Lab. Records

MASTER

X-822

OAK RIDGE NATIONAL LABORATORY
Operated by
UNION CARBIDE NUCLEAR COMPANY
Division of Union Carbide Corporation
Post Office Box X
Oak Ridge, Tennessee

ORNL
CENTRAL FILES NUMBER
58-12-43

COPY NO. 65

DATE: December 30, 1958

SUBJECT: A Preliminary Investigation of a Chromatographic Column Separation of Rare Earths Using Di(2-ethylhexyl)phosphoric Acid

TO: Distribution Shown

FROM: John W. Winchester*

Abstract

A new chromatographic separation of small amounts of rare earths has been devised and tested with carrier-free radiotracers of Nd^{147}, Pm^{147}, and Eu^{155}. The method uses di(2-ethylhexyl)orthophosphoric acid (HDEHP) as a stationary phase supported on a column of aluminum oxide, and elution is with dilute aqueous hydrochloric acid. Column behavior is similar to solvent extraction using HDEHP where separation factors average 2.5 for adjacent rare earths.

*ORINS University Research Participant, Summer, 1958, assigned to the Analytical Chemistry Division, ORNL. Present address: Department of Geology and Geophysics, Massachusetts Institute of Technology, Cambridge 38, Massachusetts

DISCLAIMER

Introduction

As part of a program to develop rapid analytical methods for the determination of rare earths in geological materials by neutron activation,[1] a new chromatographic separation procedure for small amounts of rare earths has been devised and tested with carrier-free tracers. The stationary phase is di(2-ethylhexyl)orthophosphoric acid (HDEHP) supported on a column of aluminum oxide and elution is with dilute aqueous hydrochloric acid solutions. The mixture of rare earths is placed on the top of the column bed and eluted at room temperature. Separation factors for adjacent rare earths average 2.5.

Di(2-ethylhexyl)orthophosphoric acid* (HDEHP), molecular weight 322, density ~ 1.0, is a clear colorless viscous oil at room temperature, sparingly soluble in neutral and acidic aqueous solutions, and resistant to hydrolysis on continued contact with dilute mineral acids. The dialkyl ester of orthophosphoric acid, $(CH_3CH_2CH_2CH_2CH(C_2H_5)CH_2O)_2PO(OH)$, is a weak acid and forms complexes with inorganic cations soluble in organic solvents. Peppard et al.,[2-7] Blake et al.[8,10] and Baes et al.[9,11] have described the use of the reagent in solvent extraction separation procedures for several elements.

Peppard et al.[2] report that trivalent rare earth carrier-free tracers may be extracted from acidic aqueous solutions by toluene solutions of HDEHP. Equilibria may be described by the equations**

---

*Also named bis(2-ethylhexyl)phosphoric acid and bis(2-ethylhexyl)hydrogen phosphate. Sometimes abbreviated D2EHPA.

**Baes et al.[9] report that HDEHP and its complexes actually exist as dimers, but that equations 1-4 nevertheless predict the observed dependence of E_a^o on H^+ and HDEHP concentrations.

$$HDEHP = H^{+} + DEHP^{-} \qquad (1)$$

$$M^{3+}_{aq} + 3\ HDEHP_{org} = M(DEHP)_{3org} = M(DEHP)_{3org} + 3H^{+}_{aq} \qquad (2)$$

$$K_{eq} = \frac{(M(DEHP)_{3org})}{(M^{3+}_{aq})} \cdot \frac{(H^{+}_{aq})^3}{(HDEHP_{org})^3} \qquad (3)$$

$$E^{o}_{a} = \frac{(M(DEHP)_{3org})}{(M^{3+}_{aq})} = K_{eq} \cdot \frac{(HDEHP_{org})^3}{(H^{+}_{aq})^3} \qquad (4)$$

Extraction coefficients, E^{o}_{a}, for carrier-free rare earth tracers were found[2] to increase regularly with increasing atomic number. In Figure 1 the apparent equilibrium constants (equation 3) have been calculated from the reported extraction data[2] and plotted vs. atomic number. The factors for separation of adjacent rare earths by a single extraction stage average 2.5.

Experimental

In the present work, it was found that HDEHP is held by columns of aluminum oxide and that a mixture of carrier-free rare earth radiotracers initially absorbed by the top of the column may be separated by elution with dilute HCl.

Figure 2 is an elution curve of carrier-free 11.6 d Nd^{147} and 2.6 y Pm^{147}. An 11 cm x 3 mm column was prepared by evaporating a slurry of aluminum oxide* (coarsely granular, as received), HDEHP (see Appendix), and petroleum ether to dryness and packing dry into a glass tube. One drop of tracer mixture was added to the top of the column, and elution

*Reagent grade ignited Al_2O_3 was found to be resistant to attack by the dilute HCl used in these experiments.

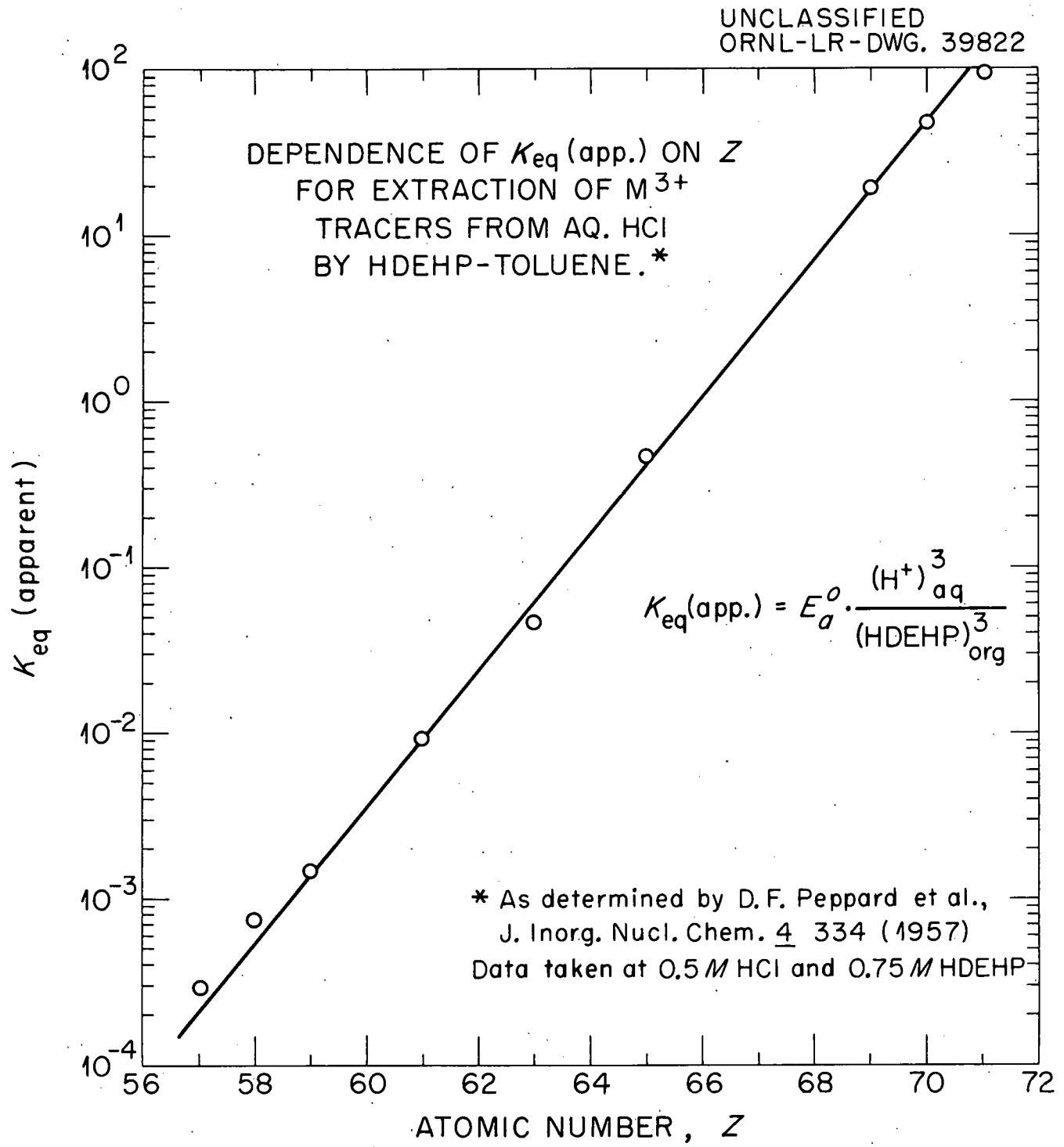
UNCLASSIFIED
ORNL-LR-DWG. 39822
DEPENDENCE OF K_{eq} (app.) ON Z
FOR EXTRACTION OF M^{3+}
TRACERS FROM AQ. HCl
BY HDEHP-TOLUENE.*
K_{eq} (apparent)
10^{2}
10^{1}
10^{0}
10^{-1}
10^{-2}
10^{-3}
10^{-4}
$K_{eq}(app.) = E_a^o \cdot \frac{(H^+)^3_{aq}}{(HDEHP)^3_{org}}$
* As determined by D. F. Peppard et al.,
J. Inorg. Nucl. Chem. 4 334 (1957)
Data taken at 0.5 M HCl and 0.75 M HDEHP
56
58
60
62
64
66
68
70
72
ATOMIC NUMBER, Z

FIGURE 1

6-4

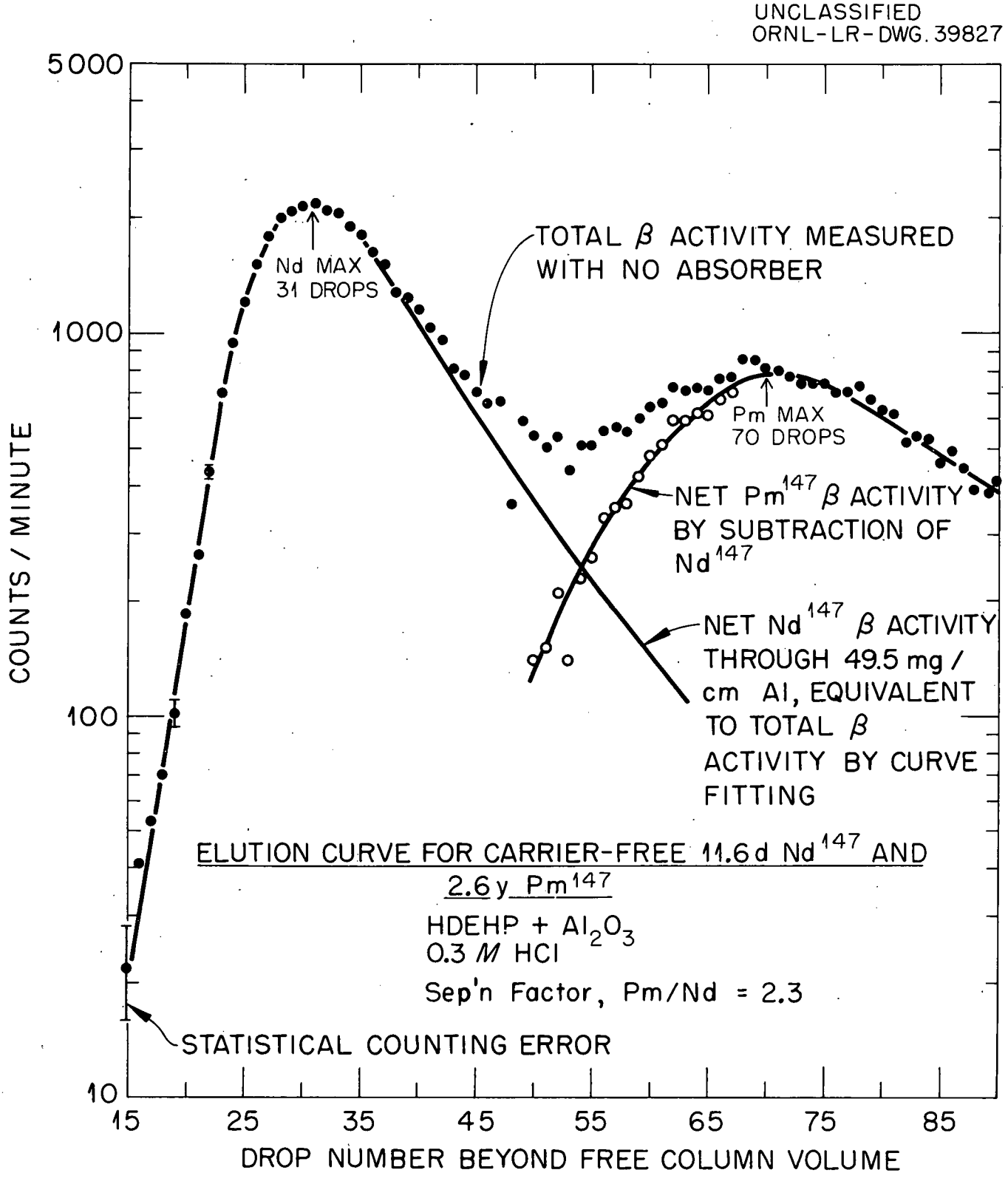
UNCLASSIFIED
ORNL-LR-DWG. 39827
5000
1000
100
10
COUNTS / MINUTE
Nd MAX
31 DROPS
TOTAL β ACTIVITY MEASURED WITH NO ABSORBER
Pm MAX
70 DROPS
NET Pm147 β ACTIVITY BY SUBTRACTION OF Nd147
NET Nd147 β ACTIVITY THROUGH 49.5 mg / cm Al, EQUIVALENT TO TOTAL β ACTIVITY BY CURVE FITTING
ELUTION CURVE FOR CARRIER-FREE 11.6 d Nd147 AND 2.6 y Pm147
HDEHP + Al2O3
0.3 M HCl
Sep'n Factor, Pm/Nd = 2.3
STATISTICAL COUNTING ERROR
15
25
35
45
55
65
75
85
DROP NUMBER BEYOND FREE COLUMN VOLUME

FIGURE 2

6-5

was carried out at room temperature with 0.3 M HCl at a flow rate of ~ 1 ml/cm^2 min (~ 2 drops/min). Drops were collected, evaporated and counted with an end-window G-M counter with and without an aluminum absorber of 49.5 mg/cm^2 (to absorb the weak 0.23 Mev Pm^{147} β radiation). The ratio of drop numbers* for the Pm and Nd maxima indicate a separation factor of 2.3. The full widths at half maximum for these two elution peaks are 44% and 48% respectively.

Figure 3 is an elution curve for the single carrier free tracer 1.7 y Eu^{155}. A 13 cm x 4 mm column was prepared by packing the glass tube with aluminum oxide (ground and sieved to 200-325 mesh) by settling from water suspension, passing an acetone solution of HDEHP through the column, and displacing the acetone by eluting with 0.01 M HCl. The tracer was absorbed by the top of the column and eluted with 0.4 M HCl (presaturated with HDEHP) at a flow rate of 0.15 ml/cm^2/min (~ 2 min/drop). Drops were collected and counted with a well-type scintillation counter. A full width at half maximum of 15% was obtained, although some tailing was observed.

Conclusions

1. A separation factor of 2.3 was obtained for the elution of Pm and Nd carrier-free radiotracers using 0.3 M HCl and an aluminum oxide column treated with HDEHP.

2. Elution peaks as narrow as 15% full width at half maximum may be obtained by careful packing of the aluminum oxide columns.

---

*It was found that drops issuing from the column during elution were constant in size within 10% or less. Therefore, numbers of drops, rather than actual volumes, have been used in comparing elution volumes.

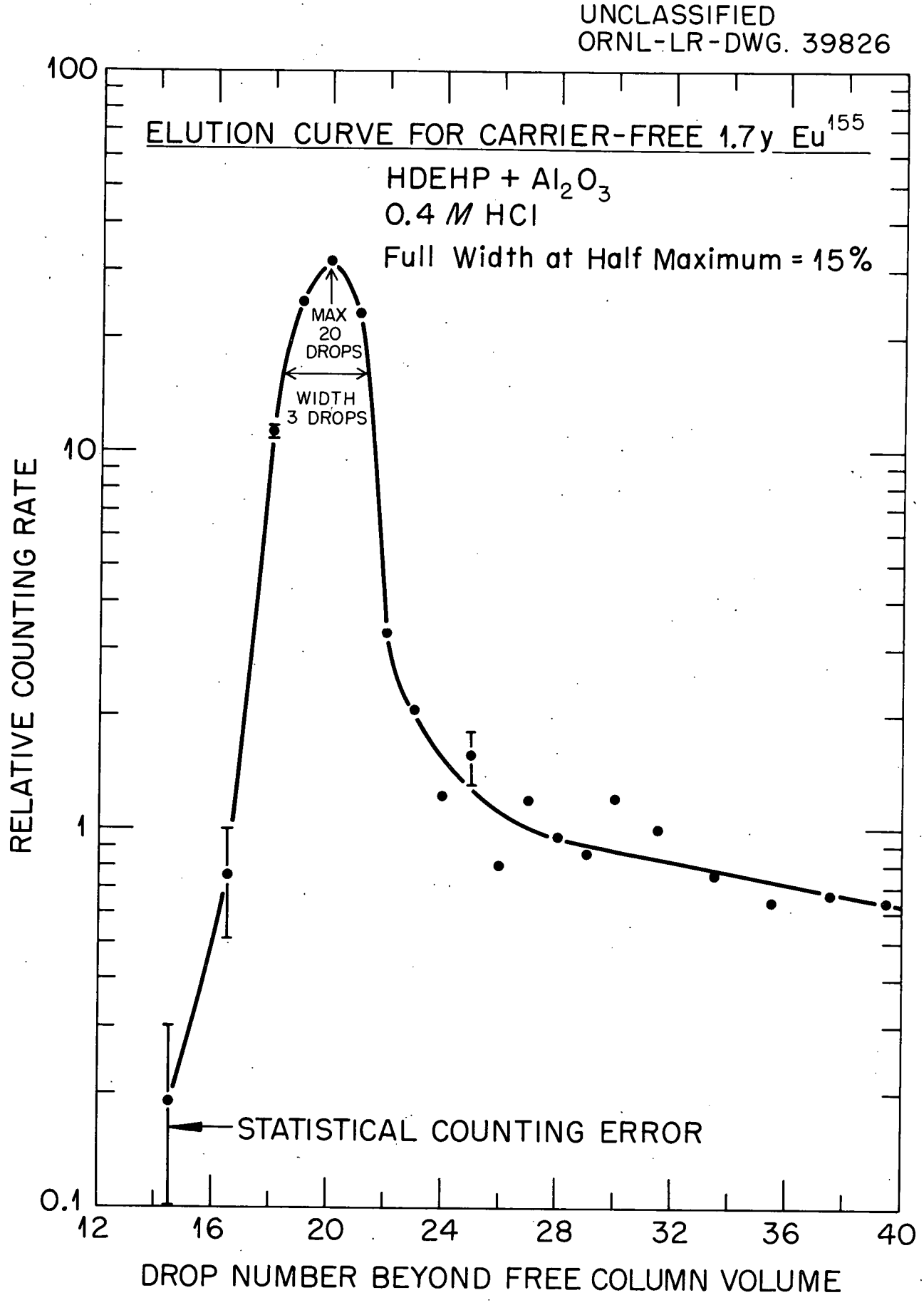
UNCLASSIFIED
ORNL-LR-DWG. 39826
ELUTION CURVE FOR CARRIER-FREE 1.7y Eu155
HDEHP + Al2O3
0.4 M HCl
Full Width at Half Maximum = 15%
MAX 20 DROPS
WIDTH 3 DROPS
STATISTICAL COUNTING ERROR
RELATIVE COUNTING RATE
100
10
1
0.1
12
16
20
24
28
32
36
40
DROP NUMBER BEYOND FREE COLUMN VOLUME

FIGURE 3

6-7

3. Column behavior is quantitatively in agreement with predictions based on solvent extraction behavior of the rare earths in HDEHP - dilute acid systems.

4. The very large separations for adjacent rare earths (about double those attainable by cation exchange resins), the liquid state of the stationary phase, and the property that low atomic number rare earths are eluted most rapidly suggest numerous applications of rare earth chromatography using HDEHP.

Appendix

Note on HDEHP Purification

The separation of rare earths by HDEHP is sensitive to impurities of mono(2-ethylhexyl)orthophosphoric acid and pyrophosphoric acid esters.[2] The HDEHP used in these experiments, synthesized and purified at ORNL, was subjected to additional purification by heating with 6 M HCl at 60°C. for 16 hours, and extracting a petroleum ether solution of the HDEHP five times with ethylene glycol. Titration of the final extraction with NaOH showed $\lesssim$ 0.1% mono(2-ethylhexyl)orthophosphoric acid as an impurity in the HDEHP.

References

1. J. W. Winchester, July 1, 1958, personal communication to M. T. Kelley.
2. D. F. Peppard, G. W. Mason, J. L. Maier, and W. J. Driscoll, J. Inorg. Nucl. Chem. 4, 334 (1957).
3. D. F. Peppard, S. W. Moline and G. W. Mason, Ibid. 4, 344 (1957).
4. D. F. Peppard, J. R. Ferraro and G. W. Mason, Ibid. 4, 371 (1957).
5. D. F. Peppard, G. W. Mason and S. W. Moline, Ibid. 5, 141 (1957).
6. D. F. Peppard, J. R. Ferraro and G. W. Mason, Ibid. 7, 231 (1958).
7. D. F. Peppard, G. W. Mason, W. J. Driscoll and R. J. Sironen, Ibid. 7, 276 (1958).
8. C. A. Blake, Jr., C. F. Baes, Jr., and K. B. Brown, Ind. Eng. Chem. 50, 1763 (1958).
9. C. F. Baes, R. A. Zingaro and C. F. Coleman, J. Phys. Chem. 62, 129 (1958).
10. C. A. Blake, Jr., C. F. Baes, Jr., K. B. Brown, C. F. Coleman, and J. C. White, Int. Conf. on the Peaceful Uses of Atomic Energy, Geneva, 1958, Vol. 28, paper 1550.
11. C. F. Baes, Jr. and H. T. Baker, to be published.

DISTRIBUTION

1. G. E. Boyd
2. M. T. Kelley
3. C. D. Susano
4.- 8. G. W. Leddicotte
9. L. T. Corbin
10. S. A. Reynolds
11. C. F. Baes
12. C. A. Blake
13. K. A. Kraus
14. A. Chetham-Strode
15. J. C. White
16. E. Lamb
17. S. J. Rimshaw
18. R. S. Pressly
19. W. H. Baldwin
20. C. Feldman
21. E. I. Wyatt
22. R. E. Meyer
23. S. Lindenbaum
24. R. A. Strehlow
25. J. A. Marinsky
26. F. L. Moore
27. T. H. Handley
28. J. S. Eldridge
29. J. E. Strain
30.-54. J. W. Winchester
55. O. Menis
56. J. A. Norris
57. P. F. Thomason
58. D. E. LaValle
59. E. J. Murphy
60. M. J. Skinner
61. W. J. Ross
62- 63. Central Research Library
64. Document Reference Section
65- 66. Laboratory Records
67. ORNL-RC