



PNNL-16775

Prepared for the U.S. Department of Energy  
under Contract DE-AC05-76RL01830

# Separation of Lanthanide Ions with Klaui Ligand Resin

TD Granger  
VA Henry  
SL Latesky

July 20, 2007



**Pacific Northwest**  
NATIONAL LABORATORY

*Proudly Operated by **Battelle** Since 1965*





## 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 Battelle Memorial Institute, 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, or Battelle Memorial Institute. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

PACIFIC NORTHWEST NATIONAL LABORATORY

*operated by*

BATTELLE

*for the*

UNITED STATES DEPARTMENT OF ENERGY

*under Contract DE-AC05-76RL01830*

Printed in the United States of America

Available to DOE and DOE contractors from the  
Office of Scientific and Technical Information,  
P.O. Box 62, Oak Ridge, TN 37831-0062;  
ph: (865) 576-8401  
fax: (865) 576-5728  
email: [reports@adonis.osti.gov](mailto:reports@adonis.osti.gov)

Available to the public from the National Technical Information Service,  
U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161  
ph: (800) 553-6847  
fax: (703) 605-6900  
email: [orders@ntis.fedworld.gov](mailto:orders@ntis.fedworld.gov)  
online ordering: <http://www.ntis.gov/ordering.htm>



This document was printed on recycled paper.

(9/2003)

## Separation of Lanthanide Ions with Kläui Ligand Resin

Trinity D. Granger

Victoria A. Henry

Dr. Stanley L. Latesky

Office of Science, FAST Program

University of the Virgin Islands

Pacific Northwest National Laboratory

Richland, Washington

July 20, 2007

Prepared in partial fulfillment of the requirements of the Office of Science, U.S.

Department of Energy and the National Science Foundation Faculty and Student Team

(NSF-FAST) and under the direction of Gregg J. Lumetta in the Radiochemical

Processing Laboratory at Pacific Northwest National Laboratory

Participant: \_\_\_\_\_

Participant: \_\_\_\_\_

Participant: \_\_\_\_\_

Research Advisor: \_\_\_\_\_

## **Table of Contents**

Abstract	3
Introduction	5
Materials and Methods	6
Results	7
Discussion and Conclusions	9
Acknowledgements	11
References	11

## ABSTRACT

Separation of Lanthanide Ions with Kläui. TRINITY GRANGER, VICTORIA HENRY, and STANLEY LATESKY (University of the Virgin Islands, 2 John Brewer's Bay, St. Thomas VI 00802) GREGG LUMETTA (Pacific North West National Laboratory, Richland WA 99352)

Separation and pre-concentration of the desired analyte is often a critical step in many radioanalytical methods. Current procedures for separating and concentrating analytes for detection are complex, and can be both expensive and time consuming. Therefore, the purpose of this research is to develop an alternative method of separating lanthanide ions through the use of an extraction chromatography resin containing a Kläui ligand salt. This research is a continuation of a concerted effort to develop new methods of detecting small concentrations of radionuclides and lanthanides using Kläui ligands. The Kläui ligands,  $C_5Me_5Co(OP(OR)_2)_3^-$  ( $R=Me, Et, n-Pr$ ) ( $L_{OR}^-$ ), have unique affinity for lanthanide and actinide ions in the presence of competing metal ions. The use of 1 wt%  $NaL_{OR}$  ( $R=Et$  or  $n-Pr$ ) adsorbed onto resin support has been shown to extract lanthanide ions from aqueous nitric acid solutions of different concentrations. In order to further evaluate the utility of these materials in radiochemical separation, the selectivity of the resins for the different lanthanide ions was examined by measuring the distribution coefficients ( $K_d$ ) for a series of lanthanides over a range of solution conditions. Based on prior research with actinide ions, it was hypothesized that the lanthanide ions would bond strongly with the Kläui ligands. The success of this research is important, because it will assist in expanding and improving current automated radiochemical methods, which will decrease the cost of developing and implementing radiochemical methods. To date,  $K_d$

values have been determined for  $\text{Eu}^{+3}$ ,  $\text{Nd}^{+3}$  and  $\text{Pr}^{+3}$  under varying nitric acid ( $\text{HNO}_3$ ) concentration, using a resin consisting of 1.0 wt%  $\text{NaL}_{\text{OPr}}$  on Amberlite XAD-7HP. The dependence of the  $K_d$  values for  $\text{Eu}^{+3}$  has also been examined as a function of the ligand-to-europium ratio and the nitrate concentration. Decreasing  $K_d$  values were obtained upon increasing the nitric acid concentration, indicating protonation of the ligand, which competes with binding of the lanthanide ions. As expected, increasing the Kläui ligand-to-europium ratio results in increasing  $K_d$ , but no conclusions could be made from these data regarding stoichiometry of the complex formed on the resin. No dependence of the  $K_d$  on the nitrate concentration was observed, supporting the notion that the  $\text{HNO}_3$  dependence is dominated by the presence of the acidic hydronium ion (as opposed to the nitrate ion). Future work will involve the determination of the  $K_d$  values for the remainder of the lanthanide series to further assess the potential of the Kläui ligand for intra-group lanthanide separations.



## INTRODUCTION

Separation and pre-concentration of a desired analyte is often a critical step in many radioanalytical methods. Traditional wet radiochemical separation methods such as precipitation, ion exchange, and liquid-liquid extraction are time consuming and labor intensive. Recent advances in separations technology such as extraction chromatography offer the possibility to automate radiochemical separations, which would lead to greater efficiency and throughput in performing analyses for radioactive isotopes. The purpose of this research is to explore the use of Kläui ligands,  $C_5Me_5Co(OP(OR)_2)_3^-$  ( $R=Me, Et, i-Pr, n-Pr$ ) ( $L_{OR}^-$ ), in separating lanthanide ions from bulk matrix components (e.g., Al, Ca, Fe, etc.) and from one another. For this purpose the Kläui ligand was deployed as an extraction chromatography resin containing 1.0 wt%  $NaL_{OPr}$  sorbed onto Amberlite XAD-7HP. In previous research, this resin had been investigated for use in the separation of actinide ions. Hence, it is hypothesized that the ligand will have similar affinity for the trivalent lanthanide ions. This work was initiated to determine the relative affinity of the Kläui ligand resin for the lanthanide ions across the lanthanide series to assess the utility of the resin for separating these ions from one another, which is a generally a difficult task.

The experiments performed involved determining the batch distribution coefficients for lanthanide ions as the nitric acid concentration was varied, as the ligand-to-metal ratio was varied, or as the nitrate concentration was varied. Distribution coefficients are a quantitative expression of how much of the metal ion is absorbed onto the resin at equilibrium, and thus can be used to assess the potential of the resin in separating the metal ion of interest. Gamma spectroscopy and inductively coupled

plasma optical emission spectroscopy was used to track the distribution of the lanthanide ions between the liquid and resin phases. Gamma spectroscopy was used for solutions traced with the radioactive isotope  $^{155}\text{Eu}$ . The data were obtained in terms of the number of gamma emission events observed per minute (counts per minute). The count rates measured before and after contact with the resin were used to determine the distribution coefficients for Eu. Inductively coupled plasma optical emission spectroscopy, on the other hand, is a process that uses light that atoms in the plasma emit. The light emitted has different wavelengths unique to each element, which can be used to quantify how much of the element is present in solution.

## **MATERIALS AND METHODS**

Nitric acid solutions of the various lanthanum nitrate salts were contacted with either the blank resin (Amberlite XAD-7HP) or the Kläui ligand resin. The three lanthanum ion salts used were  $\text{Eu}^{+3}$ ,  $\text{Nd}^{+3}$  and  $\text{Pr}^{+3}$ . Solutions of different concentrations of nitric acid (e.g. 0.1, 0.5, 1.0, 2.5, and 5.0 molar) were prepared by diluting a 10 molar stock solution with deionized water. Normally, 50 mg of the blank resin or the Kläui resin was used; however, in one experiment when the concentration of nitric acid remained constant, the resin varied from approximately 20, 50, 100, 150, 200, and 250 mg.

A total of sixteen experiments were executed under varying conditions in order to find out which method separated the lanthanide ions most efficiently. The solutions that contained  $\text{Eu}^{+3}$  were executed slightly differently from those that contained  $\text{Nd}^{+3}$  and  $\text{Pr}^{+3}$  in that the solutions were spiked with the radioactive tracer  $^{155}\text{Eu}$ . The solutions were

contacted with the resin by mixing on a reciprocating shaker set on the oscillating mode for at least 20 hours. Samples of the solutions were taken before and after contact with the resin and analyzed by either gamma spectroscopy (for  $^{155}\text{Eu}$ ) or ICP-OES (for Nd and Pr). The  $K_d$  values were calculated using the equation  $K_d = \frac{C_i - C_f}{C_f} \times \frac{V}{M}$ , where  $C_i$  represents the initial concentration of the lanthanide ion solution,  $C_f$  the final concentration after contact with the resin,  $V$  represents the volume of the solution placed in the gamma counter, and  $M$  represents the mass of the resin. As mentioned in the introduction, the  $K_d$  values are a quantitative measure for the amount of ion absorbed.

## RESULTS

The relative affinity of the XAD-7HP resin containing 1%  $\text{NaL}_{\text{OPr}}$  for  $\text{Pr}^{+3}$ ,  $\text{Nd}^{+3}$ , and  $\text{Eu}^{+3}$  was examined by measuring the batch distribution coefficients ( $K_d$ ) for each of the ions as a function of nitric acid concentration. Table 1 and Figure 1 present the data from this experiment. No sorption of  $\text{Pr}^{+3}$ ,  $\text{Nd}^{+3}$ , and  $\text{Eu}^{+3}$  was detected for the blank XAD-7HP resin. According to the data collected in Table 1, as the nitric acid concentration increased the  $K_d$  values decreased, refer to Figure 1. The results are consistent with the results for  $\text{Eu}^{+3}$  previously measured at PNNL (Table 2), giving confidence in the experimental techniques use in this work.

Table1: Log  $K_d$  vs.  $[\text{HNO}_3]$  for  $\text{Pr}^{+3}$ ,  $\text{Nd}^{+3}$ , and  $\text{Eu}^{+3}$

$[\text{HNO}_3]$	Log $K_d$ of $\text{Nd}^{+3}$	Log $K_d$ of $\text{Pr}^{+3}$	Log $K_d$ of $\text{Eu}^{+3}$
0.1	2.97	2.52	4.29
0.25	2.45	2.12	
0.50	1.61	1.67	2.18
0.75	1.32	1.17	
1.00	0.91	0.76	1.40

Figure 1: Log  $K_d$  vs.  $[\text{HNO}_3]$  for  $\text{Pr}^{+3}$ ,  $\text{Nd}^{+3}$ , and  $\text{Eu}^{+3}$

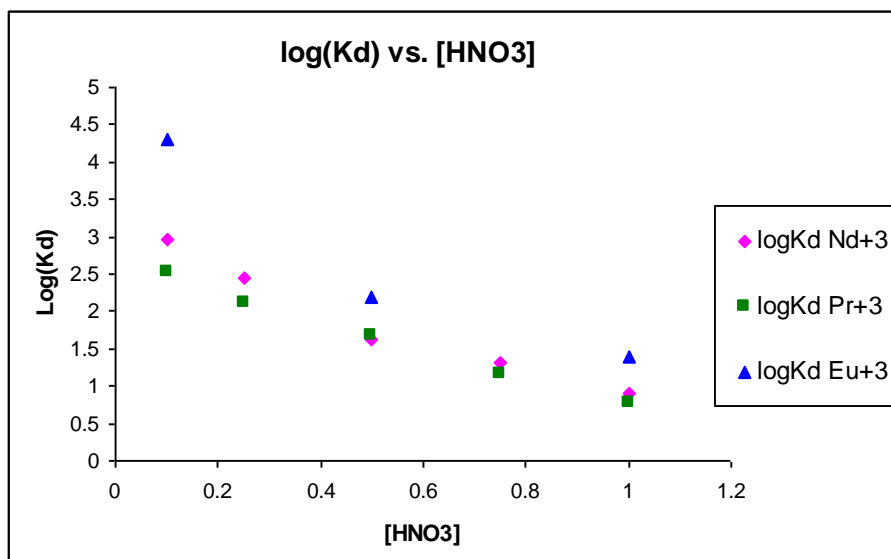


Table 2. Varying Concentrations of  $[\text{HNO}_3]$  vs.  $\text{Eu}^{+3} K_d$  (previously measured at PNNL)

$[\text{HNO}_3]$	<b>Eu log <math>K_d</math></b>
0.1	4.26
0.15	3.66
0.2	3.40
0.3	2.86
0.4	2.45
0.6	2.02
0.8	1.63
1.0	1.32

The second part of our experiment (Table 3) shows the dependence of the  $\text{Eu}^{+3} K_d$  on the amount of resin used. Varying the amount of resin was done to provide an indication of the influence of the Kläui ligand-to-europium molar ratio on the  $\text{Eu}^{+3} K_d$ . Table 3 and Figure 2 present the results of that experiment (L:M represents the ligand to metal ratio between the lanthanide metal and Kläui ligand). Although there are large

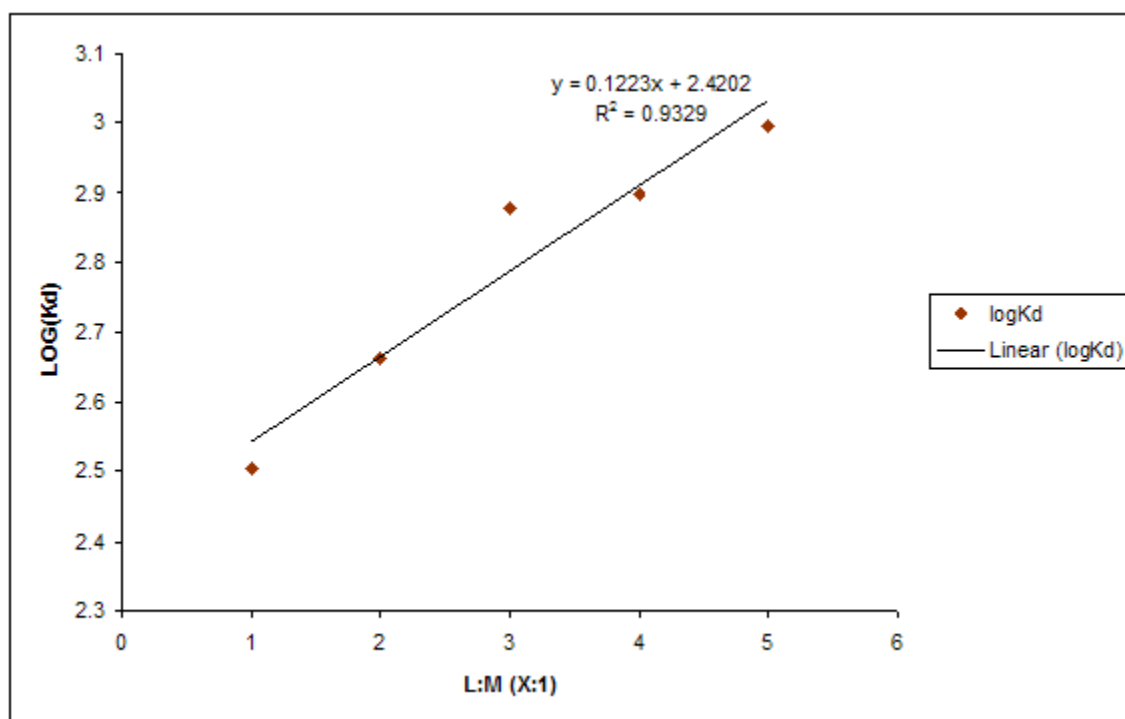
experimental uncertainties in the data, there is a general trend of increase Eu  $K_d$  with increasing ligand-to-europium molar ratio.

Table 3: Variation of the  $\text{Eu}^{+3}$   $K_d$  With Respect to Amount of Resin

Note: The empty spaces in the table mean that there was not any test run on that sample at that particular concentration.

L:M	Sample1 $K_d(\text{mL/g})$	Sample2 $K_d(\text{mL/g})$	Sample3 $K_d(\text{mL/g})$	$K_d(\text{average})$	Standard Deviation	Log ( $K_d$ )	Log(standard deviation)
0.5	132.0	230.0	51.3	138	69	2.1	1.8
1	349.0	289.0		319	42	2.5	1.6
2	503.0	413.0		458	64	2.7	1.8
3	1577.0	598.0	79.0	751	692	2.9	2.8
4	877.0	703.0		790	123	2.9	2.1
5	1051.0	934.0		992	83	3.0	1.9

Figure 2: Binding of  $\text{Eu}^{+3}$  ions as a Function L:M



## Discussion and Conclusion

The Kläui resin has a strong affinity for lanthanide and actinide ions, especially at low nitric acid concentrations. Based on the data collected, one can conclude that this affinity can be useful in separation procedures. Our data shows that varying the acid concentrations and the amount of resin present in each batch of XAD-7HP resin and 1%  $\text{NaL}_{\text{OPr}}$  for  $\text{Pr}^{+3}$ ,  $\text{Nd}^{+3}$ , and  $\text{Eu}^{+3}$  can affect the distribution coefficient ( $K_d$ ).

In our first experiment the acid was varied in three separate batches of the resin and a metal. Each batch contained a different metal. The praseodymium batch had the lowest  $K_d$  verses  $[\text{HNO}_3]$  concentrations. At lower concentrations  $\text{Nd}^{+3}$  was binding noticeably more to the Kläui ligand than the praseodymium (III), and the  $\text{Eu}^{+3}$  binding with the Kläui ligand was the strongest of the three metals.  $\text{Eu}^{+3}$  was only tested with three concentrations of nitric acid here, but previously a more extensive data set was obtained (Table 2). Past research tells us that not much binding occurs above 1 molar and our data on  $\text{Nd}^{+3}$  and  $\text{Pr}^{+3}$  shows that it is true. This occurs because the ligand becomes protonated at the high  $\text{HNO}_3$  concentrations. The Kläui anion, acting as a weak base, exhibits little or no binding at high acid concentrations due to the equilibrium protonation of the  $\text{L}_{\text{OPr}}^-$  anion forming  $\text{HL}_{\text{OPr}}$ . The neutral  $\text{HL}_{\text{OPr}}$  is unable to bind metal ions.

Our second experiment dealt only with the metal  $\text{Eu}^{+3}$  and its dependence on the amount of resin used. Figure 2 shows that the  $\text{Eu}^{+3}$   $\log K_d$  value is directly proportional to the ligand to metal ratio. As the amount of resin used increased the  $K_d$  value increased; therefore, the more ligand added to the metal, the more the lanthanide ions will bind.

This research can assist in expanding and improving current automated radiochemical methods. Future work will involve the determination of the  $K_d$  values for the remainder of the lanthanide series and experimenting to find out if the influence of electrons plays a role in the  $K_d$  value.

### **ACKNOWLEDGMENTS**

The research was conducted at the Pacific Northwest National Laboratory. We thank the U.S. Department of Energy and National Science Foundation Faculty and Student Team for giving us the opportunity to participate in the FaST program and the chance to have an incredible learning experience. A heart filled thanks go to our mentor, Dr. Gregg J. Lumetta for his patience, ability to explain, humor, and knowledge. We would like to also thank Tim Hubler, for allowing us to use his laboratory at EMSL and Yuanxian Xia for performing the ICP-OES measurements for us.

### **REFERENCES**

- [1] R. Overman, "Basic Concepts of Nuclear Chemistry", Reinhold Publishing Corporation (1963) 78
- [2] G. Lumetta, K. Nash, S. Clark, J. Friese, "Separations for the Nuclear Fuel Cycle in the 21<sup>st</sup> Century." American Chemical Society (2006) 26-28
- [3] G. Lumetta, R. Addleman, B. Hay, T. Hubler, T. Levitskaia, S. Sinkov, L. Snow, M. Warner, "Selective Media for Actinide Collection and Pre-Concentration:

- Results of FY 2006 Studies.” Pacific Northwest National Laboratory (2006) 2.1-3.18
- [4] B. Kilbourn, “A Lanthanide Lanthology.” Molycorp, Inc (1994) 10
- [5] “Gamma Spectroscopy.” Wikipedia.  
[http://en.wikipedia.org/wiki/Gamma\\_spectroscopy](http://en.wikipedia.org/wiki/Gamma_spectroscopy)
- [6] “Gamma Spectroscopy.” Nuclear Fundamentals.  
[http://www.tpub.com/content/doe/h1013v2/css/h1013v2\\_73.htm](http://www.tpub.com/content/doe/h1013v2/css/h1013v2_73.htm)
- [7] “Inductively coupled plasma atomic emission spectroscopy.” Wikipedia.  
[http://en.wikipedia.org/wiki/Inductively\\_coupled\\_plasma\\_atomic\\_emission\\_spectroscopy](http://en.wikipedia.org/wiki/Inductively_coupled_plasma_atomic_emission_spectroscopy)
- [8] T. Geoff, “ICP-AES Instrument at Works.” Varian. (1991, September) 3.  
<https://www.varianinc.com/media/sci/apps/icpes003.pdf>