Conf-911107--34

To be presented at the 1991 Winter Meeting of the American Nuclear Society, San Francisco, CA, November 10-14, 1991.

ANL/CP--73634

DE92 001913

New Chromatographic Materials for the Separation and Concentration of Uranium from Environmental Matrices*

E. Philip Horwitz, Mark L. Dietz, Renato Chiarizia, and Herbert Diamond
Chemistry Division, Argonne National Laboratory
Argonne, IL 60439

Introduction/Description of Work

Numerous methods have been described for the determination of uranium in a variety of samples. In many instances, the low concentrations of uranium encountered and the presence of high levels of matrix constituents make a direct determination difficult. Consequently, various separation and preconcentration techniques are frequently employed prior to analysis. Liquid-liquid extraction, for example, has been widely applied. It is, however, too time consuming for routine use on large numbers of samples. Similarly, a number of separation procedures based upon ion exchange have been described. The lack of specificity of ion exchange resins, however, often complicates sample treatment.

Extraction chromatography, in which an inert support is impregnated with an extractant solution to form a chromatographic resin, combines the specificity of extraction with the ease of operation of an ion exchange column, thereby overcoming the principal drawbacks of the two methods. Previous work in this laboratory on the design of selective extractants for use in nuclear fuel reprocessing[1] and in nuclear waste treatment[2] has led to the development of several new phosphorus-based neutral organic extractants. In this report, we examine the use of two of these materials as stationary phases in extraction chromatography for the isolation of uranium from environmental samples.

* Work performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy, under contract number W-31-109-ENG-38.

The submitted manuscript has been authored by a contractor of the U. S. Government under contract No. W-31-109-ENG-38. Accordingly, the U. S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U. S. Government purposes.

MASTER

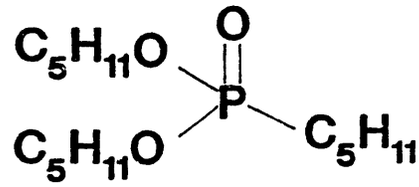
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Results and Discussion

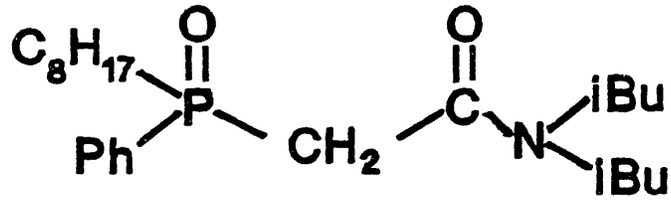
Figure 1 shows the structures of the organic extractants used and the relevant extraction equilibria. (Here, E represents either extractant and the bars denote organic phase species.) The first compound, dipentyl pentylphosphonate, is a liquid and is applied undiluted to the support (Amberchrom CG-71ms). The other, octyl(phenyl)N,N-diisobutylcarbamoylmethylphosphine oxide, requires addition of a suitable solvent, usually tri-n-butyl phosphate, before application.** As indicated by the extraction equation, uranium extraction (and therefore its retention by the resin) is favored by high nitrate ion concentration.

Figure 2 shows the capacity factors (i.e., the number of void volumes of eluent required to reach peak maximum) for each of the chromatographic materials for uranium and several other actinide ions as a function of aqueous nitric acid concentration. As can be seen, U is strongly retained by either resin at nitric acid concentrations of 1-6 M. This strong retention indicates that it should be possible to thoroughly rinse the column to remove matrix constituents following sample loading without appreciable loss of uranium. As shown in Table I, which summarizes the elution behavior of a number of elements commonly encountered in environmental samples, relatively few sample constituents will exhibit significant retention on either the DPPP or CMPO column. Note, however, that the lanthanides are retained on the latter. Note also (Fig. 1) that actinide elements other than uranium are retained to varying degrees on the two columns. These can be removed prior to uranium elution, however, with a small volume of an appropriate water-soluble complexing agent. Uranium can then be eluted with either dilute nitric acid or water (U•TEVA/Spec) or dilute ammonium carbonate (TRU•Spec).

** Both chromatographic materials are now available under the names U•TEVA/Spec and TRU/Spec, respectively, from EIChroM Industries, Inc., Darien, IL.



DP[PP]



CMPO

$$UO_2^{2+} + 2NO_3^- + \overline{2E} \rightleftharpoons \overline{UO_2(NO_3)_2 \cdot E_2}$$

Acid dependency of k' for various ions at 23°C.

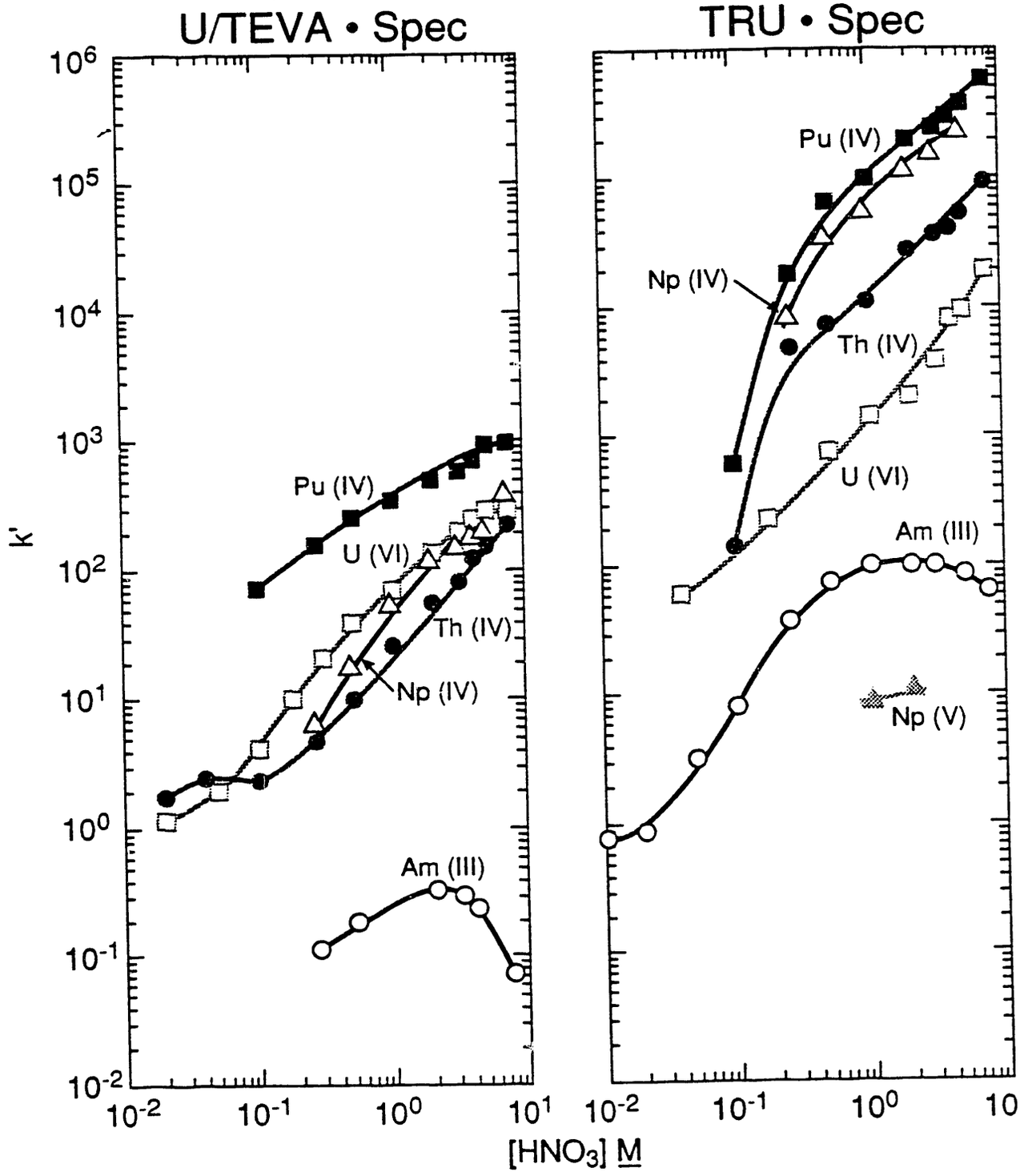


Table 1:
Elution of Selected Elements on a U/TEVA•Spec Column
(fine particles)

Element	Fraction Eluting (%) by number of free column volumes						
	1–5	6–10	11–15	16–20	21–25	26–30	31–40
Li	99.4	–	–	–	–	–	–
Na	95.0	<1.2	–	–	–	–	–
Mg	101	–	–	–	–	–	–
Al	92.0	<5.8	–	–	–	–	–
K	>100	–	–	–	–	–	–
Ca	92.4	<13.3	–	–	–	–	–
Cr	94.7	<3.3	–	–	–	–	–
Mn	96.5	<0.7	–	–	–	–	–
Fe	94.0	<0.3	–	–	–	–	–
Co	99.1	<7.1	–	–	–	–	–
Ni	97.9	<2.0	–	–	–	–	–
Cu	98.1	<2.6	–	–	–	–	–
Zn	96.8	<1.2	–	–	–	–	–
Sr	101	–	–	–	–	–	–
Y	97.9	<2.9	–	–	–	–	–
Zr	56.4	35.7	(1.4)	–	–	–	–
Ru	59.6	<19.2	<19.2	–	–	–	–
Rh	91.7	–	–	–	–	–	–
Ag	103	–	–	–	–	–	–
Cd	96.4	<0.7	–	–	–	–	–
Ba	96.6	<14.4	–	–	–	–	–
La	108	–	–	–	–	–	–
Ce	96.3	<25	–	–	–	–	–
Pr	>100	–	–	–	–	–	–
Nd	99.0	–	–	–	–	–	–
Sm	>100	–	–	–	–	–	–
Eu	>100	–	–	–	–	–	–
Hg	(>100)	(21.4)	–	–	–	–	–
Pb	98.4	<5.8	–	–	–	–	–
U*	–	–	–	–	–	–	>99

* radiometric
1–30 f.c.v. : 2M HNO_3
31–40 f.c.v. : 0.02M HNO_3

Elution of Selected Elements on a TRU•Spec Column
(fine particles)

Element	Fraction Eluting (%) by number of free column volumes						
	1–5	6–10	11–15	16–20	21–25	26–30	31–40
Li	98.4	<19	–	–	–	–	–
Na	92.8	<1.2	–	–	–	–	–
Mg	100	–	–	–	–	–	–
Al	99.8	<2.9	–	–	–	–	–
K	81.8	40.9	–	–	–	–	–
Ca	100	–	–	–	–	–	–
Cr	100	–	–	–	–	–	–
Mn	100	–	–	–	–	–	–
Fe	102	12.3	–	–	–	–	–
Co	100	–	–	–	–	–	–
Ni	100	–	–	–	–	–	–
Cu	100	–	–	–	–	–	–
Zn	100	–	–	–	–	–	–
Sr	100	–	–	–	–	–	–
Y	23.4	76.8	3.5	–	–	–	–
Zr	–	–	–	–	–	–	75.0
Ru	82.6	<19.2	–	–	–	–	–
Rh	100	–	–	–	–	–	–
Ag	100	–	–	–	–	–	–
Cd	100	–	–	–	–	–	–
Ba	100	–	–	–	–	–	–
La	–	–	–	–	–	30.0	72.0
Ce	–	–	–	–	–	<25.0	75.0
Pr	–	–	–	–	–	–	100
Nd	–	–	–	–	–	–	96.0
Sm	–	–	–	–	–	–	100
Eu	–	–	–	–	–	–	>99
Hg	(100)	(60)	(19)	–	–	–	–
Pb	100	–	–	–	–	–	–
Am*	–	–	–	–	–	–	>99

* radiometric
1–30 f.c.v. : 2M HNO_3
31–40 f.c.v. : 0.05M HNO_3

note: Because of uncertainties inherent in the ICP-AES method, the fractions shown for each element may not total to 100%. Values in parentheses are subject to considerable uncertainty and are intended only as a rough guide.

References

1. Mason, G. W.; Griffin, H. E. in Actinide Separations (ACS Symposium Series, Volume 117), J. D. Navratil and W. W. Schulz, eds., American Chemical Society, Washington, DC, 1980.
2. Howitz, E. P.; Kalina, D. G.; Diamond, H.; Vandegrift, G. F.; Schulz, W., Solvent Extr. Ion Exch. 3, 75 1985.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

END

DATE FILMED

12/04/91