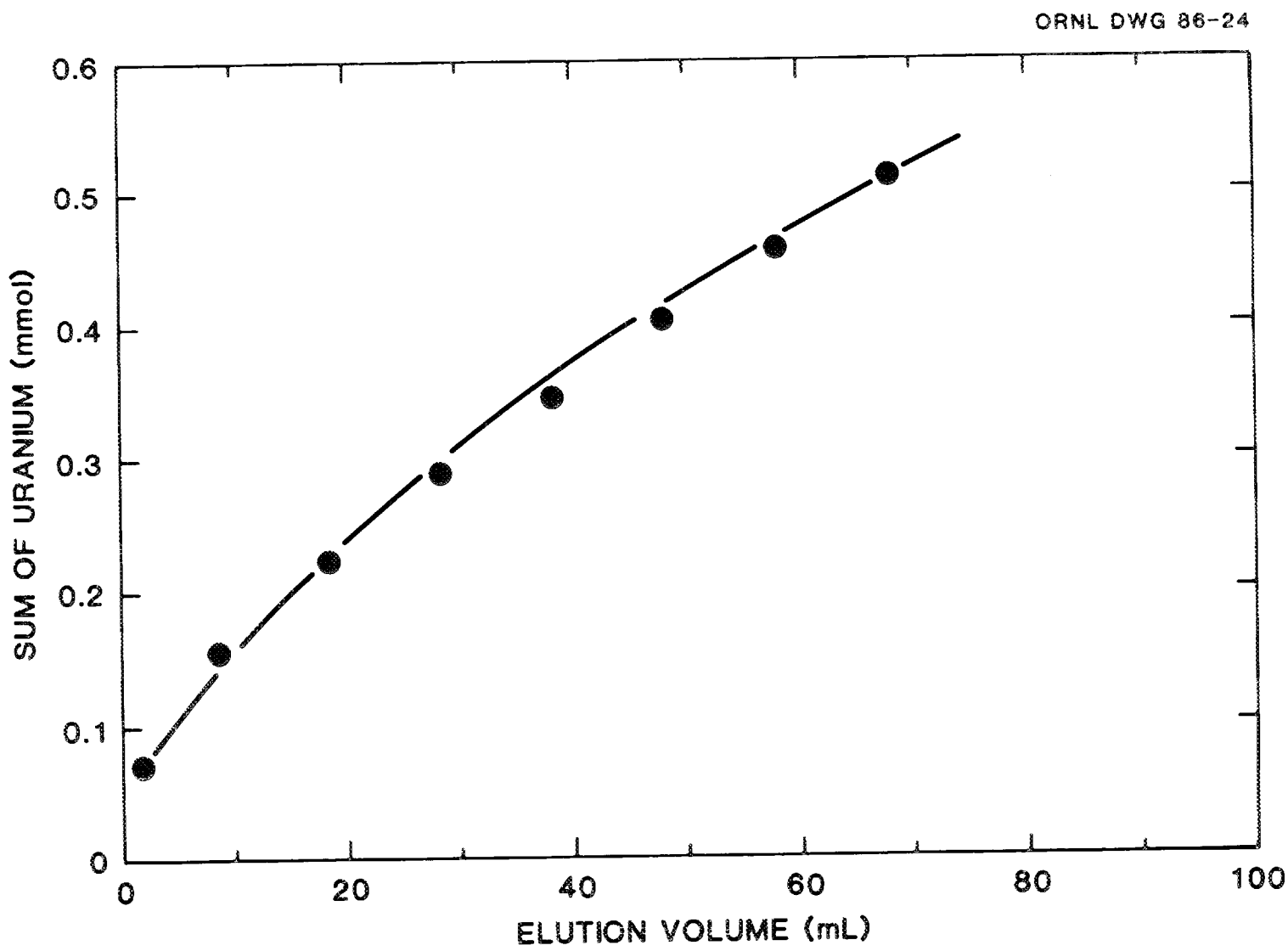

Fig. 8. Uranium eluted from 1 mL of Dowex 50W-X4 cation-exchange resin (H^+ form) by 30% TBP solvent containing 0.06 M HNO_3 at 22°C. The solvent flow rate was 1 mL/min.

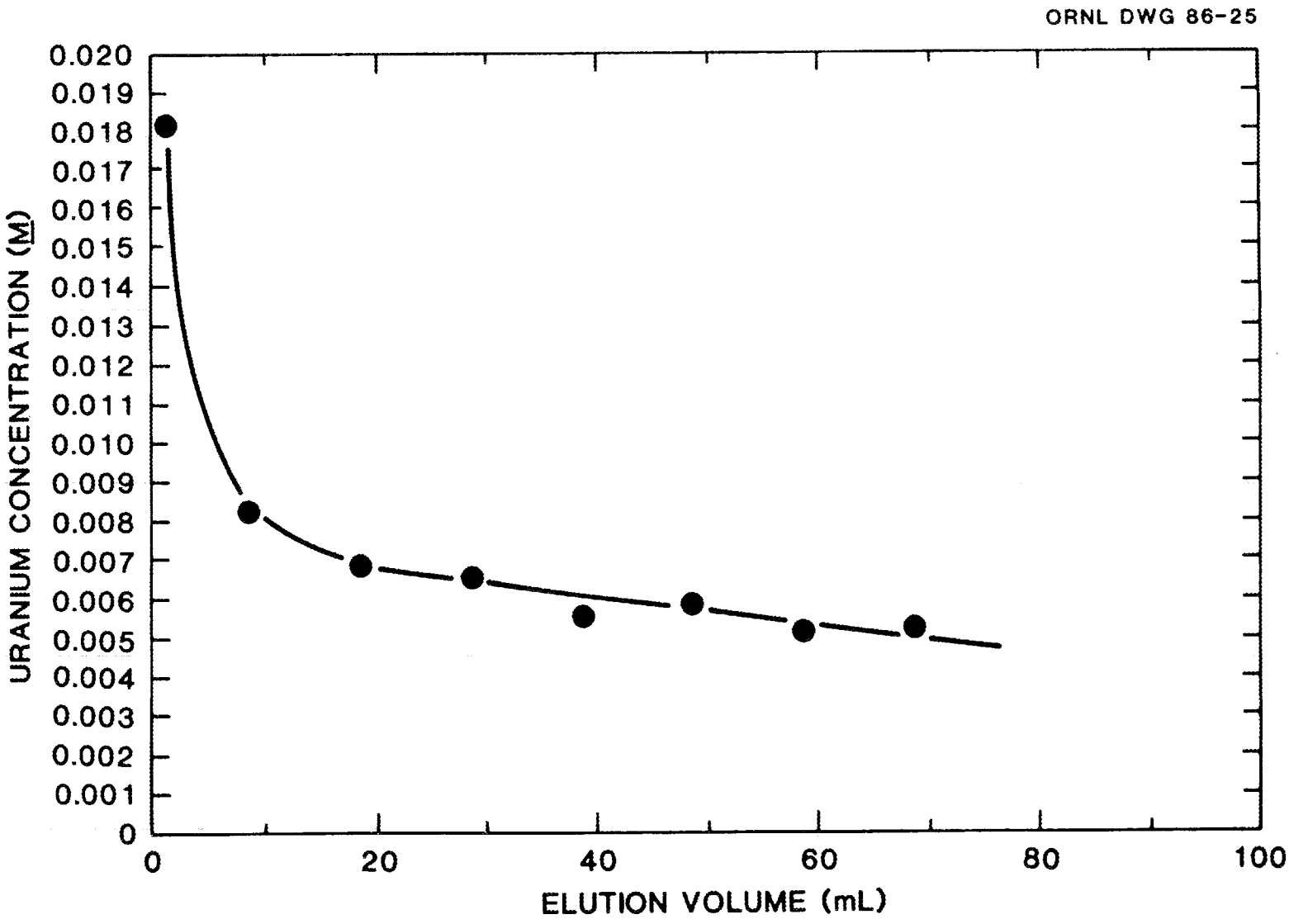

Fig. 9. Elution of uranium from 1 mL of Dowex 50W-X4 cation-exchange resin (H^+ form) by 30% TBP solvent containing 0.06 M HNO_3 at 22°C. The solvent flow rate was 1 mL/min.

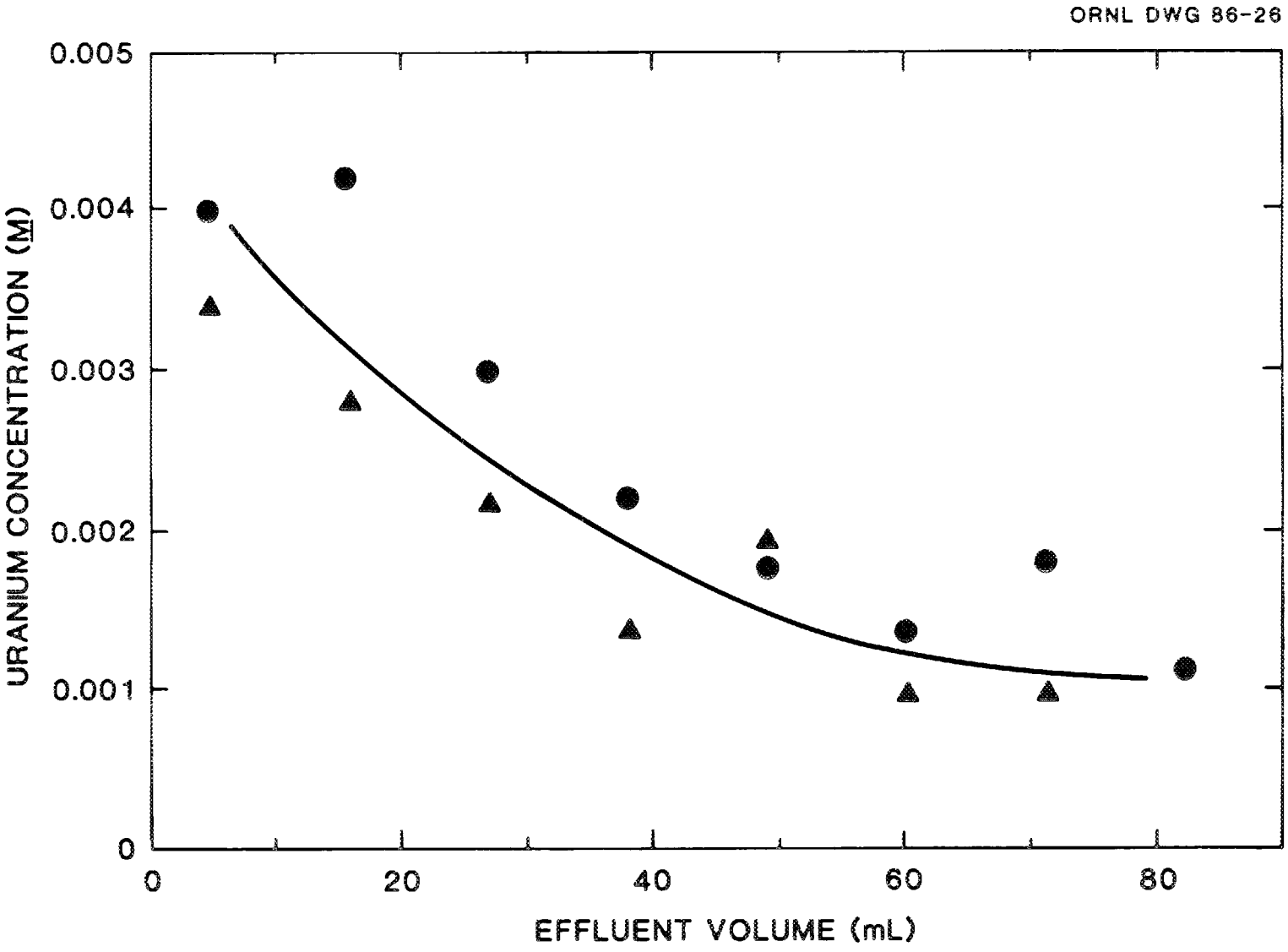

Fig. 10. Duplicate tests of elution of uranium from 1 mL of Dowex 50W-X4 cation-exchange resin (H^+ form) at 22°C with 30% TBP solvent which had been equilibrated with an equal volume of 2 M HNO_3. The flow rate of the solvent was 1 mL/min.

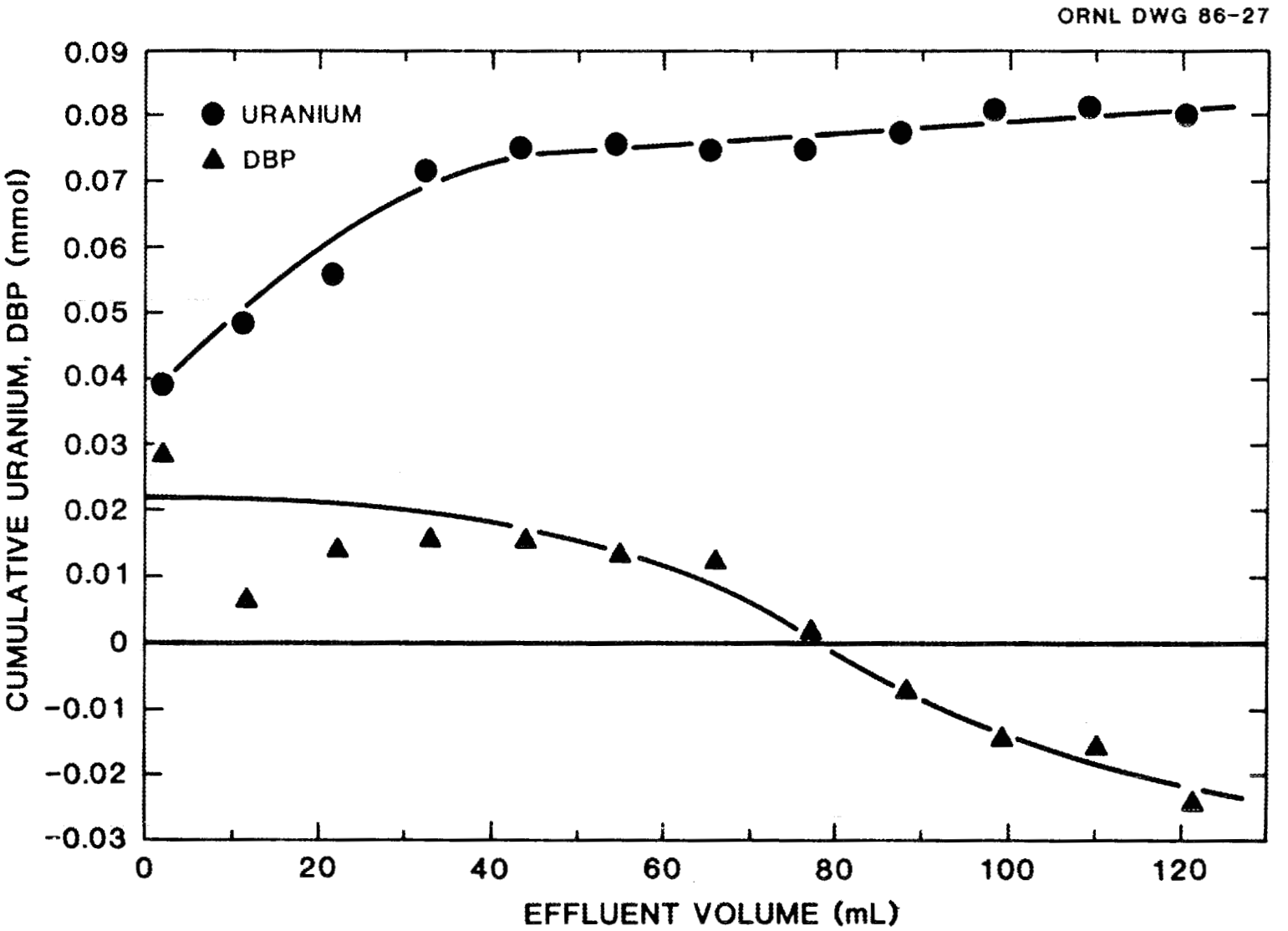

Fig. 11. Cumulative loadings of uranium and DBP on 1 mL of damp activated alumina at 22°C. The solvent flow rate was 1 mL/min.

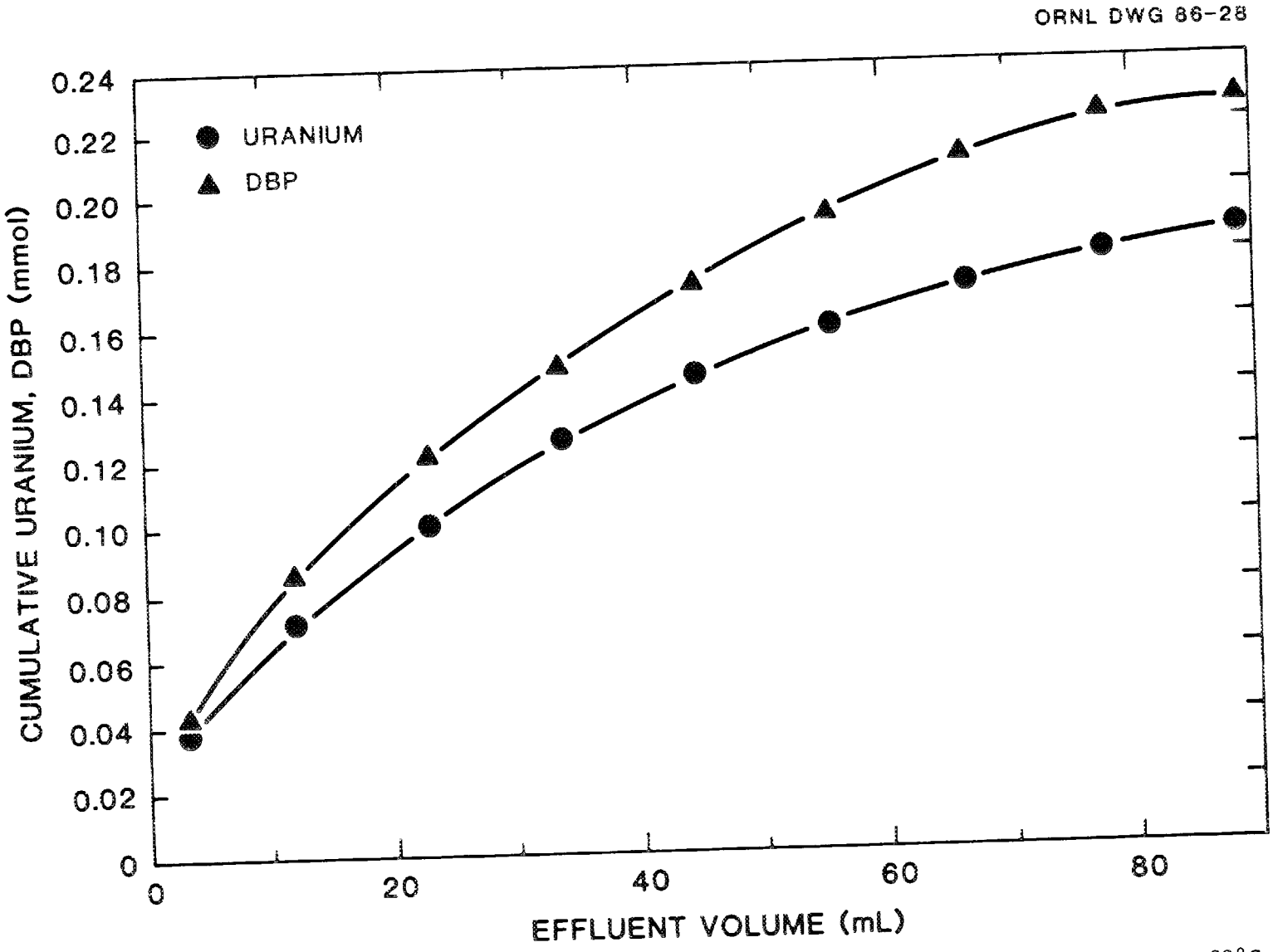

Fig. 12. Cumulative loadings of uranium and DBP on 1 mL of dry activated alumina at 22°C. The dry solvent flow rate was 1 mL/min.

DBP were loaded in approximately their ratio in the solvent (solvent ratio, DBP/U = 1.17; sorbent ratio = 1.24). Significantly greater capacities for uranium and DBP were obtained with the dry system.

2.4.4 Eluting 60–120 Mesh Alcoa F-1 Activated Alumina

Uranium was eluted from loaded activated alumina using 30% TBP solvent containing 0.36 M HNO_3. These results are shown in Fig. 13. The uranium was more easily eluted than from the cation-exchange resin, with an initial concentration in the solvent of about twice the amount that was found when eluting the cation-exchange resin. The volume required to elute the resin was also reduced by about one-half.

2.4.5 Loading a Column Containing DTPA on 3-mm Glass Beads

A column of 3-mm glass beads coated with ~0.2 g of diethylenetriamine pentaacetic acid (DTPA) (pH adjusted to ~7) was tested for the removal of uranium and DBP from the solvent (Fig. 14). At about 40 mL of effluent, the temperature of the column was increased from 22° to 50°C. At the lower temperature, the loading of uranium and DBP was minimal; at the higher temperature, the loading of uranium was significantly increased. This material appears to be usable for preferential removal of uranium from the uranium-DBP mixture. Removal of the loaded DTPA from the column is very simple because it is water soluble. Passage of a small amount of water (10 to 20 column volumes) through the column removed all the coating, with its uranium, from the column.

2.4.6 Loading Dowex 21K (Hydroxide Form)

A solvent containing ~0.01 M uranium and ~0.015 M DBP was used to load a hydroxide-form anion resin (Figs. 15 and 16). The ratio on the resin was approximately the same as that in the feed solvent.

2.4.7 Miscellaneous Tests

Literature information[3] indicates that DBP can be removed from nitric acid solutions containing uranium by extracting the DBP with 2-ethylhexanol. This reference indicated that extraction occurs by hydrogen bonding of the HDBP to the hydroxyl of the alcohol. The extraction is most effective when the nitric acid concentration is greater than 3.5 M.

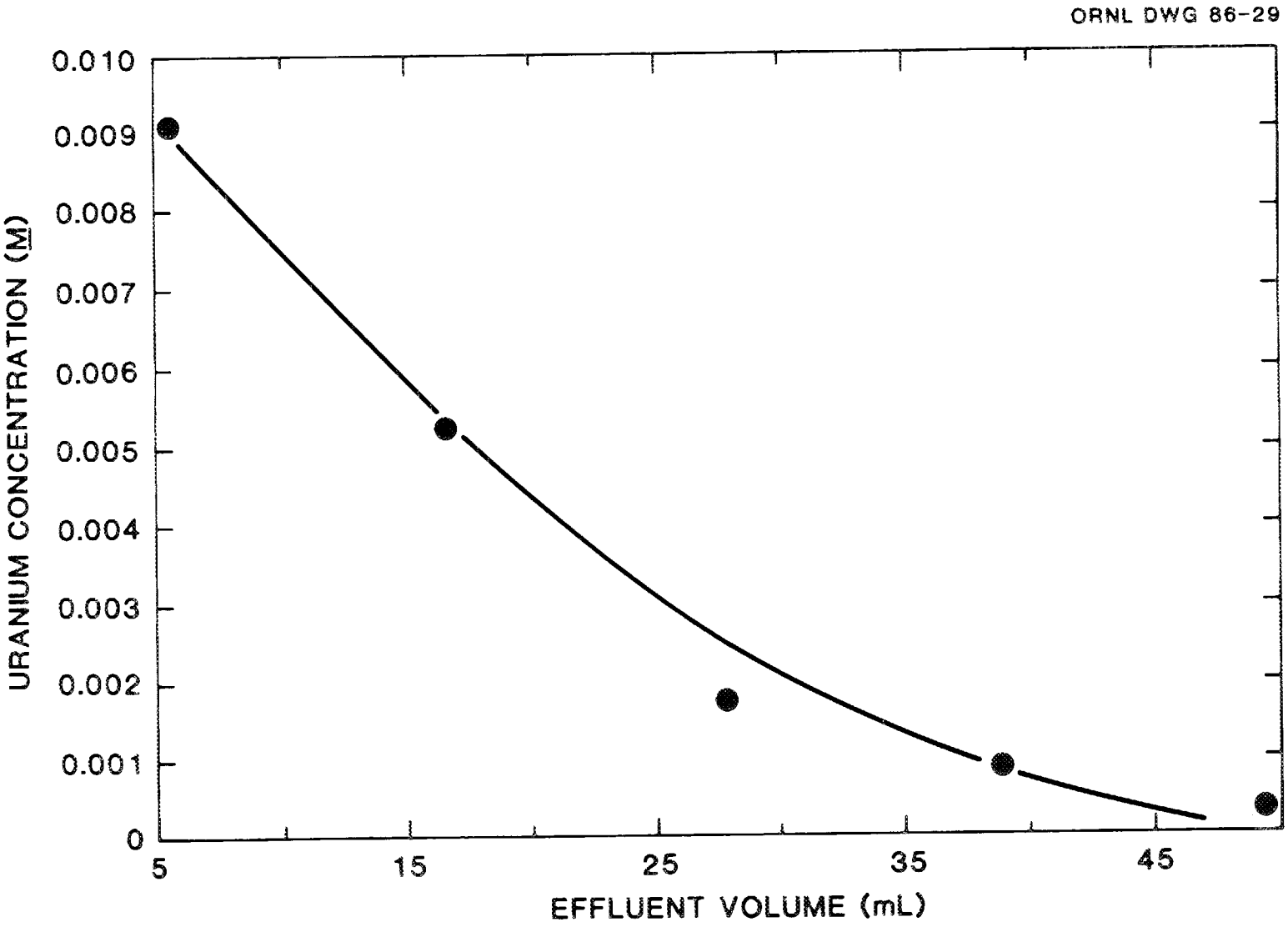

Fig. 13. Uranium removal from activated alumina by 30% TBP solvent which was equilibrated with an equal volume of 2 M HNO_3. The solvent flow rate was 1 mL/min.

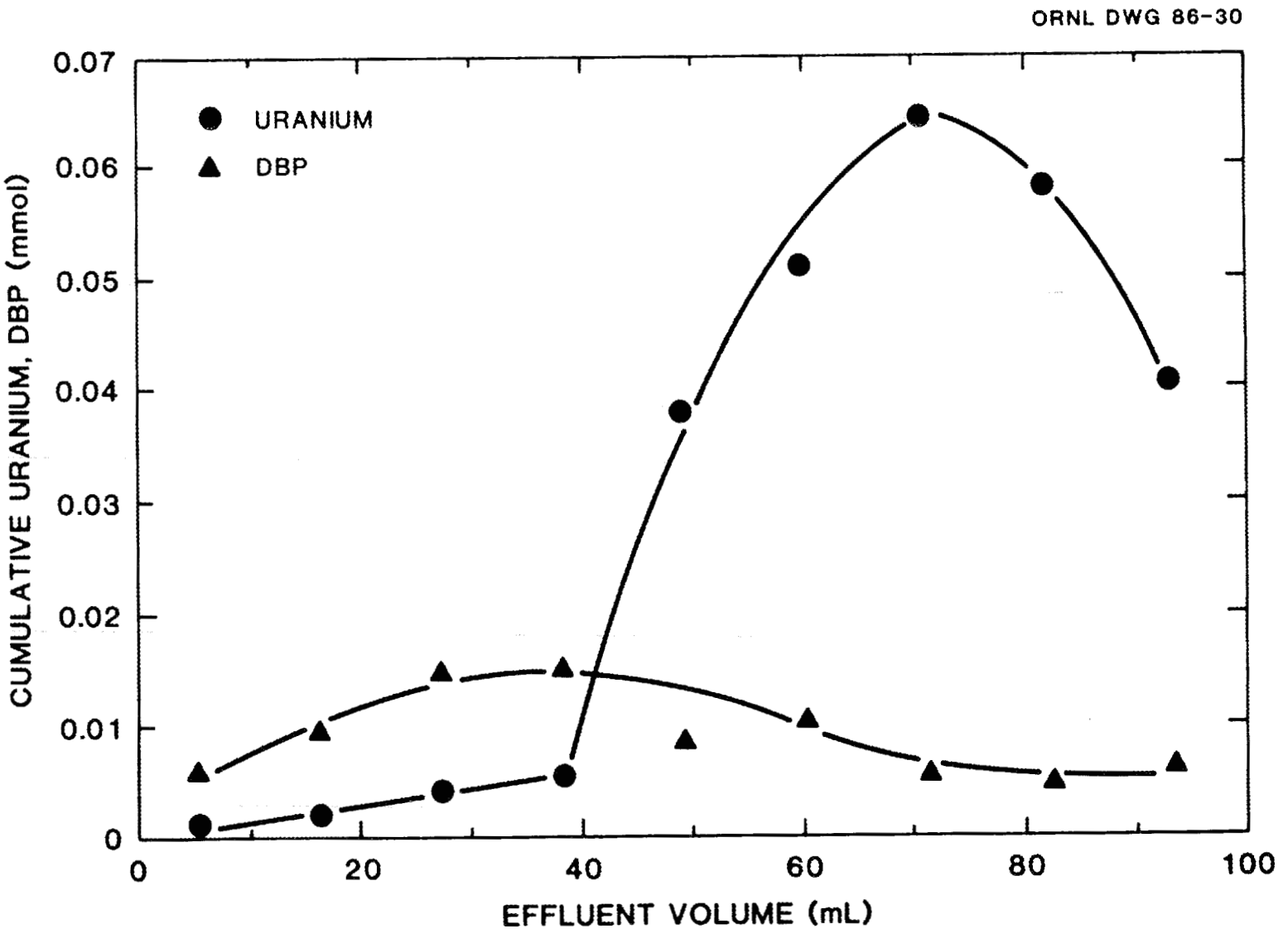

Fig. 14. Uranium and DBP loading on a column of glass beads coated with 0.2 g of DTPA. The solvent flow rate was 1 mL/min. The temperature was increased from 22° to 50°C at 40 mL of effluent volume.

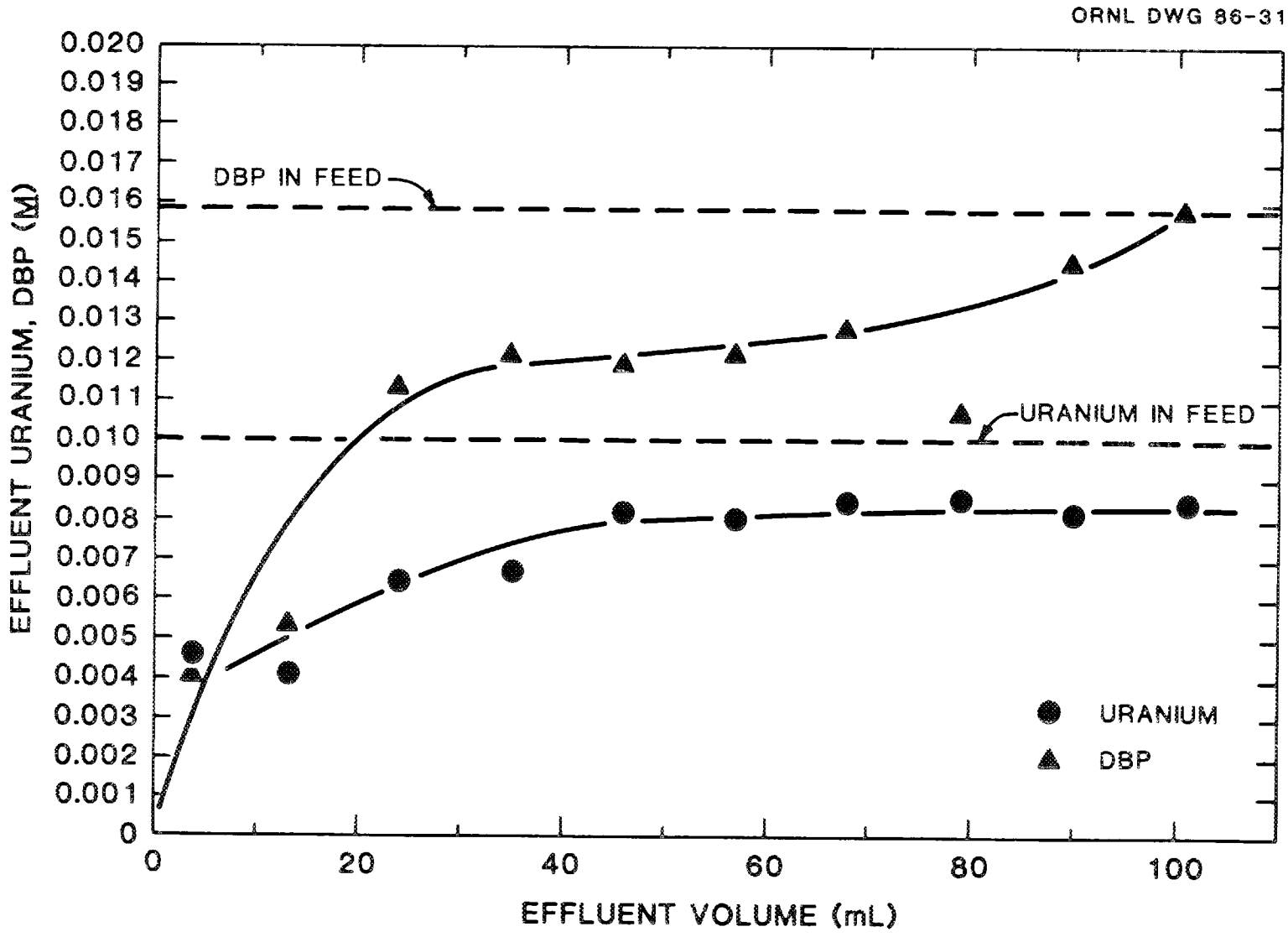

Fig. 15. Uranium and DBP loading on 1 mL of Dowex 21K resin (hydroxide form) at 22°C. The solvent flow rate was 1 mL/min.

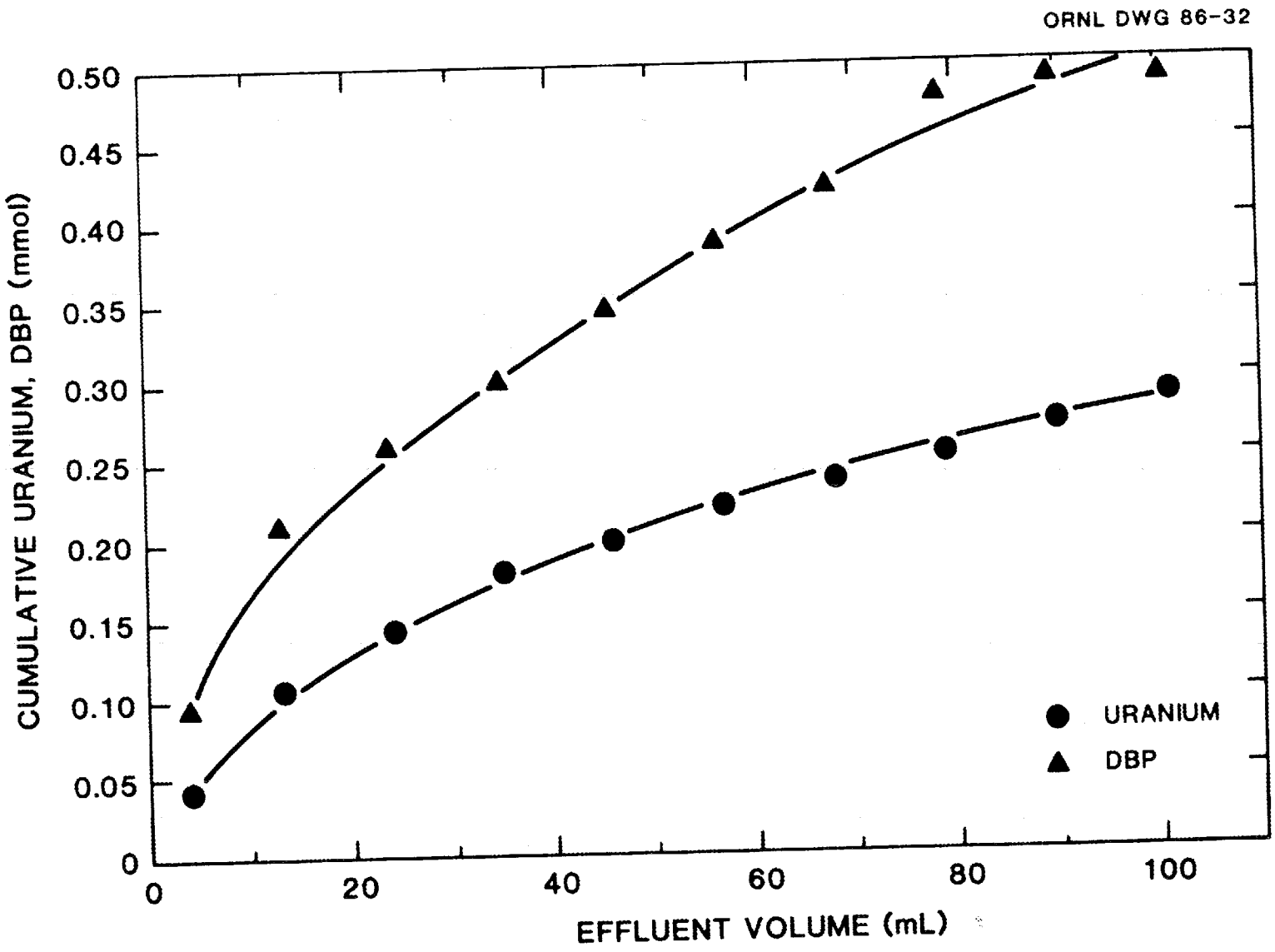

Fig. 16. Cumulative uranium and DBP loading on 1 mL of Dowex 21K resin (hydroxide form) at 22°C. The solvent flow rate was 1 mL/min.

Brief scouting experiments examined the possibility that DBP could be sorbed on sucrose (silica gel substrate) or cellulose; both of these materials contain large numbers of hydroxyl groups. The solvent used in the tests contained about 0.01 M each of uranyl nitrate and DBP. The sucrose-coated silica gel was tested with a solvent of low acidity and with a solvent equilibrated with 1 or 4 M nitric acid. Cellulose (adjustable pipette filters) was tested with a solvent of low acidity and a solvent equilibrated with 4 M HNO_3. DBP was not preferentially removed in any test. A similar scouting experiment tested Duolite CS-100 (Diamond Shamrock Chemical Co., Cleveland, Ohio). This material did not preferentially remove DBP.

It is known that iron forms a relatively strong DBP complex. A cation-exchange resin (BIO-RAD AG MP-50) was loaded with ferric iron, treated with ammonium hydroxide to precipitate the iron, and washed with water to remove the excess ammonia. Solvent containing uranyl nitrate and DBP (22°C, with a flow rate of 1 mL/min) was then passed through a column containing 1 mL of the treated resin. The cumulative sorbed uranium and DBP are shown in Fig. 17. Uranium was preferentially loaded with an apparent capacity of 0.14 mmol per mL of resin. This value represents about 40% of the capacity (under similar conditions) of the untreated cation-exchange resin for uranium. It appears likely that the iron was ineffective and occupied some of the sorption sites on the resin.

Tests with anion-exchange resins indicated that the chloride and nitrate forms of the resin could not remove DBP from the solvent. This inability to remove the DBP is likely due to the relatively strong bonding of chloride and nitrate to the resin. Resin in the hydroxide form successfully removes DBP but also removes the uranium. This uranium removal is thought to be caused by the removal of nitrate from the uranyl nitrate complex, resulting in the precipitation of uranyl hydroxide on the resin. A test was performed using the anion-exchange resin in the carbonate/bicarbonate form. The resin was prepared by suspending the hydroxide-form resin in water and sparging with CO_2 for about 1 h. The

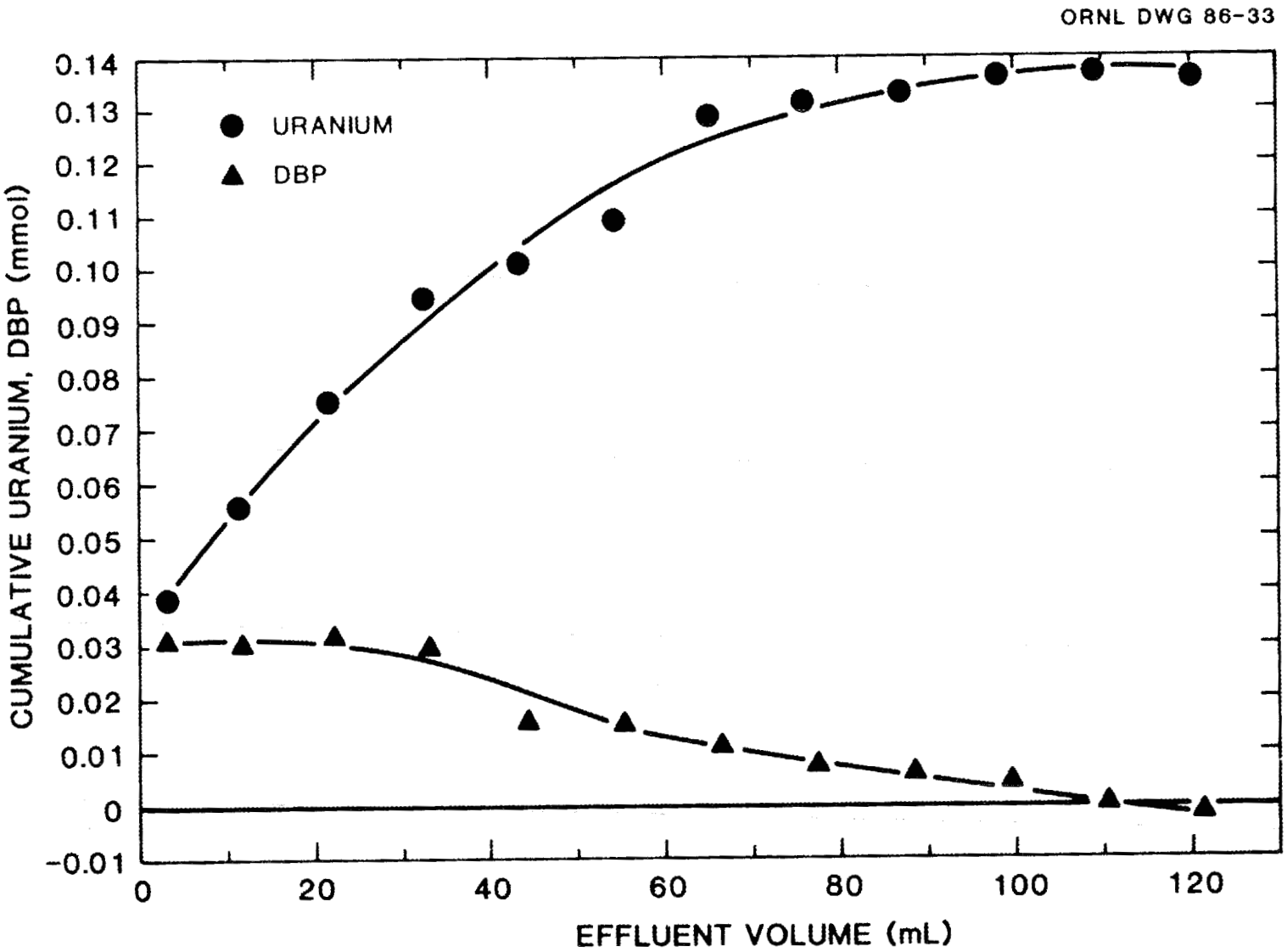

Fig. 17. Cumulative uranium and DBP loading on 1 mL of Dowex 50W-X4 cation-exchange resin (H^+ form) which had been partially loaded with iron, followed by precipitation of iron hydroxide. The solvent flow rate was 1 mL/min.

pH of the water (initially measuring 8 to 9) was decreased to about 7 at the end of sparging. This resin was tested and found that it had removed both the DBP and the uranium.

It may be possible to separately elute uranium and DBP from a sorbent that loads both components such as hydroxide-form, anion-exchange resins or activated alumina. HDBP can be extracted from acidified aqueous solutions containing both uranium and DBP by 2-ethylhexanol.[3] Elution of the DBP by 2-ethylhexanol (containing ~0.7 M HNO_3), followed by elution of the uranium by 30% (containing ~0.6 M HNO_3), was attempted. The uranium stayed on the hydroxide-form, anion-exchange resin and the activated alumina during the treatment with acidified 2-ethylhexanol, and it was removed by the treatment with acidified TBP. Both of these observations were visual; analyses for the components in the eluates were not successful.

3. SOLVENT CLEANUP MATHEMATICAL DEVELOPMENT

The following development assumes that a small sidestream will be withdrawn from the solvent extraction system and passed through a packed column that will remove nearly all of the DBP from that portion of the solvent. A sidestream treatment would be preferable for the incorporation of a new treatment in an existing plant since the ongoing, necessary operations of the plant would be affected only slightly. Additionally, if the solvent treatment system should fail, as by plugging of the column, it could be automatically bypassed. This feature would eliminate any possibility of a major disturbance to the operability of the plant.

For a system without solvent cleanup, the rate of change of the concentration of DBP is given by:

$$dC/dt = n/V,$$

where

C = concentration of DBP in main inventory, mol/L (zero subscript is initial concentration);

t = time, h;

n = rate of DBP production, assumed constant, mol/h;

V = total inventory of solvent, L.

Integration gives:

$$C - C_o = nt/V.$$

For a system with solvent cleanup, the rate of change of the concentration of DBP is given by:

$$dC/dt = n/V - CF/V,$$

where

F = solvent flow rate to cleanup system, L/h.

Rearranging gives:

$$dC/(n-CF) = dt/V.$$

Let $x = n - CF$,

then $dx = -FdC$,

and

at $t = 0$, $C = C_o$, and $x = n - C_oF$;

at $t = t$, $C = C$, and $x = n - CF$.

Substitution gives:

$$dx/-Fx = dt/V.$$

Rearranging gives:

$$dx/x = -F/V\ dt.$$

Integration gives:

$$\ln[(n - CF)/(n-C_oF)] = -Ft/V.$$

Simplifying,

$$C = n/F + [(C_oF-n)/F]e^{-Ft/V}.$$

After an extended period, the equation simplifies to:

$$C = n/F.$$

The solvent extraction system of the Y-12 Plant is estimated to reach ~0.01 M DBP in about 30 d of operation.[4] For a hypothetical system containing an inventory of 100 L, this concentration would require a rate of DBP production, n, of 0.0015 mol/h. If a sidestream of 5% of the inventory per hour is passed through a solvent cleanup system (the

cleanup system assumed to remove ~100% of the contained DBP), the equilibrium concentration of DBP will be 0.0003 mol/L. Without cleanup this level would be reached in 20 h.

This simple examination of the system demonstrates that treatment of more than 5% of the inventory per hour does not produce significant further improvement in solvent quality. Further, large amounts of unstripped uranium are present in the solvent stream to be treated. The only systems found which separately remove uranium and DBP from the solvent remove the uranium preferentially. The use of such a system (an example is cation exchange followed by DBP removal) on the total solvent flow would require handling impractical amounts of uranium. Thus, systems that remove the uranium preferentially are not suited for use in systems which cannot tolerate a sidestream treatment.

4. CONCLUSIONS

The tests performed show that it is relatively easy to preferentially remove uranium from solvents containing uranium and DBP, but quite difficult to remove DBP preferentially. The current methods could be used by removing the uranium (as by a cation-exchange resin) and then using either an anion exchange resin in the hydroxyl form or a conventional treatment with a basic solution to remove the DBP. The uranium could then be recovered from the cation-exchange resin. Such a method may not be suitable for the Y-12 facility because of accountability requirements (sampling the uranium content of the cation-exchange resin would require elution of the uranium). Such a system would be most useful for the treatment of a sidestream, as illustrated in Sect. 3.

5. ACKNOWLEDGMENTS

F. I. Case (ORNL Chemistry Division) performed all the testing and analyses reported. M. L. Baker (Y-12 Development Division) participated in planning and in performance of several of the tests and in preparation of solid sorbents. The advice of B. A. Moyer (ORNL Chemistry Division) in solvent extraction chemistry is gratefully acknowledged.

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