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APPLICATION NOTE

LIBS DIAGNOSTICS OF MOLTEN SALT REACTOR OFF-GAS STREAMS: BROADBAND AND ISOTOPIC ANALYSIS ENABLED BY AVANTES SPECTROMETERS

INTRO

LIBS DIAGNOSTICS OF MOLTEN SALT REACTOR OFF-GAS STREAMS: BROADBAND AND ISOTOPIC ANALYSIS ENABLED BY AVANTES SPECTROMETERS

Molten Salt Reactors (MSRs) represent a next-generation nuclear technology that promises enhanced safety, improved economics, and carbon-free energy production. Unlike conventional solid-fueled reactors, MSRs use liquid fuel dissolved in a high-temperature molten salt coolant, typically fluoride or chloride salt mixtures containing fissile materials. This liquid fuel circulates continuously in the primary loop, undergoing fission and producing a complex mix of fission products, some of which volatilize or aerosolize into the gas phase[1].

Real-time monitoring of molten salt chemistry and off-gas composition is critical to reactor safety and efficiency. However, challenges arise due to extreme operating conditions—high temperature, corrosiveness, and the mobility of radioactive species—can complicate traditional analytical measurement techniques. Historically, gamma spectroscopy was used during early MSR experiments to monitor fission gases, but high background signals in complex gas streams limited accuracy.

Recent advances by researchers at **Oak Ridge National Laboratory (ORNL),** supported by the **U.S. Department of Energy's Office of Nuclear Energy (DOE-NE),** have identified Laser-Induced Breakdown Spectroscopy (LIBS) as a promising alternative for real-time, remote elemental and isotopic monitoring in molten salt environments. LIBS offers rapid, sensitive detection of multiple elements and isotopes simultaneously without direct contact with the hazardous medium[2].

This application note details a study employing a modular LIBS system incorporating Avantes multichannel spectrometers to characterize molten salt aerosols. The system successfully detected key elements (Na, K, N, O, H) and resolved hydrogen isotopes (protium and deuterium), providing new insight into salt–gas interactions relevant for MSR operation and safety.

OBJECTIVE

The goal was to develop a LIBS-based diagnostic platform capable of:

- Broadband elemental identification in aerosolized molten salt samples, including sodium, potassium, nitrogen, and oxygen.
- Real-time hydrogen isotope discrimination (protium vs. deuterium) via spectral line shifts in the Hα Balmer line (~656.3 nm)
- High-speed, multi-spectral data acquisition using a combination of spectrometers synchronized for optimal performance.

An Avantes' 6-channel multichannel spectrometer was integrated into a modular LIBS system to provide fast, simultaneous spectral coverage over a broad wavelength range, complementing high-resolution spectrometers for isotopic analysis[1].

EXPERIMENTAL SETUP

A modular LIBS platform was assembled to analyze aerosol streams generated by sparging a $NaNO_3$–KNO_3 eutectic salt heated to ~350 °C within a stainless-steel vessel. Argon or hydrogen-based sparging produced aerosols were transported to a LIBS measurement cell approximately one meter away[1].

Spectrometers employed:

- Avantes 6-channel multichannel spectrometer: Provided broad, simultaneous elemental spectral coverage with high temporal resolution. The spectrometers used for the configuration were the AvaSpec-Mini2048 but these are now replaced by the **AvaSpec-NEXOS™.**
- EMU-165 echelle spectrometer: Enhanced detection of light elements like hydrogen and oxygen.
- DEMON high-resolution spectrometer: Resolved fine isotopic shifts in hydrogen emission lines.

All spectrometers were fiber-coupled and triggered synchronously at 20 Hz laser pulse repetition, with optimized delay and integration times per instrument.

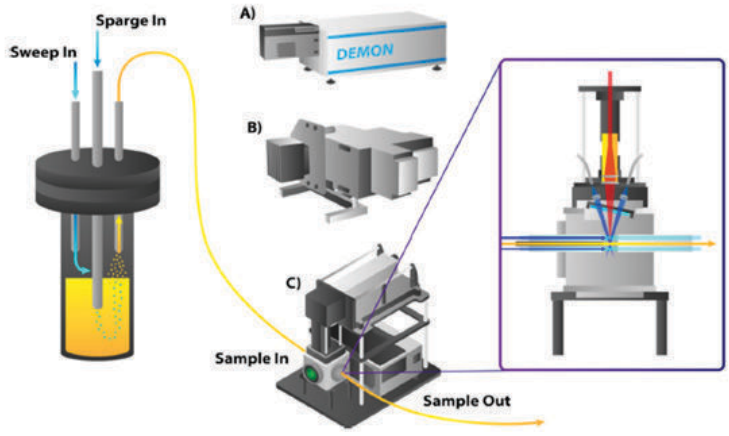


FIGURE 1 Schematic of LIBS system where C represents Avantes spectrometer multichannel module[1].

IMPORTANCE OF THE AVANTES MULTICHANNEL SPECTROMETER

The Avantes system was essential for:

Broadband elemental detection: The Avantes 6-channel multichannel spectrometer provided wide spectral detection, enabling clear identification of key salt constituents in the LIBS plasma emissions. This included[1]:

-Sodium (Na): Emission peaks observed at 588.99 nm and 589.59 nm.
-Potassium (K): Strong peaks at 766.49 nm and 769.90 nm.
-Nitrogen (N): Peak around 746.8 nm.
-Oxygen (O): Emission near 777.2 nm.
-Hydrogen (H): Peak at 656.28 nm.
-**Argon (carrier gas):** Dominant peaks, notably at 763.5 nm and 772.4 nm.

These emissions were verified against the NIST Atomic Spectral Database, ensuring accurate elemental identification.

Versatility and Reliability in Harsh Conditions: Deployed in a high-temperature, aerosol-based sampling environment simulating molten salt reactor off-gas streams, the Avantes spectrometer showed resilience and effectiveness in capturing accurate spectral data without requiring direct exposure to the extreme salt conditions—facilitated by the aerosol sampling approach.

High-speed, real-time monitoring: Recording plasma spectra at 20 Hz allowed visualization of elemental concentration changes during sparging cycles, crucial for dynamic gas diffusion studies.

Reference signal normalization: Its stable, wide-range response served as a reference baseline for interpreting the high-resolution DEMON isotope data, improving quantitative accuracy.

Modularity and integration: Compact fiber-coupled design enabled seamless synchronization with other spectrometers, creating a versatile hybrid LIBS platform.

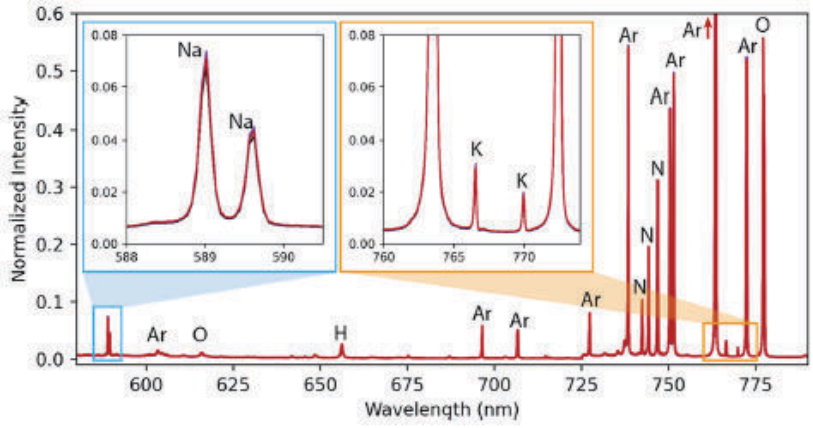


FIGURE 2 LIBS spectra showing simultaneous detection of Na, K, H, and O emission lines using the Avantes multichannel system[1].

RESULTS AND PERFORMANCE

The LIBS system successfully detected elemental signatures of sodium, potassium, nitrogen, oxygen, and hydrogen within molten salt aerosols in real-time. Hydrogen isotope shifts between protium and deuterium (~178 pm difference) were clearly resolved, marking a novel demonstration of LIBS for in situ isotope discrimination in molten salt environments[1].

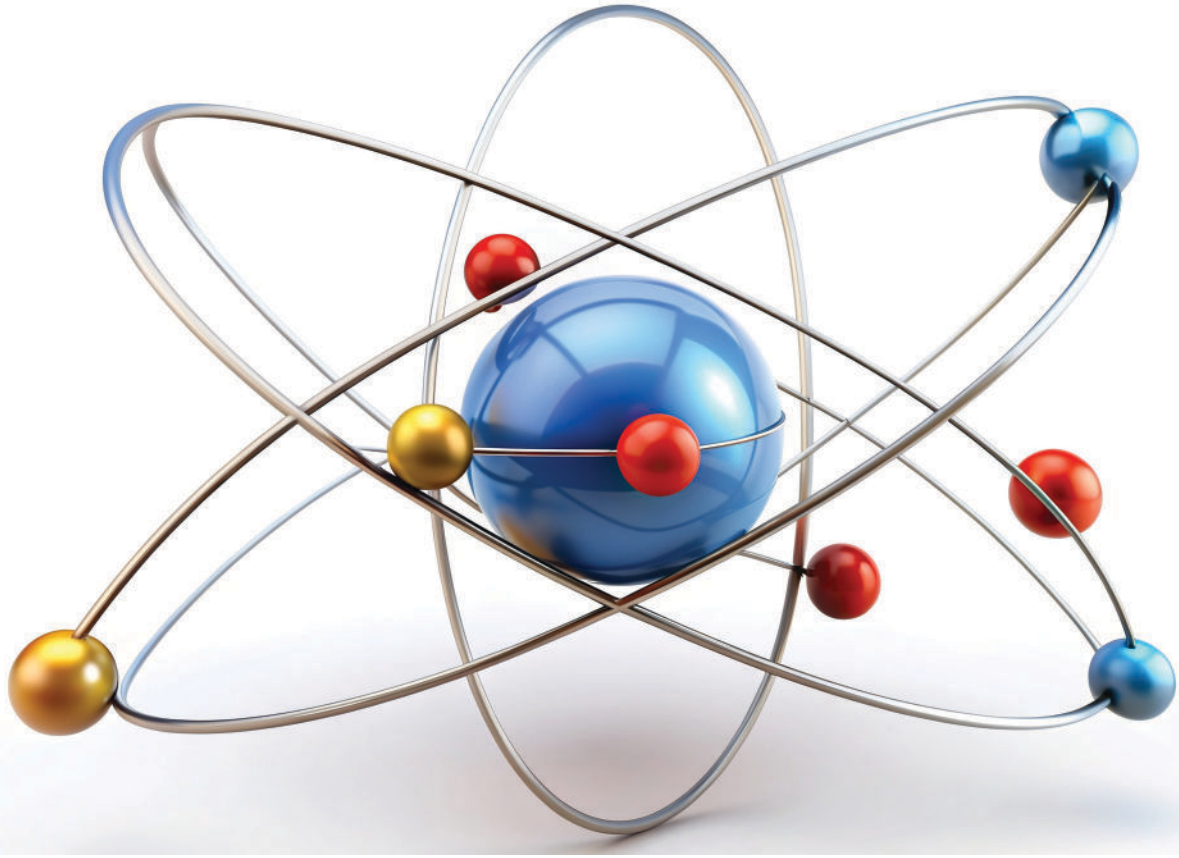
Continuous multi-spectral acquisition enabled dynamic monitoring of salt–gas interactions, providing critical insights into fission product behavior, gas retention, and impurity transport relevant for MSR off-gas monitoring and safety[1].

CONCLUSION AND OUTLOOK

This study, conducted at Oak Ridge National Laboratory and supported by the U.S. Department of Energy, demonstrates that a LIBS platform incorporating Avantes multichannel spectrometers enables real-time, non-radiometric monitoring of molten salt reactor environments. The system provides rapid elemental and isotopic information with high temporal resolution, advancing molten salt process diagnostics.

FUTURE WORK

Efforts are underway to optimize LIBS detection of impurities in molten salt aerosols and develop real-time off-gas monitoring models for engineering-scale MSR testbeds. The ultimate goal is to deploy LIBS sensors in commercial molten salt reactors for enhanced operational safety and performance.[2]



RECOMMENDED AVANTES CONFIGURATIONS

Avantes offers a variety of spectrometer options which are suitable for LIBS. The **AvaSpec-NEXOS™** (Figure 3) is comparable to the instruments used in this application. The range of this spectrometer is from 190-1100 nm with resolution as high as 0.08 nm (FWHM). This spectrometer is sold as individual, independent modules which can be joined together with interface cables from Avantes. Also available is the **AvaSpec-VARIUS™** (Figure 4) which covers the same range and resolution specifications (190-1100 nm & 0.07 nm resolution). Avantes also has a popular configuration of multi-channel spectrometers (Figure 5 & 6) which are housed in a single enclosure allow for improved interoperability between the spectrometers. Currently the multi-channel spectrometers are only available with the **AvaSpec-ULS2048CL-EVO** and **AvaSpec-ULS4096-EVO** models both of which are well suited to the LIBS application.

FIGURE 3 AvaSpec-NEXOS™ Spectrometer

FIGURE 4 AvaSpec-VARIUS™ Spectrometer

FIGURE 5 Example of an Avantes 8-channel Multichannel Rackmount

FIGURE 6 Example of an Avantes 4-channel Multichannel Rackmount

REFERENCES

1) Andrews, H. B., Kitzhaber, Z. B., Orea, D., & McFarlane, J. (2024). Real-time elemental and isotopic measurements of molten salt systems through laser-induced breakdown spectroscopy. Journal of the American Chemical Society. https://doi.org/10.1021/jacs.4c13684

2) U.S. Department of Energy, Office of Nuclear Energy. (2024, June 10). National lab develops new way to monitor molten salts. https://www.energy.gov/ne/articles/national-lab-develops-new-way-monitor-molten-salts

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