EIChroM
EIChroM
EIChroM
EIChroM

Ideas

PUBLISHED BY EICHROM INDUSTRIES, INC.

Volume 4

Issue No. 1

March 1997

As Eichrom's resins have become more popular in the radioanalytical industry, we have promoted their use and acceptance by developing step-by-step methods, holding Users' Seminars regularly throughout the world, and disseminating a bibliography of published papers. Our efforts have resulted in exceptionally broad use of these resins worldwide and a generally intimate working knowledge in most laboratories.

But, as the industry's hands-on experience with our resins has grown, in many cases the specific knowledge of the underlying chemical characteristics of extraction chromatography is sometimes missing. Without this understanding it can be difficult to modify a method for a new sample matrix or troubleshoot the cause of a poor analytical result. To bridge this gap, in our next few issues of *Eichrom Ideas* we will present the basic characterization data for our various resins. This will provide you with a solid understanding of the fundamental properties of our products.

This issue of *Eichrom Ideas* concentrates on Eichrom's TRU Resin — a product that is used in the analysis of actinide elements in a variety of applications including bioassay, environmental and waste sample analysis. And as many of you already know, TRU Resin

simplifies these analyses, reduces the volumes of acid used, and eliminates the need for hazardous organic extractants like DDCP. These distinct benefits have made TRU Resin a standard reagent in the radiochemical analysis of actinides worldwide.

"TRU Resin has become a standard reagent in the radiochemical analysis of actinides worldwide by simplifying analysis, reducing the volumes of acid used, and eliminating the need for hazardous organic extractants like DDCP."

TRU Resin

Eichrom's TRU Resin is an extraction chromatographic material, in which the extractant system is octylphenyl-N,N-di-isobutyl carbamoylphosphine oxide (abbreviated CMPO) dissolved in tri-n-butyl phosphate (TBP). The CMPO molecule is shown in figure 1.

The CMPO/TBP solvent system complexes actinide elements and extracts them out of certain aqueous solutions. Figure 2 shows the uptake of various actinide elements from nitric acid solutions by the TRU Resin. The y-axis, k', is a measure of uptake, corresponding to the number of free column volumes to peak maximum in a chromatographic column. Values higher than 100 indicate strong uptake, values between 1 and 50 indicate weak uptake, and values below 1 indicate no retention on a column.

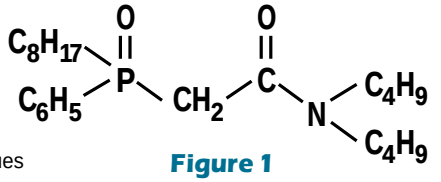

Figure 1

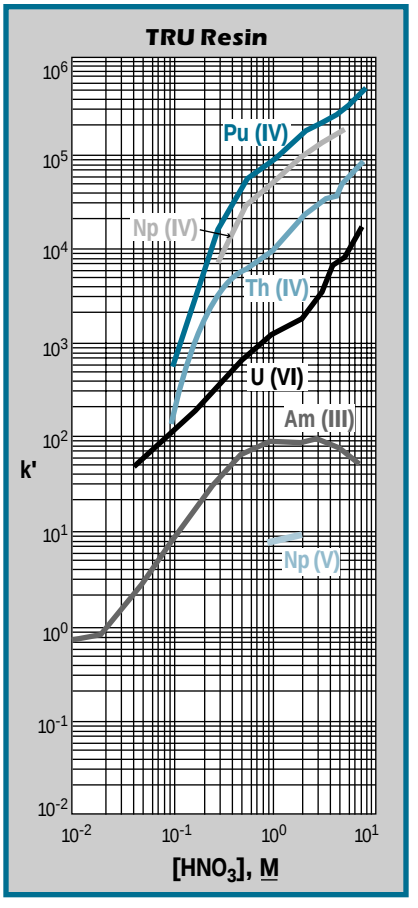

Figure 2: Nitric Acid Dependency of k' for Actinide Ions

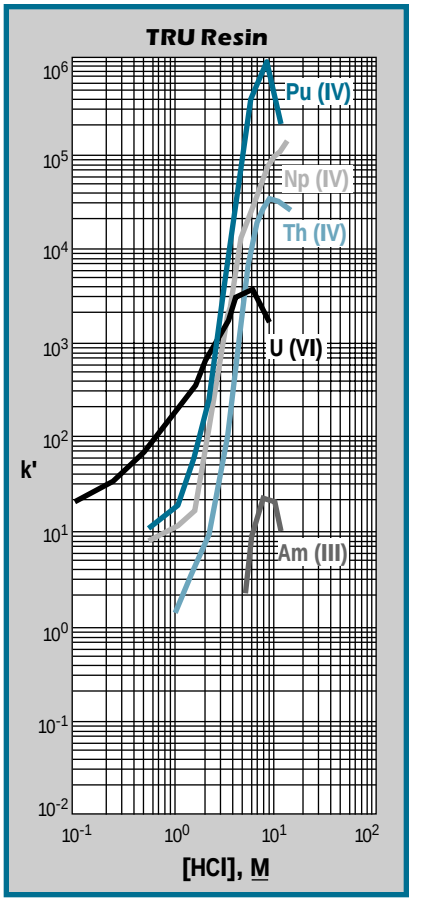

Figure 3: Hydrochloric Acid Dependency of k' for Actinide Ions

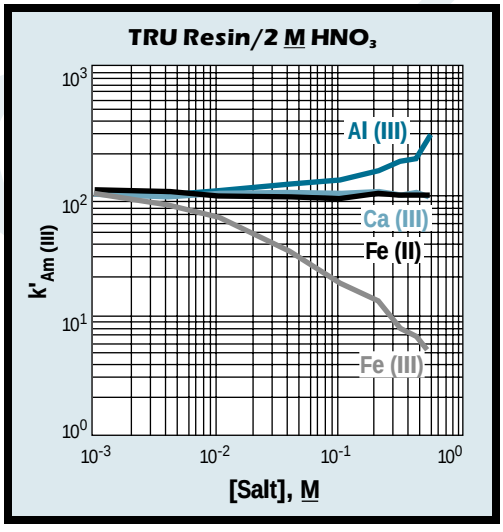

Figure 4: Effect of Matrix Cations on Americium Retention

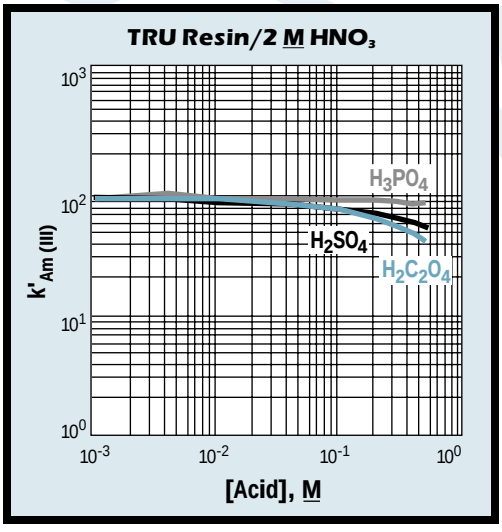

Figure 5: Effect of Matrix Anions on Americium Retention

The tetravalent actinides show extremely high retention on the column, with k' in the range of 10^4–10^6 at nitric acid concentrations in excess of 2M. Hexavalent uranium is approximately one order of magnitude lower. The k' curve for trivalent americium plateaus at about 100 free column volumes in the range of 1–5M nitric acid. It is important to note that pentavalent neptunium exhibits very low retention at any nitrate concentration.

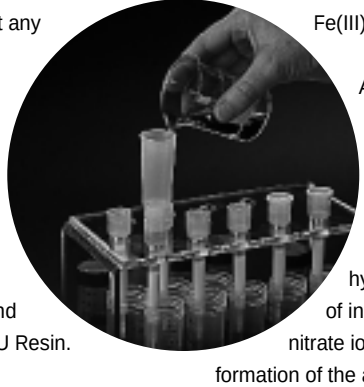

Figure 3 shows the retention behavior of the actinides in HCl. The very low affinity of the column for Am in chloride media forms the basis for the selective stripping of Am (and trivalent plutonium) from TRU Resin.

The data in figures 2 and 3 shows the behavior of the actinide elements without any interference from other ions in solution. Figures 4 through 6 show the effect of a number of matrix components on the uptake of the actinides.

The effect of various cations on the retention volume (k') of americium in 2M nitric acid on the TRU Resin is plotted in figure 4. Among the cations shown, calcium and divalent iron show no effect on americium retention. This is particularly valuable since both calcium and iron are present in large quantities in many environmental and bioassay samples, and are often added as carriers in precipitation steps. Trivalent iron shows a significant, negative effect on Am retention. If it is suspected that iron is present in a sample, a reducing agent such as ascorbic acid should be added to ensure that all Fe(III) is reduced to Fe(II).

Aluminum actually increases the uptake of Am on the TRU Resin column. This happens because the aluminum (III) cation in solution is readily hydrated. The has the effect of increasing the activity of nitrate ions in solutions, driving the formation of the americium nitrato complex which is readily extracted by the CMPO/TBP extractant system.

As shown in figures 5 and 6, the commonly occurring polyatomic anions show no real effect on americium retention on the TRU Resin, but have a dramatic effect on the retention of the tetravalent actinides. While this graph shows only the effects on the retention of neptunium, the behavior of the other tetravalent actinides under the same conditions is analogous. The curve for plutonium is nearly identical to the neptunium curve; that for thorium would be parallel, but approximately one order of magnitude lower.

Fortunately, the retention of neptunium (and the other tetravalent actinides, Th and Pu) is high enough that even relatively large concentrations of sulfate and phosphate do not cause breakthrough of the column for "normal" load and rinse volumes totaling less than 50–75 mL. The effect of oxalate is quite significant for the tetravalent actinides which readily form oxalato complexes that are not extracted by the CMPO/TBP solvent system. Often solutions of oxalate salts are used to strip these actinides efficiently from the TRU Resin.

SOURCE: E. P. Horwitz, R. Chiarizia, M. L. Dietz, H. Diamond, and D. Nelson, "Separation and Preconcentration of Actinides from Acidic Media by Extraction Chromatography," *Analytica Chimica Acta,* 281 (1993) 361–372.

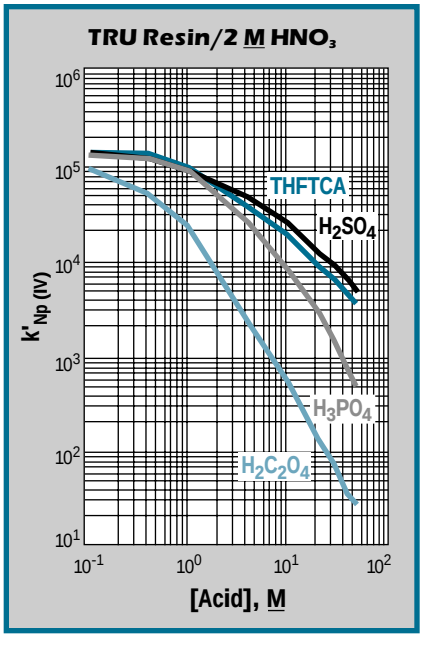

Figure 6: Effect of Matrix Constituents on Neptunium Retention

Frequently Asked QUESTIONS

...About Eichrom TRU Resin

1 What is the purpose of $Al(NO_3)_3$ which is used in many procedures involving TRU Resin?

Aluminum is a good complexing agent for potentially interfering phosphates and fluorides and reduces the negative impact these anions can have on the retention of actinides.

The additional nitrate combined with the salting out effect of the aluminum also enhances the retention of most actinides due to an increase in the overall nitrate activity in solution. This effect is not necessary for tetravalent and hexavalent actinides. The retention of trivalent americium in straight nitric acid is low enough that $Al(NO_3)_3$ can be an important addition to Am load solutions.

2 Does iron interfere with the uptake of actinides on TRU Resin?

Trivalent iron can interfere with the uptake of americium on the TRU Resin. It does not seem to affect the retention of the other actinides to any significant degree. As shown in the first part of table 1 below, the presence of iron reduces the k' (or elution volume) of americium from about 100 in 2M nitric acid to as low as 9.1 for 100 mg Fe/10mL. Table 1 also demonstrates that adding ascorbic acid to reduce ferric, Fe(III), to ferrous, Fe(II), significantly increases the k' of americium.

3 What is the capacity of the TRU Resin?

The experimentally measured capacity of Am on the TRU Resin is 6.8 mg per mL of resin bed or about 14 mg per 2mL pre-packed column. Eichrom recommends a working capacity of 10 to 20% of the total capacity or 1.5–3 mg Am per 2 mL pre-packed column of TRU Resin. The theoretical capacities of tetravalent plutonium and neptunium and hexavalent uranium are approximately 50% higher. In most radioanalytical situations Am, Pu and Np will never exceed the working capacity of the TRU Resin. Capacity may become a limitation if large samples containing high levels of uranium are to be analyzed.

4 Are there other uses for TRU Resin?

A number of laboratories are using TRU Resin in an Fe^{55}/Fe^{59} method. The sample is loaded onto TRU Resin in 8M nitric acid. Iron is selectively stripped with 2M nitric acid.

Table 1: Effect of Fe and Ascorbic Acid on Am Uptake by TRU Resin 2M HNO_3, 23°C

mg Fe/10 mL	molarity of ascorbic acid	k' (americium)
0	-	98
25	-	28
50	-	17
100	-	9.1
25	0.3	88
50	0.3	72
100	0.3	65

Source: Horwitz, et al., "Separation and Preconcentration of Actinides from Acidic Media by Extraction Chromatography," *Analytica Chimica Acta,* 281 (1993) 361–372.

New References in 1996 on Extraction Chromatography with Eichrom Resins. References

Alvarez, A. and Navarro, N.
"Method for Actinides and Sr-90 Determination in Urine Samples." *Applied Radiation & Isotopes.* Vol. 47, No. 9/10, (1996) pp. 869–873. (AL196).

Burnett, W. and Yeh, C.C.
"Separation of Protactinium from Geochemical Materials via Extraction Chromatography." *Radioactivity & Radiochemistry.* 6 (4) (1995) pp. 22–26. (BW395).

Cadieux, J.R. et al.
"Separation and Analysis of Actinides by Extraction Chromatography Coupled with Alpha-Particle Liquid Scintillation Spectrometry." *Radioactivity & Radiochemistry.* 7 (2) (1996) pp. 30–34 (CA196).

Gale, N.H.
"A New Method for Extracting and Purifying Lead from Difficult Matrices for Isotopic Analysis." Accepted for publication in *Analytica Chimica Acta.* 332 (1996) pp. 15–21.

Harduin, J.C. et al.
"Analytical Determination of Actinides in Biological Samples." *Radioprotection.* 31 (1996) 2, pp. 229–245. (HJ196).

Sloof, Joyce E. et al.
"Determination of Lead in Phosphate Ore and Phosphogypsum." *Fresenius' Journal of Analytical Chemistry.* 354 (1996) pp. 16–20. (SJ196).

Uchida, S. and Tagami, K.
"Preconcentration and Purification of Technetium using an Extraction Chromatographic Resin," *Eco-Informa '96,* Poster N-10, 6 November, 1996, Lake Buena Vista, FL, USA

A complete bibliography of papers on Eichrom products is available. Contact Eichrom or your local representative to receive your updated copy.

Upcoming Events...

SPRING 1997

- **Northwest Users' Seminar** ..... Idaho Falls, Idaho
- **Southwest Users' Seminar** ..... Albuquerque, New Mexico
- **East Users' Seminar** ..... Oak Ridge, Tennessee
- **German Users' Meeting** ..... Karlsruhe, Germany

SUMMER 1997

- **French Users' Meeting** ..... To be announced

AUTUMN 1997

- **37th ORNL-DOE Conference on Analytical Chemistry in Energy Technology** ..... Gatlinburg, Tennessee
- **The 43rd Annual Conference on Bioassay, Analytical and Environmental Radiochemistry** ..... Charleston, South Carolina
- **Symposium on "Recent Advances in Metal Ion Separation and Preconcentration" at the 214th ACS National Meeting** ..... Las Vegas, Nevada

If you are interested in receiving additional information on any of these events please check the appropriate box on the fax-back form below or call:

Lynda Gates in the US at: **(800) 422-6693** –or– **(630) 963-0320**
Lesley Robertson in the UK at: **+44 (0) 1337 827 715**

Please help us update our mailing list...

- If corrections to or deletion of your mailing address are required, transfer the peel and stick address label from the front of this newsletter to the form below. Hand write any corrections in the space provided or place an X across the label to indicate deletion from our list and fax the form back to us.
- Or, if you know someone who would like to be on our mailing list, please complete the form with their information and fax it back to us.
- This form can also be used to request information on any of the upcoming events listed above. Our fax numbers are:

North America: (630) 963-1928 Europe: +44 (0) 1337 827 716

Mailing List Update/Event Information Request Form:

Name _____ Title _____

Company _____

Address _____

Place Label Here

City _____ State/Province _____

Country _____ Zip/Postal Code _____

Phone _____ Fax _____ e-mail _____

Please send information on the following events:

☐ Northwest Users' Seminar, Idaho Falls, ID ☐ Southwest Users' Seminar, Albuquerque, NM ☐ East Users' Seminar, Oak Ridge, TN

☐ French Users' Meeting ☐ German User's Meeting, Karlsruhe

Special TRU Resin Issue...

Plus: Frequently Asked Questions • Upcoming Events • New References for 1996

EIChroM INDUSTRIES, INC

Eichrom Industries, Inc.
8205 S. Cass Avenue, Suite 107
Darien, Illinois 60561 U.S.A.

First Class
U.S. Postage
PAID
Permit No. 216
Des Plaines, IL

EIChroM INDUSTRIES, INC

Did You Know...

...The 43rd Annual Conference on Bioassay, Analytical and Environmental Radiochemistry is being hosted by Eichrom Industries, Environmental Physics, Florida State University, Westinghouse Savannah River, and the College of Charleston. This year's meeting will be held November 9-13 in Charleston, SC.

...Eichrom supplies Nickel Resin both as pre-packaged columns and in bulk resin. Columns are available in packages of 50 and 200. Bulk resin is supplied in 25 and 50 gram bottles.

...ASTM has published another method using an Eichrom resin. C1345-96, "Uranium and Thorium in Soils by ICP-MS" uses Eichrom's TRU Resin in the sample preparation steps.

For additional information, contact:

North America

Eichrom Industries, Inc.
8205 S. Cass Ave, Suite 107
Darien, IL 60561

Phone: 630/963-0320
Toll-free: 800/422-6693
Fax: 630/963-0381

Europe

Eichrom Industries, Inc.
P.O. Box 3
Cupar, Fife KY15 7SE
Scotland, U.K.

Phone: +44 (0) 1337 827 715
Fax: +44 (0) 1337 827 716