

Basis for developing samarium AMS for fuel cycle analysis

Bruce A. Buchholz^{a,*}, Steven R. Biegalski^b, Scott M. Whitney^b, Scott J. Tumey^a, C. Jordan Weaver^b

^a CAMS L-397, LLNL, 7000 East Avenue, Livermore, CA 94551, USA

^b Nuclear Engineering Teaching Laboratory, University of Texas, Austin, TX 78741, USA

ARTICLE INFO

Article history:

Available online 7 October 2009

Keywords:

Nuclear fuel cycle

Fission products

^{146}Sm

AMS

Samarium

ORIGEN

ABSTRACT

Modeling of nuclear reactor fuel burnup indicates that the production of samarium isotopes can vary significantly with reactor type and fuel cycle. The isotopic concentrations of ^{146}Sm , ^{149}Sm , and ^{151}Sm are potential signatures of fuel reprocessing, if analytical techniques can overcome the inherent challenges of lanthanide chemistry, isobaric interferences, and mass/charge interferences. We review the current limitations in measurement of the target samarium isotopes and describe potential approaches for developing Sm-AMS. AMS sample form and preparation chemistry will be discussed as well as possible spectrometer operating conditions.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Isotopes produced from fission and capture reactions in nuclear reactors vary with reactor fuel, moderator, fuel cycle, operational parameters, and overall reactor design. Some design and operation features produce distinct profiles in the spent fuel or dissolved waste. The isotope profiles can identify the type of reactor, the length of reactor fuel cycle, neutron flux, neutron fluence, and other parameters.

We previously performed fuel cycle modeling to determine which long-lived or stable fission products vary with irradiation history and found the isotopic concentrations of ^{146}Sm , ^{149}Sm , and ^{151}Sm to be illustrative [1]. Isotope ratios of specific elements contained in the waste after spent fuel reprocessing can indicate the length of the fuel cycle as well as reactor type when sensitive detecting techniques are utilized. It is important to note that isotopic ratios of individual elements are utilized in contrast to ratios of different elements since isotopic ratios are least affected by chemical fractionation that can occur during processing or environmental transport.

Using open source Oak Ridge Isotope Generation and Depletion codes, ORIGEN-ARP and ORIGEN-2.2 [2,3] we modeled fuel cycles in Pressurized Water Reactor (PWR), Boiling Water Reactor (BWR), Canada Deuterium Uranium Reactor (CANDU), and Liquid Metal Fast Breeder Reactor (LMFBR) nuclear reactors [1]. Short, low burnup (1 month) and long, high burnup (18 months typical of a commercial power reactor) fuel cycles were modeled. We assumed 1 year of cooling after removing the fuel from the core for

the decay of short-lived isotopes. The ORIGEN codes are a well substantiated set of codes that have been used for decades in nuclear engineering research and reactor fuel management.

The ratios of the rare, long-lived fission product ^{146}Sm to a high yield fission product ^{151}Sm and to a stable isotope ^{149}Sm produced in a typical power PWR with 15 day and 500 day fuel cycles is graphed in Fig. 1. Measurement of stable Sm isotopes by TIMS is reported with a small dynamic range, isotope ratios were on the order of 0.1–10 [4,5]. The use of ICP-MS is now preferred for measuring Sm isotopes in spent nuclear fuel [5–7]. ICP-MS routinely measures stable isotopes at the ppm level, but again has only been used for high abundance stable isotopes. Neither TIMS nor ICP-MS appear capable of measuring $^{146}\text{Sm}/^{149}\text{Sm}$ and $^{146}\text{Sm}/^{151}\text{Sm}$ to 10^{-9} or lower over a large dynamic range likely to be encountered (see Fig. 1).

The relative isotopic concentrations of ^{146}Sm , ^{149}Sm , and ^{151}Sm are potential signatures of fuel reprocessing, if analytical techniques can overcome the inherent challenges of very low ^{146}Sm concentration, separatory lanthanide chemistry, isobaric interferences, and mass/charge interferences. We review the current limitations in measurement of the target samarium isotopes and describe potential approaches for developing Sm-AMS. AMS sample form and preparation chemistry will be discussed and considerations for spectrometer operating conditions will be briefly suggested.

2. Sm sample processing options

Producing a high quality sample cathode material suitable for AMS sputter ion sources will likely be the most difficult task in developing Sm-AMS. The starting sample matrix for this application

* Corresponding author. Tel.: +1 925 422 1739; fax: +1 925 423 7884.

E-mail address: bbuchholz@llnl.gov (B.A. Buchholz).

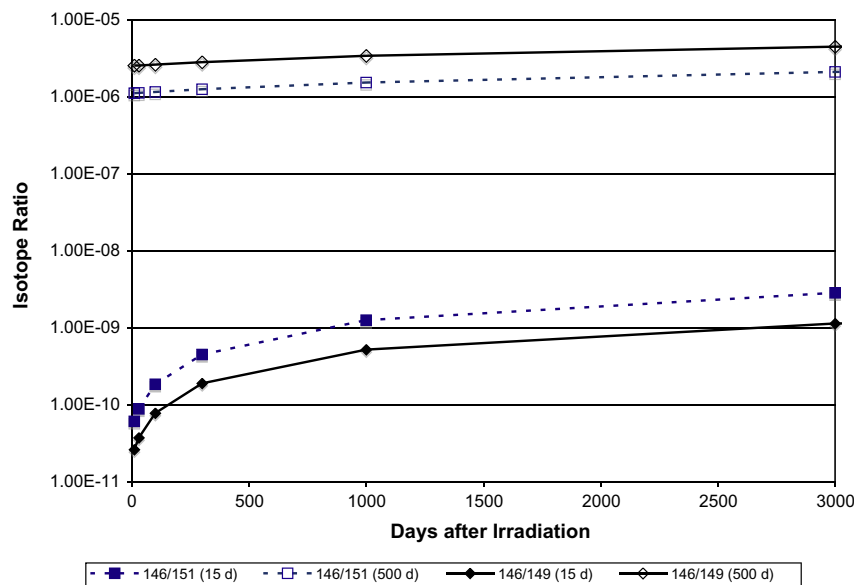


Fig. 1. Samarium isotope ratios after cooling predicted with ORIGEN models assuming long and short fuel cycles for a pressurized water reactor.

is likely to be an aqueous waste stream, waste organic solvent, spent separatory column, or precipitated solids inside a tank or drum. All of these matrices will be rich in lanthanides and other fission products, not a purified isotopic target typically used in nuclear physics experiments. An initial aqueous chemistry clean-up step to remove or reduce the soup of elements will need to be done. Luckily, lanthanide chemistry is well developed and a variety of approaches have been used to separate Sm from other lanthanides and other trivalent aqueous ions [8–13]. Many isobars exist in the range of interest. A list of some possible injection isobars capable of carrying a 1[−] charge is provided in Table 1.

Middleton demonstrated intense SmH₂[−] and SmH₄[−] beams using a gas cathode, which flowed H₂ gas over metallic Sm [14]. The gas cathode is not conducive to sample switching, but suggests that samarium hydride might make a good cathode material. Several techniques for producing a variety of samarium hydrides for specialized applications are in the literature. The diffusion of H₂ gas into hot Sm metal [15,16], production as a thin film layer [17,18], an organometallic complex [19,20] or a nano-particle [21] are not readily transferred to typical AMS sample processing. The hydride is likely to be very reactive with water, and probably not a first choice as a cathode material if other suitable materials can be found.

SmF₂ and SmF₃ are also possible cathode materials. SmF₃ sputtering targets are commercially available in semiconductor and vapor deposition applications. Most halogenated molecules form negative ions well, and F has been useful in the past [22–24]. Recent work at CAMS has focused on SrF₂ cathodes to get improved current over oxide without the difficult sample prep of the hydride

[25]. We believe samarium fluoride may present a similar compromise compared to samarium hydride, better sample stability at the expense of current and energy resolution. A variety of procedures for producing lanthanide fluorides from oxides are in the literature because the trifluoride is a precursor to metal production [26–28]. The procedure for producing SmF₃ most amenable to batch processing dissolves Sm₂O₃ in hydrochloric or nitric acid, precipitates the fluoride by adding HF, and dries the precipitate under vacuum or in an inert atmosphere at 300 °C to yield anhydrous SmF₃ [27,29].

Tests of output from the LLNL ion source [30] produced up to 300–400 nA of ¹⁵²SmF[−] and ¹⁵⁴SmF[−] from cathodes of SmF₃ mixed with Nb metal powder (Table 2). The ion source was operated under typical conditions with a cathode voltage of 9.0 kV and ion currents were measured in an in-line Faraday cup after traversing the 90° bend of our injector magnet. The cathode currents improved over time, starting at about 100 nA and increasing to 300–400 nA over 30 min and retaining the maximum current for an additional 40 min. We did not attempt to exhaust the samples. The currents of the SmF[−] of the naturally occurring Sm isotopes of masses 147, 148, 149, 150, 152, and 154 were proportional to their natural abundances aside from mass 173 (¹⁵⁴Sm¹⁹F), which was about 20% too high. We did not identify the interference. We checked production of SmF₃[−] since there are typically fewer isobars above mass 200. Unfortunately, the current was under 10 nA, and probably not worth pursuing. We also observed low SmH[−] production from SmF₃ cathodes for about 15 min, probably due to absorbed water in the targets. The SmH[−] current disappeared after the target was thoroughly heated in the sputter source.

Table 1
Potential isobaric interferences for isotopes of Sm, Sm¹⁶O and Sm¹⁹F.

Mass	Desired ion	Isobars
146	¹⁴⁶ Sm	¹¹⁴ Sn ¹⁶ O ₂ , ¹³⁰ Ba ¹⁶ O, ¹⁴⁴ NdH ₂ , ¹⁴⁵ NdH, ¹⁴⁶ Nd, ¹⁴⁵ PmH, ¹⁴⁶ Pm, ¹⁴⁴ SmH ₂
149	¹⁴⁹ Sm	¹¹⁷ Sn ¹⁶ O ₂ , ¹³³ Cs ¹⁶ O, ¹³² Ba ¹⁷ O, ¹³³ Ba ¹⁶ O, ¹⁴⁸ NdH, ¹⁴⁷ SmH ₂ , ¹⁴⁸ SmH
151	¹⁵¹ Sm	¹¹⁹ Sn ¹⁶ O ₂ , ¹³³ Cs ¹⁸ O, ¹³⁴ Ba ¹⁷ O, ¹³⁵ Ba ¹⁶ O, ¹⁵⁰ NdH, ¹⁴⁷ SmH ₄ , ¹⁵¹ Eu, ¹⁵⁰ GdH
162	¹⁴⁶ Sm ¹⁶ O	¹⁴³ Nd ¹⁹ F, ¹⁴⁵ Nd ¹⁶ OH, ¹⁴⁶ Nd ¹⁶ O, ¹⁴⁵ Pm ¹⁶ OH, ¹⁴⁵ Pm ¹⁷ O, ¹⁴⁶ Pm ¹⁶ O, ¹⁶² Dy, ¹⁶² Er
165	¹⁴⁹ Sm ¹⁶ O	¹⁴⁶ Nd ¹⁹ F, ¹⁴⁸ Nd ¹⁶ OH, ¹⁴⁶ Pm ¹⁹ F, ¹⁴⁸ Sm ¹⁶ OH, ¹⁴⁸ Sm ¹⁷ O, ¹⁴⁶ Sm ¹⁹ F, ¹⁶³ DyH ₂ , ¹⁶⁴ DyH, ¹⁶⁴ ErH
167	¹⁵¹ Sm ¹⁶ O	¹⁵⁰ Nd ¹⁶ OH, ¹⁴⁸ Sm ¹⁸ OH, ¹⁴⁹ Sm ¹⁸ O, ¹⁵⁰ Sm ¹⁶ OH, ¹⁵⁰ Sm ¹⁷ O, ¹⁵¹ Eu ¹⁶ O, ¹⁵⁰ Gd ¹⁶ OH, ¹⁵⁰ Gd ¹⁷ O, ¹⁶⁵ HoH ₂ , ¹⁶⁶ ErH, ¹⁶⁷ Er
165	¹⁴⁶ Sm ¹⁹ F	¹⁴⁶ Nd ¹⁹ F, ¹⁴⁸ Nd ¹⁶ OH, ¹⁴⁶ Pm ¹⁹ F, ¹⁴⁸ Sm ¹⁶ OH, ¹⁴⁸ Sm ¹⁷ O, ¹⁴⁹ Sm ¹⁶ O, ¹⁶³ DyH ₂ , ¹⁶⁴ DyH, ¹⁶⁴ ErH
168	¹⁴⁹ Sm ¹⁹ F	¹³³ Cs ³⁵ Cl, ¹⁵⁰ Gd ¹⁸ O, ¹⁶⁶ ErH ₂ , ¹⁶⁷ ErH, ¹⁶⁸ Er, ¹⁶⁸ Yb
170	¹⁵¹ Sm ¹⁹ F	¹³³ Cs ³⁷ Cl, ¹⁵² Gd ¹⁸ O, ¹⁵⁴ Gd ¹⁶ O, ¹⁵¹ Eu ¹⁹ F, ¹⁷⁰ Er, ¹⁶⁹ TmH, ¹⁶⁸ YbH ₂ , ¹⁷⁰ Yb

Table 2

¹⁵²Sm ion currents produced by various Sm cathode materials. All cathodes contained Nb powder to improve electrical and thermal conductivity.

Cathode Ion	SmF ₃				Sm ₂ O ₃		Sm ₂ O ₃ + CaF ₂
	Sm [−]	SmH [−]	SmF [−]	SmF ₃ [−]	Sm [−]	SmO [−]	SmF [−]
Current (nA)	~1	<10	300	<10	~1	~30	~30

The sesquioxide Sm₂O₃ would seem to be a good cathode material since it is relatively inert and easy to make. Lanthanide oxides are prepared by pyrolysis of insoluble lanthanide salts, often an oxalate, carbonate, nitrate, or sulphate [31]. Middleton observed unexpectedly poor current for SmO[−] using a solid samarium oxide cathode, however, and blamed it on ionizer poisoning [14]. Middleton suggested flowing O₂ gas over a metallic Sm target, similar to his approach with H₂, to improve source output [14]. The simple chemistry of samarium oxide warrants investigation as a cathode, despite gloomy predictions of source output. SmO[−] output from the LLNL source peaked at 30–50 nA, about 10% the output from SmF[−]. We did not observe ionizer poisoning as noted by Middleton [14], with robust SmF[−] currents produced after sputtering Sm₂O₃ targets for a couple hours.

Since the molecular form of the cathode is destroyed in the sputtering process, we investigated the use of Sm₂O₃ doped with a high purity fluoride salt as a cathode to produce SmF[−]. The oxide is easy to make at high purity and is relatively inert. It is also the starting material for the production of the fluoride. Mixing CaF₂, Sm₂O₃, and Nb metal at ratios of 1:1:1, 1:2:1, and 2:2:1 did produce some SmF[−], but currents were about the same as SmO[−].

Kinoshita et al. used a metallic target and an ECR source in their measurements of ¹⁴⁶Sm [32]. A metallic target is not likely to produce a good Sm[−] beam. Middleton also observed very low Sm[−] output, with hydrides producing much larger current, even when there was no H₂ gas feed [14]. We observed Sm[−] currents of only 1–2 nA from both SmF₃ and Sm₂O₃ targets. The metal does not seem to be a promising target material for a negative ion source.

3. Spectrometer operation

Spectrometer operational parameters will depend in part upon the quality and identity of the ion beam produced by the source and will vary among AMS facilities. The large number of potential isobars (Table 1) presents challenges in obtaining a clean background for ¹⁴⁶Sm. Both ¹⁴⁹Sm and ¹⁵¹Sm will have relatively high concentrations in spent fuel, and will be amenable to current measurement in an off-axis Faraday cup. Based on the experience of Kinoshita et al. [32], it appears as though high energy and high positive charge state are needed to resolve ¹⁴⁶Sm from ¹⁴⁶Nd and other ions in the detector. But the ECR source and metal target may produce more interferences than a traditional AMS ion source.

It is likely that real applications will be sample limited, so measurement efficiency is an important consideration. The need to operate at a reasonably well-populated charge state to make measurements will need to be balanced against the need for energy separation in the detector. We calculated stripping yield for a variety of terminal potentials on the LLNL FN accelerator. Operating at a terminal voltage of 9 MV yields a 21% conversion to the +11 charge state. Many of potential isobar and lighter ion scattering interferences can be removed through the use of the +11 charge state and multiple high energy (HE) filters. The specific operational parameters will vary with facility.

4. Conclusions

¹⁴⁶Sm AMS is likely a niche measurement capability, requiring reasonable measurement efficiency due to limited samples but without the need for high sample throughput. TIMS and ICP-MS can routinely measure stable Sm isotopes now, often at part per million concentrations. Our modeling indicates that the limited production of ¹⁴⁶Sm over a wide dynamic range will produce isotopic ratios beyond measurement capabilities of these techniques and will require AMS. As in most new applications of AMS, sample chemistry is probably more of a challenge than spectrometer operation. Of the potential target materials, SmF₃ seems most promising from ease of preparation and negative ion production. We believe the potential usefulness of the measurement warrants the development of ¹⁴⁶Sm/¹⁴⁹Sm and ¹⁴⁶Sm/¹⁵¹Sm AMS.

Acknowledgements

Support was provided by HDTRA1-08-1-0032. This work performed in part under the auspices of the US Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

References

- [1] S.M. Whitney, S. Biegalski, B. Buchholz, Nucl. Sci. Eng. 157 (2007) 200.
- [2] U.P. Jenquin, R.J. Guenther, Trans. Am. Nucl. Soc. 61 (1990) 76.
- [3] T. Adachi et al., J. Nucl. Sci. Technol. 31 (1994) 1119.
- [4] C. Pin, P. Telouk, J. Imbert, J. Anal. Atom. Spectrom. 10 (1995) 93.
- [5] H. Isnard, R. Brennetot, C. Caussignac, N. Caussignac, F. Chartier, Int. J. Mass Spectrom. 246 (2005) 66.
- [6] S.F. Wolf, D.L. Bowers, J.C. Cunnane, J. Radioanal. Nucl. Chem. 263 (2005) 581.
- [7] I. Günther-Leopold, N. Kivel, J.K. Waldis, B. Wernli, Anal. Bioanal. Chem. 390 (2008) 503.
- [8] F.H. Spedding, E.I. Fulmer, T.A. Butler, E.M. Gladrow, M. Gobush, P.E. Porter, J.E. Powell, J.M. Wright, J. Am. Chem. Soc. 69 (1947) 2812.
- [9] Y. Marcus, F. Nelson, J. Phys. Chem. 63 (1959) 77.
- [10] S. Maji, S. Lahiri, B. Wierczinski, G. Korschinek, Analyst 131 (2006) 1332.
- [11] J.M. Schwantes, R.S. Rundberg, W.A. Taylor, D.J. Viera, J. Alloys Compd. 418 (2006) 189.
- [12] C. Pin, J.F.S. Zalduegui, Anal. Chim. Acta 339 (1997) 79.
- [13] F. Luo, D.Q. Li, Y.L. Wu, Solvent Extr. Ion Exch. 22 (2004) 105.
- [14] R. Middleton, A Negative Ion Cookbook, University of Pennsylvania, Philadelphia, 1989.
- [15] C.E. Messer, M.K. Park, J. Less-Common Met. 26 (1972) 235.
- [16] O. Greis, P. Knappe, H. Müller, Solid State Chem. 39 (1981) 49.
- [17] M. Ouwerkerk, Solid State Ionics 113 (1998) 431.
- [18] P. Kumar, L.K. Malhotra, Thin Solid Films 491 (2005) 270.
- [19] T. Dube, S. Gambarotta, G.P.A. Yap, Organometallics 19 (2000) 817.
- [20] I. Castillo, T.D. Tilley, J. Am. Chem. Soc. 123 (2001) 10526.
- [21] T. Liu, Y.H. Zhang, H.Y. Shao, X.G. Li, Langmuir 19 (2003) 7569.
- [22] G. Korschinek, J. Sellmair, A. Urban, M. Müller, Nucl. Instr. Meth. A 271 (1988) 328.
- [23] R.L. Fitzgerald, D.J. Hillegonds, D.W. Burton, T.L. Griffin, S. Mullaney, J.S. Vogel, L.J. Deftos, D.A. Herold, Clin. Chem. 51 (2005) 2095.
- [24] S.P.H.T. Freeman, R.E. Serfass, J.C. King, J.R. Southon, Y. Fang, L.R. Woodhouse, G.S. Bench, J.E. McAninch, Nucl. Instr. Meth. B 99 (1995) 557.
- [25] S.J. Tumey, T.A. Brown, T.F. Hamilton, D.J. Hillegonds, Nucl. Instr. Meth. B 266 (2008) 2242.
- [26] O.N. Carlson, F.A. Schmidt, in: F.H. Spedding, A.H. Daane (Eds.), The Rare Earths, John Wiley & Sons, New York, 1961, pp. 77–88.
- [27] A.H. Daane, F.H. Spedding, J. Electrochem. Soc. 100 (1953) 442.
- [28] J.H. Melman, T.J. Emge, J.G. Brennan, Inorg. Chem. 40 (2001) 1078–1081.
- [29] B.V. Strizhkov, E.D. Ruchkin, V.S. Krikorov, V.A. Pchelkin, L.S. Nikitenko, D.A. Khromov, Inorg. Mater. 8 (1972) 1258.
- [30] J. Southon, M. Roberts, Nucl. Instr. Meth. B 172 (2000) 257.
- [31] N.E. Topp, The Chemistry of the Rare-Earth Elements, Elsevier Publishing Company, London, 1965, p. 85.
- [32] N. Kinoshita et al., J. Phys. G: Part. Phys. 35 (2008) 014033 (7 pp).