EICHROM

ideas

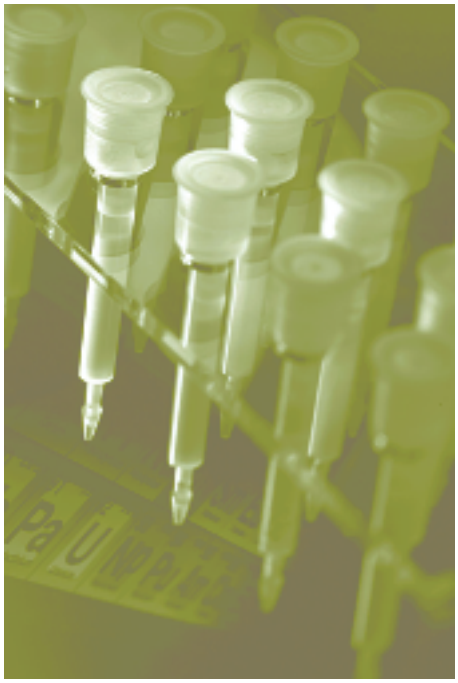
Volume 5

Issue No. 1

April 1998

PUBLISHED BY EICHROM INDUSTRIES, INC.

Two of Eichrom's resins are named to indicate their usefulness in the separation and analysis of lanthanides, or rare earth elements. These are Ln Resin and RE Resin. One question often asked of Eichrom over the years has been what is the difference between the two and what should each be used for.



The answer to that question, and, indeed, to most questions regarding the application of chemical products to specific analytical problems is, "It depends." It depends on many factors including the specific analyte to be measured, the type of matrix involved, and the impurities from which decontamination is needed. In this issue of *Eichrom Ideas* we address these two resin products by describing what is known of their basic characteristics and the situations in which they have been successfully applied. We hope you can use the experience presented here as a guide for determining which of these tools is appropriate for your analytical requirements.

This issue will help provide an answer to the commonly asked question, "What is the difference between Eichrom's Ln Resin and RE Resin?" And it will hopefully provide a guide for determining which is appropriate for your analytical requirements.

ElChroM INDUSTRIES, INC

C A L E N D A R

Upcoming Events...

SPRING 1998

- **Eastern Regional Users' Meeting**
  May 19, 1998 ..... Augusta, Georgia
- **Scandinavian Users' Meeting, English language presentations**
  May 25, 1998 ..... Helsinki, Finland

SUMMER 1998

- **Western Regional Users' Meeting, (in conjunction with the meeting of the American Chemical Society, Richland Section.)**
  June 18, 1998 ..... Pasco, Washington

AUTUMN 1998

- **French Users' Meeting, French/English simultaneous translation to be provided.**
  Date to be determined ..... To be announced

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:

Terra Collier in the US at: **(800) 422-6693** –or– **(630) 963-0320**
Lesley Robertson in Europe at: **+33 (01) 53 34 17 24**
From the UK, dial: **(01337) 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: +33 (01) 47 70 36 88

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 indicate your language preference: ☐ English ☐ French ☐ German

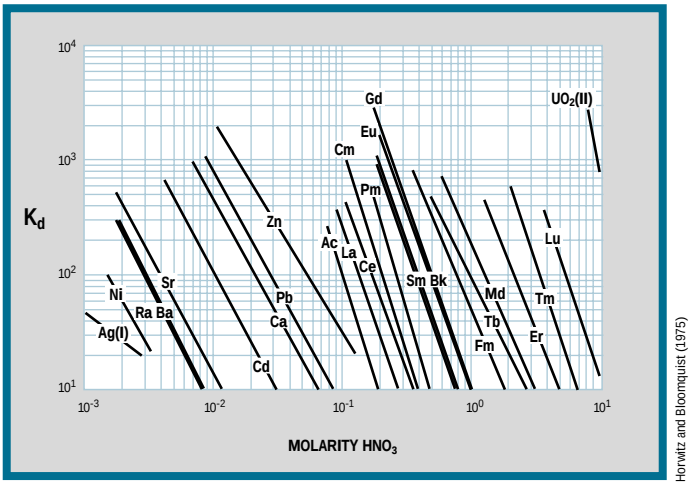
Please send information on the following events:

☐ Eastern Regional Users' Meeting, Augusta, GA
☐ Western Regional Users' Meeting, Pasco, WA
☐ Scandinavian Users' Meeting, Helsinki, Finland
☐ French Users' Meeting

Ln Resin

Ln Resin, like most of Eichrom's products, grew out of the transformation of a selective organic extractant into an extraction chromatographic resin. The extractant used in Ln Resin is di(2-ethylhexyl) orthophosphoric acid (HDEHP). References to HDEHP in a chromatographic system date back more than thirty years. A number of these references are shown in the bibliography section of this issue.

Early work by Horwitz et al. (1975)[1], provided distribution coefficients (K_d) versus nitric acid for various metal ions using HDEHP on a hydrophobic support. This data is reproduced in figure 1 and has been used as the starting point for a number of radiochemical separations in use today. Note that for Eichrom's Ln Resin, K_d can be converted into k' (an approximation of free column volumes to peak maximum) by dividing by 4.33. The application of Ln Resin in methods for the analysis of radium, neodymium, promethium and samarium are discussed in this article. As the data in figure 1 might indicate, many more analytical applications are possible and may already be operational.



Horwitz and Bloomquist (1975)

Figure 1: Chemical Separations Using HDEHP Resin

Bill Burnett et al.(1995)[2] provided an excellent reference for the determination of ^{228}Ra using Ln Resin. Although this reference also demonstrates that Eichrom's TRU Resin can be used to separate ^{228}Ra from its direct beta particle-emitting daughter, ^{228}Ac, Ln Resin may find favor with regulators as it relies on the same HDEHP extractant used in EPA Method RA-05-1 (EPA Procedures Manual 520/5-84-006) without the generation of mixed organic waste. An outline of Bill Burnett's method is provided as figure 2. After a barium sulfate precipitation and conversion to barium carbonate, the sample is loaded in 10 mL 0.095M HNO_3 onto a prepackaged Ln Resin column (0.7 g). The column is rinsed with 15 mL of the same nitric acid to remove alkali earths, lead and some other interference. Finally 10 mL of 0.35M HNO_3 is used to quantitatively elute actinium. A source can then be prepared for gas flow proportional counting. For routine work a minimum detectable activity (MDA) of <1.0 pCi/L may be obtained for a 2-L sample with 80% barium recovery with less than a 30 minute count. This method is able to reproduce the EPA's EMSL results for a number of Ra-228 samples at the 95% (2σ) confidence interval.

Ln Resin is also useful in the analysis of Pm-147[3,4,5]. A 0.5–2 L water sample can be concentrated by a $CaHPO_4$ scavenge or by evaporation. The resulting sample is dissolved in 0.2M HNO_3 with ascorbic acid. The ascorbic acid reduces any Fe(III) to Fe(II). A test with 55 mg Fe(II) in solution resulted in no breakthrough of Pm after 35 mL of 0.2M HNO_3. A typical procedure would use a total of 18–20 mL to load and rinse a standard prepackaged Ln Resin column. Potentially interfering americium is rinsed through the column along with strontium. Promethium is retained along with bismuth, yttrium and the potential tracers samarium or gadolinium. The promethium along with any samarium or gadolinium tracer is eluted with 5 mL of 1M HNO_3. Corrected recoveries of Pm-147 were >88% using Gd-148 as a yield monitor in one reported test. Excellent decontamination were achieved from Co-60, Cs-134,137 and Sr-89,90. One other potential interference is Ce-144, a beta and gamma emitter. A check with gamma spectroscopy could be used to eliminate this as a potential false positive.

Christian Pin et al. (1996)[6] recently reported a method for the sequential separation of Sm, Nd, Th and U in silicate rocks. The method uses

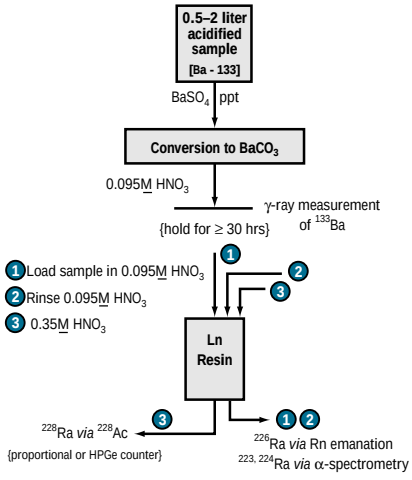


Figure 2: Radium Method Flow Chart

Source: Burnett & Cable (1995).

Eichrom's TRU Resin in series with Ln Resin. For samples high in iron, such as basaltic samples, a 50WX4 strong acid cation exchange column (available from Eichrom) is used up front. After dissolution and possible treatment with cation exchange resin, the sample is loaded onto a TRU Resin column in 1M HNO_3. Unwanted cations are eluted with rinses of the same acid. The light rare earth elements (LREE) can then be stripped with 0.05M HNO_3. This fraction from the TRU Resin column can be loaded directly onto an Ln Resin column to sorb the LREE. The Pin work used a 0.3 gram Ln Resin column of our S-grade 50–100 micron bulk resin. Figure 3 shows the

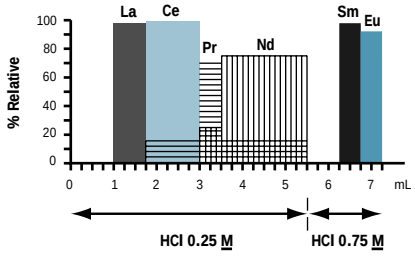


Figure 3: Neodymium and Samarium Elution on a 300 mg Ln Resin S-grade Column

Source: Pin et al. (1996).

elution of La, Ce, Pr, Nd, Sm and Eu. A total of 5.5 mL of 0.25M HCl was used to strip the La, Ce, Pr and Nd with no detectable Sm (ID-TIMS). Then after passing 0.75 mL of 0.75M HCl, Sm appeared in the next 0.5 mL. Finally Eu was collected in the next 0.5 mL of 0.75M HCl. Comparison with 15 international standard reference materials of silicate rocks showed good agreement. Element concentrations were at the mg/g to µg/g level.

Research continues on the use of Ln resin. An investigation of our fine particle size 20–50 micron Ln Resin is being undertaken by a number of researchers to improve the peak resolution of various metals. Interest in separation of Cm(III) and Cf (III) has also recently been expressed with the work of Horwitz (1969)[7] providing an excellent starting point. We hope to report references to many more metal separations in the future.

RE Resin

Eichrom's RE Resin is an extraction chromatographic material which consists of 1M octyl(phenyl)-N,N-diisobutylcarbamoyl-methylphosphine oxide (abbreviated as CMPO) in tributyl phosphate(TBP) coated on an inert polymeric support. The CMPO molecule is shown in figure 4.

RE Resin is a favorable tool for the group separation of rare earth elements and has been used in conjunction with geological dating and radionuclide transport studies. Due to the high retention of yttrium on RE Resin it has also been applied to the purification of yttrium (Y^{90}) used in cancer therapy.

The RE Resin is analogous to Eichrom's TRU Resin. Both are composed of the same extractant system (CMPO/TBP), but the concentration of CMPO is higher in the RE Resin. This increases its affinity for rare earth elements and yttrium out of acidic solutions. Figures 5 and 6 compare the uptake of selected lanthanide elements on the two resins. It can be seen that the uptake of these elements is typically twice as high on RE Resin as on TRU Resin.

Figures 7 and 8 show plots of k' vs. nitric acid for all of the lanthanide elements, as reported by Huff and Huff[8]. Note that for all the lanthanide elements, k' increases with increasing nitric acid up to 4M. At higher acid concentrations, k' increases for the heavier lanthanides, but falls off for the lighter lanthanides. Considering that values higher than 100 indicate a strong uptake, RE Resin is suitable to achieve a group separation of the rare earth elements out of 8M nitric acid. At 1M nitric acid, the k' value for Eu and lighter rare earth elements are greater than 100 (with the exception of La, $k' \approx 90$), while the k' value for the heavier rare earths (Gd and above) are less than 100. This data may be exploited to develop a separation of light and heavy rare earths on RE Resin.

Table 1 indicates that elements which are commonly present in environmental samples do not interfere with the uptake of the lanthanides.

Table 1: Elution Behavior of Selected Elements on RE Resin
[Portion eluting (%) in each fraction]

	2M HNO_3					
Element	**1**	**2**	**3**	**4**	**5**	**6–8**
Na	74.3	27.8	–	–	–	–
Mg	78.5	28.3	–	–	–	–
Al	79.4	26.8	–	–	–	–
K	81.8	27.3	–	–	–	–
Ca	75.3	33.7	–	–	–	–
Fe	<0.5	53.4	44.9	2.2	<1.1	–
Y	–	–	–	3.8	20.8	67.5

Fractions 1–6 correspond to 1.8 free column volume (FCV) each and fractions 7 and 8 correspond to 3.6 FCV each. Source: Huff & Huff (1993).

Figure 5: Acid Dependency of k' for Selected Lanthanide Elements on TRU Resin

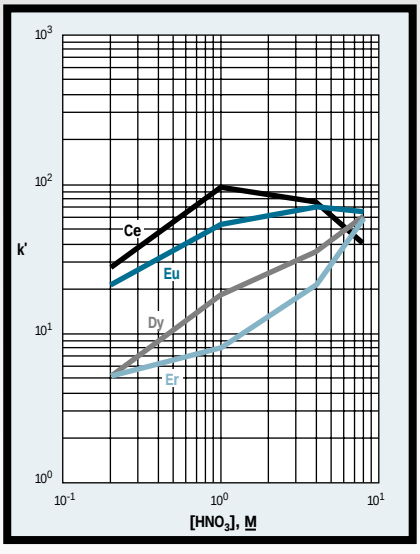
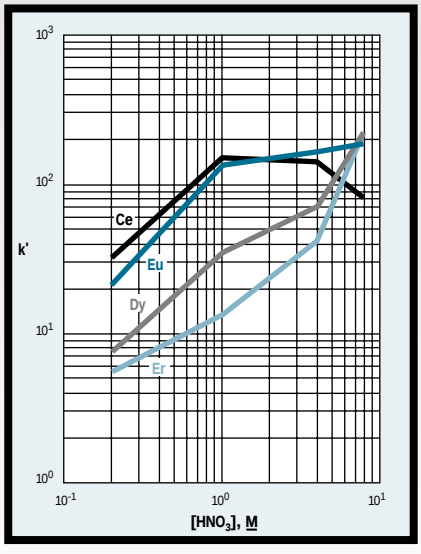


Figure 6: Acid Dependency of k' for Selected Lanthanide Elements on RE Resin



Source: Data reported by Huff & Huff as k_d was converted to k' and is plotted in Figures 5, 6, 7 and 8.

n

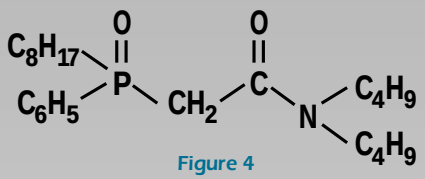


Figure 4

Esser et al. (1994)[9] developed a method for measuring rare earth elements in environmental water samples. They observed breakthrough of the heavier lanthanides during load/rinse steps when the nitric acid concentration was in the 2–4N range. At 6N no breakthrough of any lanthanides was observed. This demonstrates the acid dependency of the heavy lanthanides shown in figure 8.

Experiments conducted by Huff & Huff show that only Zr, Th and U are retained on RE Resin over the whole nitric acid range. These researchers did not evaluate the retention of other actinide elements, but, by extension from known data on TRU Resin, it is expected that all the actinides would show strong retention at 1M and higher nitric acid.

Dietz and Horwitz (1992)[10] investigated the use of RE Resin in the production of ^{90}Y for medical application. In this application, the radiation stability of the resin is quite important because of the high activities loaded onto the column. RE Resin was exposed to increasing doses of absorbed radiation and the k' for americium from low and high acid concentrations was measured. The data presented in Table 2 indicates that the RE Resin was unaffected by the radiation exposure.

This article has summarized the more pertinent information currently available on the characteristics and use of Eichrom's Ln and RE Resins. Complete references are shown in the bibliography section of this issue. Please refer to the complete text for more details.

Table 2: Effect of Radiolysis on the Uptake of Americium by RE Resin

Absorbed Dose (Gy)	k' 0.05M HNO_3	k' 2M HNO_3
0	4.53	155
36,000	3.42	141
72,000	3.44	143
144,000	4.09	139
288,000	5.11	137

Source: Dietz & Horwitz (1992).

Figure 7: Acid Dependency of k' for the Light Lanthanide Elements on RE Resin

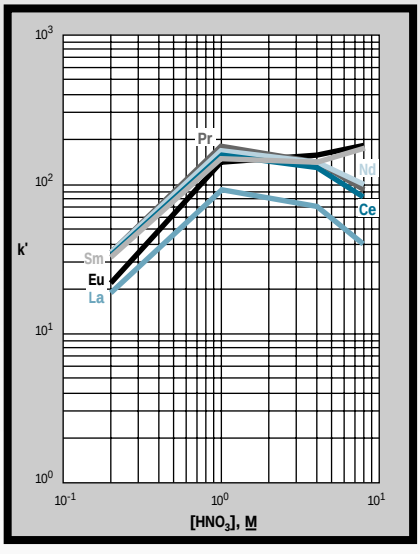
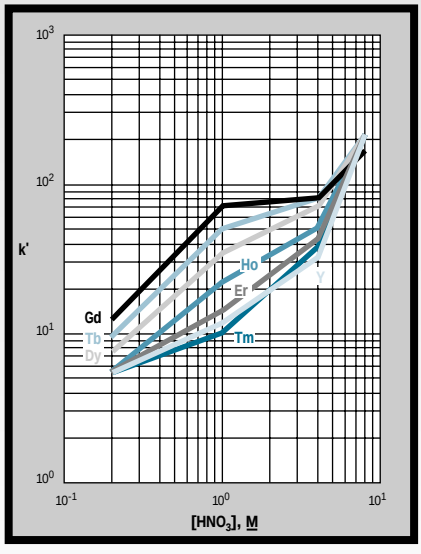


Figure 8: Acid Dependency of k' for the Heavy Lanthanide Elements and Yttrium on RE Resin



Values in figure 8 for Tb, Dy, Ho, Er, Tm and Y at 8M HNO_3 were reported as >215.

References

Selected Papers Highlighting Eichrom's Ln and RE Resins...

Ln Resin

[1]Horwitz E.P. et al. "Chemical Separations for Super-Heavy Element Searches in Irradiated Uranium Targets." *Inorganic & Nuclear Chemistry*. 37 (1975) 425–434. (HP175).

[2]Burnett, W. & Cable, Peter. "Determination of Radium-228 in Natural Waters Using Extraction Chromatographic Resins." *Radioactivity & Radiochemistry*. Vol. 6, No. 3 (1995) 36–44 (BW295).

[3]Burnett, W. et al. "Pm/Sm Separation via Ln Resin." *Eichrom 1996 Cincinnati Users' Seminar*. Cincinnati, OH. August, 1996. (BW296).

[4]Cable, Peter et al. "Analysis of Promethium in Aqueous Samples" *43rd Annual Conference on Bioassay, Analytical and Environmental Radiochemistry*. Charleston, SC. November, 1997.

[5]Sigg, R.A. et al. "Promethium Separation Using Eichrom Ln Resin" *43rd Annual Conference on Bioassay, Analytical and Environmental Radiochemistry*. Charleston, SC. November, 1997.

[6]Pin, Christian et al. "Sequential Separation of Rare-earth Elements, Thorium and Uranium by Miniaturized Extraction Chromatography: Application to Isotopic Analyses of Silicate Rocks." *Analytica Chimica Acta*. 339 (1996) 79–89. (PC196).

[7]Horwitz, E.P. et al. "The Extraction Chromatography of Americium, Curium, Berkelium and Californium with Di(2-Ethylhexyl)Orthophosphoric Acid." *J. Inorganic & Nuclear Chem.* 31, (1969) 3255–3271. (HP169).

RE Resin

[8]Huff, E.A. and Huff D.R. "TRU•Spec and RE• Spec Chromatography: Basic Studies and Applications." *34th ORNL/DOE Conference On Analytical Chemistry In Energy Technology*. Gatlinburg TN. October 1993 (HD193).

[9]Esser, B.K. et al. "Preconcentration and Purification of Rare Earth Elements in Natural Waters Using Silica-Immobilized 8-Hydroxyquinoline and a Supported Organophosphorus Extractant." *Analytical Chemistry*, 66 (1994), 1736-1742 (EB194).

[10]Dietz, M. and Horwitz, E.P. "Improved Chemistry for the Production of Yttrium-90 for Medical Applications." *Applied Radiation and Isotopes*, 43 (1992) 1093 (DM192).

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. 445
Northbrook, IL
60062

EIChroM
INDUSTRIES, INC

For additional information, contact:

North America

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

Phone: 630/963-0320
Toll-free: 800/422-6693
Fax: 630/963-1928
Web: www.eichrom.com
E-mail: info@eichrom.com

Europe

Eichrom Europe, S.A.R.L.
50, rue de Paradis
75010 Paris FRANCE

Phone: (01) 53.34.17.24
Fax: (01) 47.70.36.88
E-mail: milanger@aol.com

From the U.K.

Phone: (01337) 827 715
Fax: (01337) 827 716

Announcements

See Eichrom at the following radiochemistry conferences in 1998:

Vortragstagung, GDCh-Fachgruppe Nuklearchemie, September 7–9, Dresden, Germany. (Conference language: German) For more information contact: tel: +49 69 7917 360, fax: +49 69 7917 475, e-mail: tg@gdch.de

Seventh International Conference on "Low Level Measurements of Actinides and Long-lived Radionuclides in Biological and Environmental Samples," September 21–25, Salt Lake City, UT, USA. For more information contact: Dr. N. P. Singh, tel: 801-278-6769, e-mail: kayenta@digitalpla.net

Eighth International Symposium on Environmental Radiochemical Analysis, September 23–25, Blackpool, UK. For more information contact: Dr. Peter Warwick, tel: +44 (1509) 222 585, fax: +44 (1509) 223 925, e-mail: p.warwick@lboro.ac.uk

Fachverband für Strahlenschutz 30, September 28–October 2, Jahrestagung, Lindau, Germany. (Conference language: German) For more information contact: Frau Ulla Schrödel, tel: +49 (8931) 87 30 30, fax: +49 (8931) 87 33 62, e-mail: schroedel@gss.de

International Symposium on Marine Pollution, October 5–9, Monaco. For more information contact the IAEA Marine Environmental Laboratory: tel: +377 92 05 22 22, fax: +377 92 05 77 44, e-mail: mel@unice.fr

International Workshop on the Application of Extraction Chromatography to Radionuclide Measurements, November 9–10, Geel, Belgium. For more information contact: Michael Bickel, tel: +32 14.57.12.53, fax: +32 14.58.42.73

44th Annual Radiochemistry Conference (Bioassay Conference), November 15–19, Albuquerque, NM, USA. For more information contact: Dr. Chuan-Fu Wu, tel: 505-234-8384, fax: 505-885-4562, e-mail: wuc@wipp.carlsbad.nm.us