PNNL-37182

ICP-MS For Analysis of Lithium Isotopic Ratios in Materials Highly Enriched in 7Li (CRADA 626) Final Report

December 2024

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

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Cooperative Research and Development Agreement (CRADA) Final Report

Report Date: December 2024

In accordance with Requirements set forth in the terms of the CRADA, this document is the CRADA Final Report, including a list of Subject Inventions, to be provided to PNNL Information Release who will forward to the DOE Office of Scientific and Technical Information as part of the commitment to the public to demonstrate results of federally funded research. **PNNL acknowledges that the CRADA parties have been involved in the preparation of the report or reviewed the report.**

Parties to the Agreement:

Pacific Northwest National Laboratory, Kairos Power

CRADA number: 626

CRADA Title: ICP-MS For Analysis of Lithium Isotopic Ratios in Materials Highly Enriched in ^{7}Li

Responsible Technical Contact at DOE Lab(PNNL): Sean Scott

Name and Email Address of POC at Partner Company(ies): Johnny Williams (jwilliams@kairospower.com)

Sponsoring DOE Program Office(s): NE

Joint Work Statement Funding Table showing DOE funding commitment:

	Funding Amounts			
CRADA Parties	**DOE Funding**	**Funds-In**	***In-kind**	**Total**
Participant(s)			77,000	77,000
DOE Funding to PNNL	205,000	205,000	N/A	205,000

Total of all Contributions	205,000	205,000	77,000	282,000

Provide a list of publications, conference papers, or other public releases of results, developed under this CRADA:

Publications

1. Scott, S.R., Williams, J., Mastromarino, A., Gajos, N., Berry, C., Anderson, I., Shen, S., Graham, T.R., Hexel, C., Wimpenny, J., Brookhart, J., Kruizenga, A. 2024. Round-robin analysis of highly depleted lithium for Generation IV nuclear reactor applications. Nuclear Engineering and Design, v. 429 (1) doi.org/10.1016/j.nucengdes.2024.113664

2. Hobbs, K., Scott, S.R., Williams, J., Mastromarino, S., Gajos, N., Berry, C., Anderson, I., Melby, K., Kruizenga, A. *in review*. Lithium isotopic analysis in depleted lithium salts. Progress in Nuclear Energy

3. Scott, S.R., Turner, G., Gartman, B., Alcantar Anguiano, S., Melby, K., Allen, B., Minton, T., RisenHuber, M., Hobbs, K. *in review*, Lithium isotope analysis on the Neoma MS/MS MC-ICP-MS. Journal of Analytical Atomic Spectrometry

4. Scott, S.R., Williams, J., Mastromarino, S. 2024. Mass spectrometry analysis of lithium in FLiBe. Transactions, American Nuclear Society, v. 130 (1), 395-397. doi.org/10.13182/T130-44793

Provide a detailed list of all subject inventions, to include patent applications, copyrights, and trademarks:

No subject inventions were generated under this CRADA.

Executive Summary of CRADA Work

The intent of this project was to determine appropriate methodologies for analysis of lithium isotopes for 1) quasi-online monitoring of isotope separations, and 2) high-precision characterization of end-products, including lithium fluoride and lithium-beryllium fluoride (FLiBe). Traditionally, isotopic analysis requires the use of expensive, sophisticated instrumentation with often relatively long analytical timelines. We determined that the use of cheaper, smaller, and easier-to-operate instruments are sufficient for rapid analysis of lithium isotopes to monitor isotope separation efficiencies. In addition, we found that the analytical precision afforded by these lower-cost instruments is comparable to the more sophisticated (i.e., more expensive) instrumentation when the isotopic composition of lithium becomes highly depleted in ^{6}Li. This finding will ultimately help lower costs of manufacturing of depleted lithium that is required for operation of certain designs of Generation IV nuclear reactors.

Technical note: Typical nomenclature for non-natural lithium describes “enriched” lithium as containing unnaturally high abundances of ^{6}Li, and “depleted” lithium as containing unnaturally high abundances of ^{7}Li.

Summary of Research Results

The statement of work (SOW) for this project included three milestones; 1) development of sample preparation and sample introduction methodologies, 2) evaluation of quadrupole inductively coupled plasma mass spectrometry (Q-ICP-MS) performance and optimization of methods for rapid turnaround, and 3) determine accuracy and precision of multi-collector (MC-) ICP-MS for QA/QC of enriched lithium. Below each milestone is addressed individually:

Development of sample preparation and sample introduction methodologies

The goal of this milestone was to determine the appropriate sample preparation methodologies for liquid and solid salt materials into the inductively coupled plasma mass spectrometer. Salt digestions were completed using dilute (5 %) nitric acid. We determined that liquids and digested salts could be diluted directly into a 2 % - 3 % nitric acid solution for analysis. This was possible on both Q- and MC-ICP-MS. On a Q-ICP-MS, the samples are diluted to maintain counting rates below the analog/pulse counting threshold. This was generally achieved at lithium concentrations in solution of ~1 ppb. Dilution factors were large, minimizing any potential matrix effects from the original solutions. On a MC-ICP-MS, the use of a desolvating nebulizer system and high sensitivity cone geometries allowed for high precision isotopic measurements at Li concentrations in solution of ~ 6 ppb. Like the Q-ICP-MS, this dilution factor minimized any potential matrix effects from the original solutions. The use of high resistance amplifiers (10^{13} Ohm) allowed for low noise measurements of the small ^{6}Li ion beam on Faraday cups. Details on this methodology were provided in two publications in *Nuclear Engineering and Design* (PNNL-SA-197586) and *Progress in Nuclear Energy* (PNNL-SA-204446).

Evaluation of Q-ICP-MS performance and optimization methods for rapid turnaround

During the first half of the project timeline, most testing occurred on a ThermoFisher iCAP TQ ICP-MS. We determined that alpha factors, which measures the difference in isotopic composition between two streams, could be determined in < 1 hour. Further recommendations included minimizing standard and blank analyses that could potentially reduce alpha factor determinations down to ~ 10 minutes. Combined with direct dilution, this methodology can provide quasi-online monitoring for isotope separation processes. To test the accuracy of this method, alpha factors were determined on stream pairs using the iCAP TQ, and these values were compared to alpha factors determined in the same samples by MC-ICP-MS. The timeline required to determine a “high-precision” alpha factor was on the order of 3 hours by MC-ICP-MS. This is due to the more stringent requirements for closely monitoring instrumental background levels and mass bias drift to produce high-precision isotopic data. Details associated with these tests were provided to Kairos Power in a limited release report (PNNL-SA-199816).

Later in the project, PNNL acquired a PerkinElmer NexION5000 multi-quadrupole (MQ-) ICP-MS, which is the same instrument used by Kairos Power in their laboratory facilities. Thus, additional tests were completed on this instrument to provide recommendations to Kairos Power on how their own instrument should be operated. The NexION5000 is equipped with an electronic dilution function that allows for attenuation of individual ion beams. For lithium with isotopic compositions far outside of the natural range, the much larger ^{7}Li beam can be attenuated. The benefit of this function is that lithium can be measured at higher concentrations, increasing the beam intensity of ^{6}Li to improve precision, while electronically attenuating the ^{7}Li beam to remain within the pulse counting threshold of the detector. The details on this analytical methodology are contained within the publication currently in review in *Progress in Nuclear Energy* (PNNL-SA-204446).

Determine accuracy and precision of MC-ICP-MS for QA/QC of enriched lithium

The new design of the Neoma MS/MS MC-ICP-MS raises additional challenges associated with analysis of lithium isotopes. Because lithium is a light element, the MS/MS portion of the instrument, equipped with a double Wien mass filtering system, causes large spreading of the lithium-ion beams through the first Wien filter before re-collimating through the inversion lens. To first determine the accuracy and precision afforded by the newly designed Neoma MS/MS, we determined lithium isotopic ratios in several reference materials with well characterized lithium isotopic compositions in the literature. Most of this work was completed under a different sponsor, however, learning the basic operation of the Neoma MS/MS fell under the scope of the CRADA as well. A manuscript containing details on the analytical methodologies, including a demonstration of accuracy for materials with nominally natural lithium isotopic abundances, is currently in review in *Journal of Analytical Atomic Spectrometry* (PNNL-SA-204992).

The accuracy and precision of MC-ICP-MS for quality assurance and quality control of lithium enriched in ^{7}Li was determined through multiple tests. First, the ^{7}Li Isoflex material characterized in the round robin exercise published in *Nuclear Engineering and Design* (PNNL-SA-197586) was measured on several MC-ICP-MS instruments, including the Neoma MS/MS. This measurement was also completed by thermal ionization mass spectrometry (TIMS), which is traditionally the “gold standard” for many isotopic analysis applications. We determined that the value and overall uncertainty of ^{7}Li abundance in this material was 99.9573 ± 0.0023 % and demonstrated that good agreement between different instruments was achieved.

Additional measurements were completed on three commercially available ^{7}Li-enriched Li salts (LiOH, LiCl, and LiF) using three different instruments (ThermoFisher Triton TIMS, ThermoFisher Neoma MS/MS MC-ICP-MS, and PerkinElmer NexION5000 MQ-ICP-MS). Comparison of results from these experiments allowed for determination of accuracy and precision afforded by the different instruments. Across instruments, precision (reported as the standard deviation) on the abundance of ^{7}Li was generally < 0.001 %, and absolute ^{7}Li abundances agreed to within 0.002 %, which is similar to the overall uncertainty reported for the ^{7}Li Isoflex material measured in the multi-laboratory study. Results were achieved using multiple reference materials for fractionation corrections, including LSVEC, IRMM-016, and ^{7}Li Isoflex, showing that data are accurate regardless of the choice of reference material. Results also showed that the best data on the Neoma MS/MS was achieved using a desolvating nebulizer and a 10^{13} Ohm resistor for ^{6}Li. The NexION5000 produced the best data when ion beams were maintained below the pulse/analog threshold, which can be accomplished using the electronic dilution function on ^{7}Li. Thus, these tests on the ICP-MS instruments provided additional insights for tasks 1 and 2 of the SOW.

The final test of analytical methodologies developed under this CRADA was to measure Li isotopic abundances in FLiBe (lithium-beryllium fluoride) that is the primary coolant in the Kairos Power Fluoride Salt Cooled High Temperature Reactor (KP-FHR). Kairos Power was able to provide several FLiBe samples from an engineering test unit (ETU), a full-scale non-radioactive testing module for their Hermes low power reactor. FLiBe from the ETU contained nominally natural Li isotopic abundances (^{7}Li from 92.4645 to 92.4583 %, Table 1), which was confirmed with measurements on the Neoma MS/MS. NIST924a was measured during the ETU

FLiBe run for quality control and returned $^{6}Li/^{7}Li$ = 0.082279 ± 0.000004, within the expanded uncertainty of NIST924a from the round robin study ($^{6}Li/^{7}Li$ = 0.08223 ± 0.00013). Subsequently, Kairos Power produced new FLiBe made from commercially available materials containing ^{7}Li-enriched lithium. This FLiBe, along with ^{7}Li-enriched LiOH and LiF salts were measured on the Neoma MS/MS and the NexION5000. These materials were measured using the ^{7}Li Isoflex material as the primary bracketing standard to reduce the impacts of instrumental background from natural Li. Results indicated that the Li maintains the enriched isotopic composition during manufacturing of the FLiBe salt (Tables 2 and 3). The ^{7}Li IsoFlex material analyzed relative to itself on the Neoma MS/MS gave $^{6}Li/^{7}Li$ = 0.0004281 ± 0.0000008, within the expanded uncertainty of the round robin value ($^{6}Li/^{7}Li$ = 0.000428 ± 0.000023). Abundances of ^{7}Li in the FLiBe agreed between the Neoma MS/MS and NexION5000 to within 0.0004 %. Analysis of the ^{7}Li-enriched FLiBe demonstrated the ability of both MC-ICP-MS and Q-ICP-MS to measure Li isotopic compositions accurately and precisely in this material, which completed the scope of the project work.

Table 1. Li isotopic compositions of FLiBe from the Kairos Power ETU

Vial	Sample	$^{6}Li/^{7}Li$	SD	% ^{7}Li	SD
Flibe 1C	P2-112-3 Ref	0.081568	0.000003	92.4583%	0.0003%
Flibe 3C	ETU1-RV-10 A	0.081525	0.000004	92.4621%	0.0004%
Flibe 4C	ETU1-RV-10 B	0.081545	0.000005	92.4603%	0.0004%
Flibe 5C	ETU1-RV-11 A	0.081533	0.000006	92.4614%	0.0005%
Flibe 6C	ETU1-RV-11 B	0.081538	0.000003	92.4609%	0.0002%
Flibe 7C	ETU1-RV-12 A	0.081557	0.000009	92.4593%	0.0008%
Flibe 8C	ETU1-RV-12 B	0.081548	0.000010	92.4600%	0.0008%
Flibe 9C	ETU1-RV-13 A	0.081536	0.000009	92.4611%	0.0008%
Flibe 10C	ETU1-RV-13 B	0.081496	0.000006	92.4645%	0.0005%
Flibe 11C	ETU1-RV-14 A	0.081528	0.000005	92.4618%	0.0004%
Flibe 13C	ETU1-RV-15 A	0.081529	0.000003	92.4617%	0.0003%

All samples measured in triplicate with uncertainties reported as the standard deviation (SD) of the three measurements.

Table 2. Li isotopic compositions of salts and ^{7}Li-enriched FLiBe measured on the Neoma MS/MS

Vial	Sample	$^{6}Li/^{7}Li$	SD	% ^{7}Li	SD
LiOH 1	LiOH	0.0004528	0.0000024	99.95474%	0.00024%
LiOH 2	LiOH	0.0004561	0.0000005	99.95441%	0.00005%
LiF 1	2410-LiF-1	0.0004505	0.0000011	99.95497%	0.00011%
LiF 2	2410-LiF-1	0.0004503	0.0000011	99.95499%	0.00011%
Flibe 1	KP-Flibe-66	0.0004566	0.0000003	99.95436%	0.00003%
Flibe 2	KP-Flibe-66	0.0004554	0.0000004	99.95448%	0.00004%

All samples measured in triplicate with uncertainties reported as the standard deviation (SD) of the three measurements.

Table 3. Li isotopic compositions of salts and ^{7}Li-enriched FLiBe measured on the NexION5000

Vial	Sample	^{6}Li/^{7}Li	SD	% ^{7}Li	SD
LiOH 1	LiOH	0.0004575	0.0000024	99.95427%	0.00024%
LiOH 2	LiOH	0.0004557	0.0000009	99.95445%	0.00009%
LiF 1	2410-LiF-1	0.0004582	0.0000004	99.95420%	0.00004%
LiF 2	2410-LiF-1	0.0004561	0.0000033	99.95441%	0.00033%
Flibe 1	KP-Flibe-66	0.0004602	0.0000011	99.95400%	0.00011%
Flibe 2	KP-Flibe-66	0.0004591	0.0000007	99.95411%	0.00007%

All samples measured in triplicate with uncertainties reported as the standard deviation (SD) of the three measurements.

Additional work

At the request of Kairos Power, Nuclear Magnetic Resonance (NMR) analyses were performed on the lithium hydroxide material that was characterized in the round-robin study that was published in *Nuclear Engineering and Design* during this project (PNNL-SA-197586). Details on the analytical procedures associated with these analyses were provided in the publication. Using the standard addition method, the lower limit for isotopic composition measured by NMR was determined at ^{6}Li/^{7}Li of ~0.001. The mass spectrometry analyses of this material determined a ^{6}Li/^{7}Li value of 0.000428 ± 0.000023.

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