



11-3-2015

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Special Issue (SI): MARC X:

LOG NUMBER OF PAPER: 439

TITLE OF PAPER:

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Radiochemistry Center of Excellence**

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

3

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7

8 **Abstract**

9 The University of Tennessee formed its Radiochemistry Center of Excellence (RCoE) in
10 2013 with support from the U.S. National Nuclear Security Administration. One of the
11 major thrusts of the RCoE is to develop deeper understanding of rapid methods for
12 radiochemical separations that are relevant to both general radiochemical analyses as well
13 as post-detonation nuclear forensics. Early work has included the development and
14 demonstration of rapid separations of lanthanide elements in the gas phase, development
15 of a gas-phase separation front-end for ICP-TOF-MS analysis, and the development of
16 realistic analytical surrogates for post-detonation debris to support methods development.

17 **Key words**

18 Separations, Rapid Radiochemistry, Nuclear Forensics, Gas-Phase,

19 Thermochemistry, Lanthanides

20 **Background**

21 The disciplines of nuclear and radiochemistry are important to a number of fields, notably

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

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

36 The University of Tennessee (UT) undertook an effort to expand and revitalize
37 radiochemistry graduate education and research on its campus with an emphasis in the
38 area of nuclear security. This was a natural outgrowth of work that UT had started in
39 2009 to develop nuclear security curricula and research as a general thrust in the
40 Department of Nuclear Engineering [4], an effort which ultimately culminated in the
41 establishment of a campus-wide Institute for Nuclear Security [5]. In 2013, this
42 radiochemistry effort was established as the Radiochemistry Center of Excellence
43 (RCoE) in the UT Institute for Nuclear Security, with financial support from the U.S.
44 National Nuclear Security Administration (NNSA).

45 **Objective of the Center in Advanced Radiochemical Separations**

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

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

68 supports the ability to move the analysis capability into the field, rather than relying on
69 traditional laboratory wet-chemistry methods.

70 **Theory and Modeling**

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

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

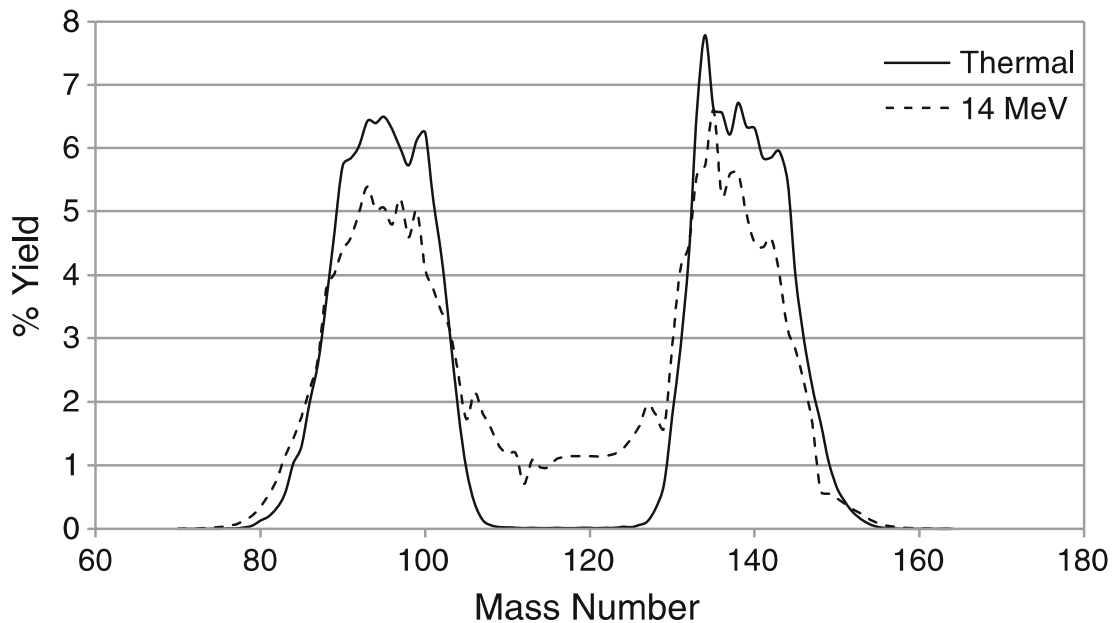
90 thermodynamics of the gas-phase separations process.

91 **Experimental Approach and Methods**

92 We determined that our first target for investigation would be the lanthanides, using
93 substituted β -diketonates as our initial ligands to promote volatility. The lanthanides
94 complexes were synthesized by dissolving the lanthanide oxides (excluding Ce and Pm)
95 into conc. hydrochloric acid (Fisher). Once dissolved the resulting chloride salts were
96 dried. The 1,1,1,5,5,5-hexafluoro-2,4-pentadione (hfac) or 6,6,7,7,8,8,8-heptafluoro-
97 2,2-dimethyl-3,5-octanedione (hfod) ligands (Acros), depending on the compound to
98 be prepared, were treated with equimolar amounts ammonium hydroxide, which both
99 ligands form white precipitates. The resulting compounds were NH_4hfac and NH_4hfod .
100 The rare earth chloride salts were dissolved in water where they were treated with either
101 NH_4hfac or NH_4hfod , to form the precipitating solids, as reported previously [16–18]. In
102 the case of 2,2,6,6-tetramethyl-3,5-heptanedione (hdpm), the ligand (Acros) is
103 prepared by treatment with sodium hydroxide (2.4 g) and dissolved in 50 mL of
104 50% ethanol (Fisher) solution under an argon atmosphere. While under argon, the
105 rare earth chloride solution was added to the reaction vessel, such that the
106 lanthanide to ligand ratio was 3:1, and allowed to vacuum reflux for 24 hours, the
107 precipitate was collected via vacuum separation [17].

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

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



116
117 Figure 1. Fission product yield of ^{235}U fission from thermal and 14-MeV neutrons
118 (Graph from Hanson [12] using data from Nichols [19]).

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

124 To completely characterize the behavior of the metal-ligand complexes for gas phase

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

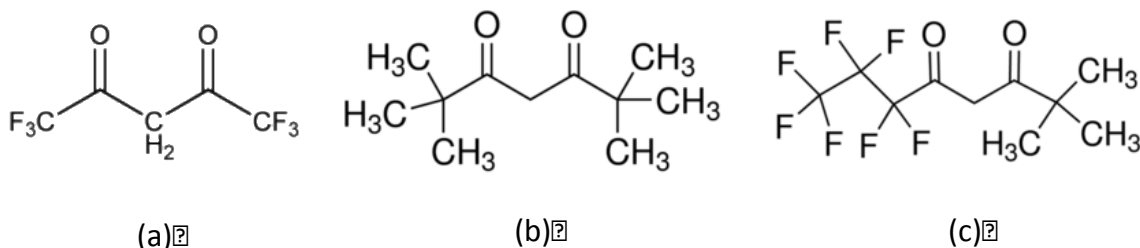
135 However, of course, analysis of stable lanthanide solutions are not our primary target and
136 ICP-TOF-MS as a detector needs to be supplemented with radiation measurement tools.
137 However, the ability to test the system with stable isotopes was extremely useful for
138 instrument development,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

145 To this end, a process for producing – in the laboratory – a synthetic melt glass was
146 developed [21]. This melt glass, doped with uranium and irradiated in a reactor to induce
147 a reasonable number of fissions in the sample, would not only provide us with realistic

148 radioactive lanthanides to separate, but would also allow us to provide a full evaluation of
149 analysis time from start of dissolution until separated high-purity lanthanide fractions
150 were prepared.

151 **Results and Discussion**

152 Several candidate ligands have been fully evaluated for suitability with stable
153 lanthanides: 1,1,1,5,5,5-hexafluoro-2,4-pentadione (denoted “hfac,” Figure 2a),
154 2,2,6,6-tetramethyl-3,5-heptanedione (denoted “hdpm,” Figure 2b), and
155 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione (denoted “hfod,” Figure 2c).



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

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

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

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

<i>Ligand system</i>	Sm		Dy	
	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

175

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

184 We have also extended the surrogate nuclear debris work into simulating debris from
 185 urban environments [23], with an approach that takes into account differences in local
 186 geology, building types, land use, population density, etc. This is important, because the

187 gross chemical composition of the melt glass can dramatically affect the performance of
188 the initial dilutions and derivatization steps.

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

194 **Conclusions**

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

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

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

211 **Acknowledgements**

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

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