11-3-2015

Exploring Rapid Radiochemical Separations at the University of Tennessee Radiochemistry Center of Excellence

Howard L. Hall
University of Tennessee - Knoxville, howard.hall@utk.edu

John D. Auxier II
University of Tennessee, Knoxville, jauxier@utk.edu

Recommended Citation

Hall, Howard L. and Auxier, John D. II, "Exploring Rapid Radiochemical Separations at the University of Tennessee Radiochemistry Center of Excellence" (2015). *Faculty Publications and Other Works -- Institute for Nuclear Security.*
https://trace.tennessee.edu/utk_nuclearpubs/1

Special Issue (SI): MARC X:

LOG NUMBER OF PAPER: 439

TITLE OF PAPER:

Exploring Rapid Radiochemical Separations at the University of Tennessee Radiochemistry Center of Excellence

AUTHOR(S): Howard L. Hall and John D. Auxier II

POSTAL ADDRESS OF EACH AUTHOR:

University of Tennessee, Institute for Nuclear Security and Department of Nuclear Engineering, Knoxville, TN 37996-2300

CORRESPONDING AUTHOR'S E-MAIL ADDRESS, TELEPHONE AND FAX NUMBERS:

howard.hall@utk.edu, 865-544-8996, no fax

Exploring Rapid Radiochemical Separations at the University of Tennessee Radiochemistry Center of Excellence

Howard L. Hall and John D. Auxier II
Institute for Nuclear Security and the Department of Nuclear Engineering, University of Tennessee, Knoxville, TN 37996-2300 USA

Abstract

The University of Tennessee formed its Radiochemistry Center of Excellence (RCoE) in 2013 with support from the U.S. National Nuclear Security Administration. One of the major thrusts of the RCoE is to develop deeper understanding of rapid methods for radiochemical separations that are relevant to both general radiochemical analyses as well as post-detonation nuclear forensics. Early work has included the development and demonstration of rapid separations of lanthanide elements in the gas phase, development of a gas-phase separation front-end for ICP-TOF-MS analysis, and the development of realistic analytical surrogates for post-detonation debris to support methods development.

Key words

Separations, Rapid Radiochemistry, Nuclear Forensics, Gas-Phase, Thermochromatography, Lanthanides

Background

The disciplines of nuclear and radiochemistry are important to a number of fields, notably nuclear medicine/radiopharmaceuticals, environmental management or remediation of radioactive or nuclear materials, and nuclear security/nonproliferation activities. These programs in the private and government sectors are significant in the United States and present an important component of the overall portfolio of nuclear work. Internationally, a number of nations are embarking on ambitious programs to develop or expand nuclear power and related industries.

However, nuclear and radiochemistry have waned in the academic community over the years. A recent study by the National Academy of Science **[1]** found that academic programs in the U.S. across all aspects of nuclear and radiochemistry were not producing enough doctoral-level radiochemists to meet estimated national need, and this was especially acute in the nuclear security/nonproliferation area (in which non-U.S. citizens are more difficult to employ due to governmental security considerations). This is not a new observation – a number of other studies have also remarked on the same loss of academic pathways for educating nuclear and radiochemists **[2, 3]**.

The University of Tennessee (UT) undertook an effort to expand and revitalize radiochemistry graduate education and research on its campus with an emphasis in the area of nuclear security. This was a natural outgrowth of work that UT had started in 2009 to develop nuclear security curricula and research as a general thrust in the Department of Nuclear Engineering **[4]**, an effort which ultimately culminated in the establishment of a campus-wide Institute for Nuclear Security **[5]**. In 2013, this radiochemistry effort was established as the Radiochemistry Center of Excellence (RCoE) in the UT Institute for Nuclear Security, with financial support from the U.S. National Nuclear Security Administration (NNSA).

Objective of the Center in Advanced Radiochemical Separations

Focused on graduate research training and education in this area, the RCoE is organized into a set of two larger and two smaller research thrusts, each selected to develop new scientific understanding in areas of strategic interest and to develop student expertise and interests that overlap with long-term NNSA needs. The two larger thrust areas are advanced radiochemical separations research (the focus of this manuscript) and the development of radiochemical probes to explore complex fluid dynamics. The smaller thrusts are in actinide materials behavior and in nuclear cross-sections (the nuclear cross-section effort also serves as a linkage and ongoing collaboration with the Center of Excellence for Radioactive Ion Beam Studies for Stewardship Science consortium **[6]** led by Rutgers University).

In the advanced radiochemical separations research thrust, work is focused on improving the specificity, timeliness, detection limits, and/or operational suitability of radiochemical separations that are relevant to NNSA mission areas. Radiochemical separations ultimately underlie all applications of radiochemistry in this area, and is easily applicable to other applications of radiochemistry as well (e.g., medical radioisotope purification). To date, we have focused primarily on exploiting unique gas-phase chemistry to develop and improve separations, with a particular emphasis on pursuing faster and higher specificity separations that support the analysis of post-detonation nuclear debris for nuclear forensic purposes. The impetus for faster and higher specificity separations is to reduce the overall analysis time, which is a limiting factor in the ability of technical nuclear forensics to support crisis-mode decision-making for governmental responses to a potential act of nuclear terrorism. Additionally, the simplicity of this approach also supports the ability to move the analysis capability into the field, rather than relying on traditional laboratory wet-chemistry methods.

Theory and Modeling

Gas-phase separations have not been routinely used on nuclear forensic studies, but variants of thermochromatography have been applied to heavy element synthesis experiments for some time **[7–11]**. Prior to the establishment of the RCoE, we had identified that thermochromatography was extensible to the types of separations needed for post-detonation debris analysis **[12]** and, through the use of modeling, shown that it was at least theoretically possible to exploit this for dramatic improvements in separation time **[13]**.

However, this modeling was dependent on thermodynamic parameters that were poorly known and in some cases contradictory. Hanson et al. **[12]** provided a thorough review of prior studies of thermochromatography, and also provides a summary of the thermodynamics that govern the separation process. An obvious conclusion from Hanson is that the earlier experimental work was tailored to separate materials for physics studies as opposed to fully understanding the thermodynamics, and the comparability and reproducibility of various investigators' work was challenging. Drawing from Table 1 of Hanson **[12]**, deposition temperatures for metals of interest varied dramatically between the reported values **[10, 14, 15]**. It should be noted that the deposition temperatures are directly relatable to the adsorption enthalpy for the reaction of the volatile compound with the wall material in the separation column. This motivated efforts to not only focus on time of separation, but to help resolve the immense uncertainties in the thermodynamics of the gas-phase separations process.

Experimental Approach and Methods

We determined that our first target for investigation would be the lanthanides, using substituted β-diketonates as our initial ligands to promote volatility. The lanthanides complexes were synthesized by dissolving the lanthanide oxides (excluding Ce and Pm) into conc. hydrochloric acid (Fisher). Once dissolved the resulting chloride salts were dried. The 1 1,1,1,5,5,5–hexafluoro-2,4-pentadione (hfac) or 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione (hfod) ligands (Acros), depending on the compound to be prepared, were treated with equimolar amounts ammonium hydroxide, which both ligands form white precipitates. The resulting compounds were NH_4hfac and NH_4hfod. The rare earth chloride salts were dissolved in water where they were treated with either NH_4hfac or NH_4hfod, to form the precipitating solids, as reported previously [16–18]. In the case of 2,2,6,6-tetramethyl-3,5-heptanedione (hdpm), the ligand (Acros) is prepared by treatment with sodium hydroxide (2.4 g) and dissolved in 50 mL of 50% ethanol (Fisher) solution under an argon atmosphere. While under argon, the rare earth chloride solution was added to the reaction vessel, such that the lanthanide to ligand ratio was 3:1, and allowed to vacuum reflux for 24 hours, the precipitate was collected via vacuum separation [17].

The lanthanides are not only useful because there was *some* thermodynamics data reported for them, but also because the lanthanides are also strongly diagnostic of neutron energy in a nuclear explosion. Figure 1 shows the dramatic change in the fission product distribution of the lanthanides between thermal neutron fission and fission induced by 14-

MeV neutrons. A thorough measurement of the lanthanides in post-detonation debris, in addition to further interpretation, can therefore help understand the neutronic environment of the exploding assembly, providing design clues that are useful in the attribution process.

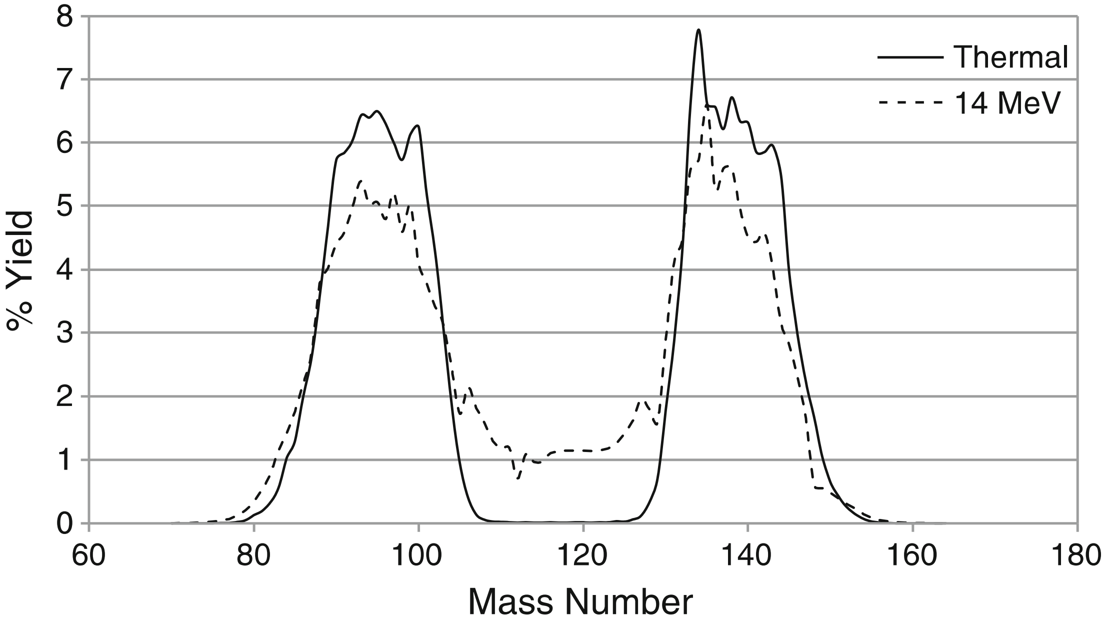


Figure 1. Fission product yield of ^{235}U fission from thermal and 14-MeV neutrons (Graph from Hanson [12] using data from Nichols [19]).

For early development work, stable lanthanides were used to determine the best method to derivatize the metals for introduction into the gas phase. Typical physical data for the compounds were determined, including single crystal structural x-ray diffraction data for those compounds which could induced to grow single crystals. This data has been reported already **[20]** for some of the metal-ligand systems under study.

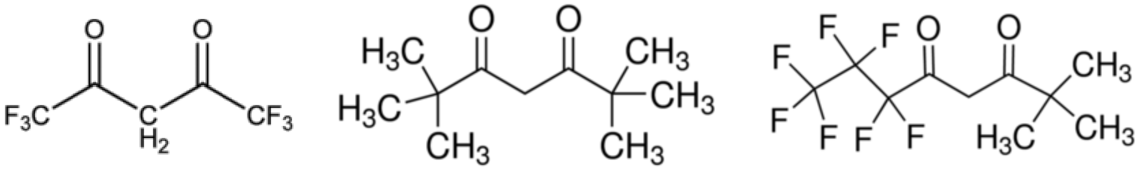
To completely characterize the behavior of the metal-ligand complexes for gas phase separations, we developed a coupled thermochromatography – inductively coupled plasma – time-of-flight mass spectrometer (TC-ICP-TOF-MS) system to measure the elution times and separation factors of the complexes using stable lanthanides as our first test cases. This involved repurposing a gas-chromatography oven (Hewlett-Packard) with an uncoated quartz capillary column, and then coupling the outflow of the column through a custom-developed thermally controlled gas transfer system into the plasma torch of the ICP-TOF-MS (GBC Scientific Opti-Mass 9500). This allows us to easily vary experimental parameters such as column temperature, carrier gas flow rates, mass-loading effects, etc., while collecting a full suite of separation data from a mixture of lanthanides in each experiment.

However, of course, analysis of stable lanthanide solutions are not our primary target and ICP-TOF-MS as a detector needs to be supplemented with radiation measurement tools. However, the ability to test the system with stable isotopes was extremely useful for instrument development, early studies, and – importantly – building confidence with the university radiation safety team that the system can be operated with risks appropriately controlled. To challenge the gas-phase separation approach with lanthanide isotopes from fission, we sought to develop a means of producing a realistic sample that was chemically, radiologically, and morphologically similar to the type of post-detonation debris that might be the sort of ideal sample – nuclear melt glass from the vicinity of the working point of a nuclear device detonation.

To this end, a process for producing – in the laboratory – a synthetic melt glass was developed **[21]**. This melt glass, doped with uranium and irradiated in a reactor to induce a reasonable number of fissions in the sample, would not only provide us with realistic radioactive lanthanides to separate, but would also allow us to provide a full evaluation of analysis time from start of dissolution until separated high-purity lanthanide fractions were prepared.

Results and Discussion

Several candidate ligands have been fully evaluated for suitability with stable lanthanides: 1 1,1,1,5,5,5–hexafluoro-2,4-pentadione (denoted “hfac,” Figure 2a), 2,2,6,6-tetramethyl-3,5-heptanedione (denoted “hdpm,” Figure 2b), and 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione (denoted “hfod,” Figure 2c).



(a) (b) (c)

Figure 2. Structures of the hfac (a), hfod (b), and hdpm (c) ligands,

Gas-phase separations studies using the TC-ICP-TOF-MS and conventional gas chromatography-mass spectrometry have yielded preliminary results that are extremely promising – very good separation factors (defined as $\Delta t_i/w_{av}$ where Δt_i is the difference in elution times and w_{av} is the average width of the elution peak at the baseline) . Separation factors of 1.5 or more are considered very good. Using hdpm ligands, we have observed separation factors exceeding 7 for adjacent lanthanides when running stable isotope lanthanide samples. Similarly, hfac ligands (which are more easily used to derivatize the lanthanides) produce separation factors of about 5. Moreover the time for separation is excellent, generally under 10 minutes for complete separation.

Hanson **[20]** has compared the absorption enthalpies and entropies derived from experimental retention times for Dy and Sm when complexed and volatilized with each of the ligands we are using, as shown in Table 1. All cases were measured with a bare (uncoated) quartz glass column, and was measured by the use of a standard gas chromatography – mass spectrometry (GC-MS) instrument that used an isothermal methods.

Table 1. Enthalpy of adsorption and entropy of adsorption for Sm and Dy ligand complexes (on quartz glass surfaces) as observed from gas-phase separations [20]**.**

	Sm		**Dy**	
Ligand system	**ΔH_{ad} (kJ/mol)**	**ΔS_{ad} (J/mol)**	**ΔH_{ad} (kJ/mol)**	**ΔS_{ad} (J/mol)**
hfac	-1±3	-49±8	31±8	26±16
hfod	-20±40	94±94	27±4	21±10
hdpm	24±2	98±5	12±4	-68±25

End-to-end analysis on reactor-produced lanthanide fission products has not yet been carried out. However, the methodology for producing synthetic melt glass similar to trinitite (produced in the first U.S. nuclear explosion, code named "Trinity" at Alamagordo, New Mexico, in 1945 **[22]**) has been developed and successfully reduced to routine practice **[21]**. Test irradiation of the synthetic trinitite has been conducted at the Oak Ridge National Laboratory High Flux Isotope Reactor, and gamma spectrometry performed on the activated glass to verify expected activation and fission product retention within the glass matrix.

We have also extended the surrogate nuclear debris work into simulating debris from urban environments **[23]**, with an approach that takes into account differences in local geology, building types, land use, population density, etc. This is important, because the gross chemical composition of the melt glass can dramatically affect the performance of the initial dilutions and derivatization steps.

Beginning with synthetic trinitite, and using microwave-assisted acid dissolution of the bulk sample followed by derivatization and gas-phase separations, we have been able to produce separate high-purity lanthanide fractions with this approach in less than two hours. This is a significant improvement over the “classical” methods for purifying the lanthanides **[24]**.

Conclusions

Gas-phase separations are proving to be an effective and rapid means to radiochemically isolate the lanthanide elements, which are of significant nuclear forensic utility. The work of the RCoE has established the experimental capability to systematically and thoroughly investigate these metal-ligand complexes, as well as prove their usefulness on realistic starting samples. Through the thermodynamic data developed, these methods also allow us to explore the thermodynamic phenomenology of the adsorption enthalpies of these compounds with a variety of surfaces. The development of synthetic nuclear melt glasses also broadens the availability for the academic community to engage in methods development for nuclear forensics, and serves as a potential quality control source for operational entities.

Last, but certainly not least, the RCoE is also educating new nuclear and radiochemistry practitioners. While the RCoE can only make a small impact on the deficit of radiochemists needed for U.S. needs (the National Academies estimate that the U.S. has a deficit of approximately 50 Ph.D.-level radiochemists per year **[1]**), the RCoE and the

Institute for Nuclear Security has been successful are building student interest and entrenching radiochemistry research into the University of Tennessee.

Acknowledgements

This work was performed in part under Grant number DE-NA0001983 from the Stewardship Science Academic Alliances Program of the National Nuclear Security Administration. Their support is gratefully acknowledged.

References

1. Moore CB, Anderson CJ, Baisden PA, et al. (2012) Assuring a Future U.S.-Based Nuclear and Radiochemistry Expertise. National Academies Press, Washington, DC
2. APS/AAAS (2008) Nuclear Forensics - Role, State of the Art, and Program Needs. American Physical Society and American Association for the Advancement of Science, Washington, DC
3. Baruzzini ML, Crabtree LI, Hall HL (2012) Nuclear forensic science educational needs - A student perspective. In: Trans. Am. Nucl. Soc. pp 128–129
4. Hall HL, Dodds HL, Hayward JP, et al. (2010) Nuclear Engineering and Nuclear Security: A Growing Emphasis at the University of Tennessee. Proc. Pac. Northwest Int. Conf. Glob. Nucl. Secur. Decade Ahead
5. Hall HL (2013) Building the Academic Nuclear Security Program at the University of Tennessee. Proc. IAEA Int. Conf. Nucl. Secur. Enhancing Glob. Efforts
6. Cizewski JA (2013) Applications of Nuclear Science for Stewardship Science. J Phys Conf Ser 420:012058. doi: 10.1088/1742-6596/420/1/012058
7. Schadel M (2015) Chemistry of the superheavy elements. Philos Trans R Soc Math Phys Eng Sci 373:20140191. doi: 10.1098/rsta.2014.0191
8. Kratz JV (2003) Critical evaluation of the chemical properties of the transactinide elements (IUPAC Technical Report). Pure Appl Chem 75:103–108. doi: 10.1351/pac200375010103
9. Eichler B, Rhede E (1980) Thermochromatographic Studies on Actinides .1. Americium in Titanium Columns. Kernenergie 23:191–195.
10. Hickmann U, Greulich N, Trautmann N, et al. (1980) Rapid Continuous Radiochemical Separations by Thermochromatography in Connection with a Gas-Jet Recoil-Transport System. Nucl Instrum Methods 174:507–513.
11. Dienstbach F, Bachmann K (1983) Gas-Solid Thermochromatographic Separation of Lanthanide Chlorides. Radiochim Acta 34:215–217.
12. Hanson D, Garrison J, Hall H (2011) Assessing thermochromatography as a separation method for nuclear forensics: current capability vis-a-vis forensic requirements. J Radioanal Nucl Chem 289:213–223. doi: 10.1007/s10967-011-1063-5

13. Garrison JR, Hanson DE, Hall HL (2012) Monte Carlo analysis of thermochromatography as a fast separation method for nuclear forensics. J Radioanal Nucl Chem 291:9. doi: 10.1007/s10967-011-1367-5
14. Hickmann U, Greulich N, Trautmann N, Herrmann G (1993) Online Separation of Volatile Fission-Products by Thermochromatography - Comparison of Halide-Systems. Radiochim Acta 60:127–132.
15. Tsalas S, Bachmann K (1978) Inorganic Gas-Chromatography - Separation of Volatile Chlorides by Thermochromatography Combined with Complex-Formation. Anal Chim Acta 98:17–24.
16. Sievers RE, Ponder BW, Morris ML, Moshier RW (1963) Gas Phase Chromatography of Metal Chelates of Acetylacetone, Trifluoroacetylacetone, and Hexafluoroacetylacetone. Inorg Chem 2:693–698. doi: 10.1021/ic50008a006
17. Eisentraut KJ, Sievers RE (1965) Volatile Rare Earth Chelates. J Am Chem Soc 87:5254–5256. doi: 10.1021/ja00950a051
18. Springer CS, Meek DW, Sievers RE (1967) Rare earth chelates of 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione. Inorg Chem 6:1105–1110. doi: 10.1021/ic50052a009
19. Nichols AL, Aldama DL, Verpelli M (2008) Handbook of Nuclear Data for Safeguards: Database Extensions, August 2008, INDC(NDS)-0534 ed. International Atomic Energy Agency, Vienna, Austria
20. Hanson D (2014) Synthesis and Thermodynamic Analysis of Volatile Beta-Diketone Complexes of Select Lanthanides via Gas-Phase Separations. PhD dissertation, University of Tennessee
21. Molgaard JJ, Auxier JD, Giminaro AV, et al. (2015) Development of synthetic nuclear melt glass for forensic analysis. J Radioanal Nucl Chem 304:1293–1301. doi: 10.1007/s10967-015-3941-8
22. Bainbridge KT (1947) Weapon data effects and instruments. Volume 24. Section G, Appendices 50-54. Los Alamos Scientific Laboratory, Los Alamos, NM
23. Giminaro AV, Stratz SA, Gill JA, et al. (2015) Compositional planning for development of synthetic urban nuclear melt glass. J Radioanal Nucl Chem. doi: 10.1007/s10967-015-4061-1
24. Kleinberg J (1990) Collected radiochemical and geochemical procedures. Los Alamos Scientific Laboratory, Los Alamos, NM