Application Note

SPORIAN® MICROSYSTEMS, INC

High-Temperature Raman Spectroscopy for Molten Nitrate Salt Mixture Monitoring

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Introduction

Molten nitrate salts are an important class of fluids for a range of high-temperature applications, including: electrolytics, metal processing, heat storage/transfer fluids for concentrating solar power (CSP) and nuclear energy, and ion-exchange chemical glass strengthening. These kinds of technologies require operation at temperature ranges for which molten salts are particularly suited due to their main characteristics: stability at molten temperatures (> 240°C), low vapor pressure, and high heat capacity.

However, maintaining salt composition control can be a challenging issue. For example, molten salt chemical strengthening methods for glass have received a great deal of attention in recent years since the display industry adopted the cover glass to protect portable devices. Significant process development has been performed to get a high compressive stress and a deep ion-exchange layer by tailoring the glass compositions and optimizing process factors such as exchange time, temperature, salt composition, impurities, and process conditions [1,2,3].

Real-time molten salt composition monitoring would be of significant value for molten-salt-based process control. There are few technical options for in-situ, high-temperature-immersed, harsh environment tolerant, real-time monitoring that can provide chemical composition information, and most can only provide partial compositional data.

Raman spectroscopy is a powerful analytical technique that quickly gives highly specific information for the analysis of chemical compounds and can be used for multi-compound analysis. Raman-active species exhibit spectra with distinct peaks and provide "fingerprint" information on the vibrational transitions within a molecule. This feature makes Raman spectroscopy ideal for implementing a robust, automated, molecular identification system.

In this application note, we'll explore the use of a high-temperature-operable Raman spectroscopy monitoring instrument for the identification and quantification of molten nitrate mixtures.

Experiment/Methods

Data presented here was collected using a Sporian Microsystems SpecIQ™ High-Temperature Raman Fluid Composition Monitoring System. The Raman-spectroscopy-based measurement system has the capability to provide in-situ, real-time monitoring of various molten salts in systems such as those used in CSP, nuclear power, fossil fuel energy storage, materials synthesis/processing, and metal making/finishing.

Key system specifications are shown in Table 1, and the system is designed to operate in one of two possible modes: (1) as an autonomous monitoring device that measures and applies machine-learning-based algorithms to provide classification of salt constituents and quantified concentrations to higher level control systems, and (2) as a user operated instrument with specific feature/function control options.

Nitrate salt reagents were purchased from Sigma Aldrich, and included sodium nitrate (ReagentPlus ≥ 99.0%) and potassium nitrate (ReagentPlus ≥ 99.0%). Mixtures were prepared by percent weight and ground with a mortar and pestle in a glove box under dry nitrogen to prevent water ingress/adsorption by the salts. Salt mixtures were melted in a quartz-lined, environmentally controlled crucible and heated to the desired temperature with an Ambrell precision induction heating system.

Table 1: Key SpecIQ™ specifications

Spec/Feature	Unit
Excitation Wavelength	532 nm
Wavenumber Range (Shift)	100-5400 cm^{-1}
Resolution	6 cm^{-1}
Communications	Ethernet
Measurement Temp. Used	25-500°C
Max Measurement Temp. Capable	950°C
Integration Times	100ms-1s

The setup included the capability to purge a dry gas through the system during operation. The high-temperature Raman probe hardware was inserted into the heat zone of the system such as to monitor the mixture when molten, at temperatures ranging from 240 to 500°C. The instrument was configured to measure and send data to a database file that could then be subsequently used to process/view resulting data.

One of the benefits of the Sporian Microsystems SpecIQ™ High-Temperature Raman Fluid Composition Monitoring System is its ability to provide very high dimensionality measurements by using many pixels to measure a broad spectral range, thereby enabling it to measure many different species within a sample. However, this poses a challenge in analyzing the data as there are many dimensions, or variables, to process.

All spectral data were processed and analyzed by performing a sequence of pre-processing, dimension reduction, and machine learning classification and/or regression. Preprocessing included the stabilization of signal fluctuations based on laser output and the removal of background signal. Then, principal component analysis (PCA) was performed to find the optimal variance in the data as well as transform the data and reduce the dimensionality. Using the optimized data, the data was then split into a train dataset and a smaller test dataset. A supervised machine learning model was implemented to train on the known dataset, analyzing their relationships. For simple identification of species, a classification model is used, and a regression model is used for quantitative species concentration predictions.

Results

Figure 1 shows the measured Raman spectra for potassium nitrate (KNO_3) and sodium nitrate ($NaNO_3$) at 400°C. All $NaNO_3$ Raman peaks are shifted 4 to 10 cm^{-1} to the right (higher energy) compared to KNO_3, except for the 1648cm^{-1} $NaNO_3$ peak assigned to the overtone of the out-of-plane bending nitrate fundamental which is shifted to the left (lower energy) compared to 1655cm^{-1} KNO_3 peak. These Raman shifts are expected with differing nitrate cations [4].

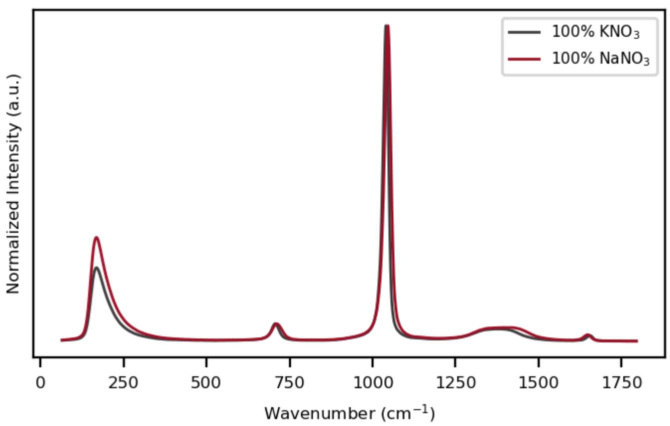

Figure 1: Raman Spectra of potassium nitrate (KNO_3) at 400°C and sodium nitrate ($NaNO_3$) at 400°C

Figure 2 shows the Raman shifts in the primary nitrate peak for a range of KNO_3/$NaNO_3$ mixture concentrations at 400°C. Such data can be used to train machine-learning-based models to predict mixture ratios of subsequent measurements and monitor changes over time. This is particularly useful in material synthesis applications, such as those that utilize nitrate ion exchange to tailor glass properties. Measurements of the salt composition during the submersion of the material in molten salts can provide a precise way to quantify and control process factors such as exchange time, temperature, salt composition, impurities, and process conditions to realize materials with the desired properties.

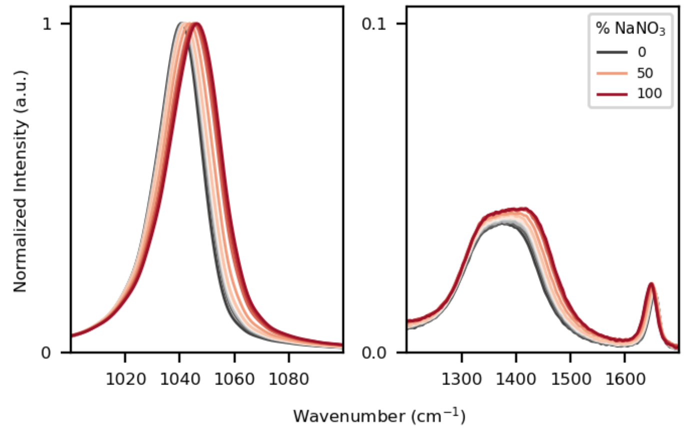

Figure 2: Raman spectra in a range of $NaNO_3$/KNO_3 concentrations at 400°C.

Figure 3 shows the regression analysis of the training data, which allows for the estimation of mixture concentration for subsequent measurements. The regression technique applied to the present data set was Support Vector Regression as it was able to fit nonlinearly with the processed data. The model was able to provide very accurate predictions as it was able to fit well with the trends in the molten salt mixtures data. The root mean squared error (RMSE) of the regression results was 1.13% $NaNO_3$, or one standard deviation of the error.

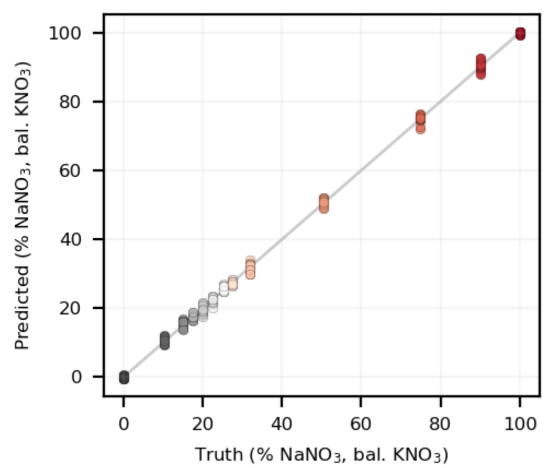

Figure 3: Multivariate regression analysis of the training data

Conclusions

Molten salts are a very challenging environment for chemical composition monitoring. Real-time molten salt composition monitoring is of significant value for industries using molten salts. Sporian Microsystems' high-temperature, real-time, Raman-spectroscopy-based measurement system is an effective tool to provide in-situ, real-time monitoring of various molten salts systems compositions, and to provide constituent and contaminant classification and quantification. Instruments capable of continuous monitoring in very harsh conditions and allowing for the use of machine-learning-based data processing are ideally suited for performing such measurements.

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[1] Lee, Hoikwan, et al. "Additive effect in salt bath for glass strengthening." Journal of the Ceramic Society of Japan 129.2 (2021): 122-125.

[2] LaCourse, William C. "Design of SLS Compositions for Accelerated Chemical Strengthening." 78th Conference on Glass Problems: Ceramic Engineering and Science Proceedings, Issue 1. Vol. 39. Hoboken, NJ, USA: John Wiley & Sons, Inc., 2018.

[3] Lyu, Xigeng, et al. "Effects of OH− anion additive concentration in nitrate salt baths on chemical strengthening of Li_2O–Al_2O_3–SiO_2 (LAS) glass." Ceramics International 46.2 (2020): 1697-1704.

[4] Janz, G. J., and James, D. W. "Raman Spectra and Ionic Interactions in Molten Nitrates." The Journal of Chemical Physics, 35.2 (1961): 739–745.