Application Note

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High-Temperature Raman Spectroscopy for Molten Salt Compositional Monitoring

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Introduction

Molten salts are an important class of fluids for a range of high-temperature applications, including: thermal energy storage and transfer fluids for concentrating solar power (CSP) and molten salt nuclear reactors (MSR), molten carbonate fuel cells (MCFC), electrolysis, metals or waste processing, and ion-exchange (IOX) chemical glass strengthening. This is due to the unique properties of molten salts as stable fluids over a wide range of temperatures, with low vapor pressures, and high heat capacities.

Eutectic salt blends have the benefit of very low melting points that are ideal for the most efficient use of molten salts. However, maintaining salt composition control of eutectics can be a challenge. 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 options 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 in a non-destructive manner. Raman-active species exhibit spectra with distinct peaks and provide "fingerprint" information on the vibrational transitions within a molecule by uniquely characterizing sample volumes in bulk. Raman systems are easily portable and can be transmitted by optical fibers over long distances for remote analyses.

These features make 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 a selection of molten salts as an example of applicable high-temperature systems.

Methods

Data presented here was collected using 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. 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.

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-^{1}s

All salt reagents were purchased from Sigma Aldrich with purity ≥ 99.0%. Salt mixtures and eutectics of interest are reported in Table 2. Each mixture was 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. 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 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.

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Table 2: Molten Salt Selection

Salt	Salt Composition	wt% Ratio	MP/Decomp Temp (°C) [1]	Interest [1,2]
Nitrates	$NaNO_3/KNO_3$	60/40	220/585	Main solar salt in CSP, minimal corrosion in air, but with decomposition at high temp
Brazes	Alu-braze-960	~20 LiCl/ ~10 NaF	~515/650	Good braze characteristics in air, but with decomposition at high temp
Chlorides	$MgCl_2/KCl$	35.6/64.4	423/>800	High temp HTF salt, corrosive
	$MgCl_2/KCl/NaCl$	55/20.5/ 24.5	383/>800	Lowest cost, low mp, high heat capacity of chlorides, corrosive
	$ZnCl_2/KCl/NaCl$	68.6/23.9/7.5	204/>800	Lower cost, lowest mp, but lowest heat capacity
Carbonates	$Li_2CO_3/Na_2CO_3/K_2CO_3$	32.1/33.4/34.5	398/800	Mainly used in MCFC, air stable, less corrosive, but more expensive salt
Sulfates	Li_2SO_4/K_2SO_4	90/10	~625/~900	Used in IOX, high mp
	KCl/K_2SO_4	54/46	~670/~900	Used in IOX, high mp

Using the optimized data, the data was then split into a training dataset and a smaller test dataset. A supervised machine learning model was implemented to train on the known dataset, analyzing its relationships. For simple identification of species, a classification model was used, and a regression model was used for quantitative species concentration predictions.

Results

Figure 1 shows the measured Raman spectra for a selection of molten salts at the reported high temperatures. Nitrates, carbonates, and sulfates are all highly Raman active (≥4 Raman peaks), with primary symmetric vibrational oxyanion stretches from 950 to 1050 cm^{-1} [3,4,5]. Chlorides are more weakly Raman active with subtle Raman peak shifts observed below 300 cm^{-1} [6]. While pure salts are mainly observed spectrally at ≤2000cm^{-1}, additional contaminants such as water and metal oxides may be seen out to 5400cm^{-1}. It should be noted that at temperatures above 725°C, blackbody radiation extends into the visible region of the electromagnetic spectrum, which may cause saturation of high energy Raman signals [7].

Figure 2 shows Raman spectra of nitrate and chloride molten salt mixtures with a range of percent weight concentrations for each salt type. 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 3 shows the regression analyses of the two sets of training data shown in Figure 2, both of which allow for the prediction of mixture concentration in subsequent measurements. A support vector regression model was able to provide accurate predictions as it was able to fit well with the non-linear trend in each of the molten salt mixtures data sets. The root mean squared error (RMSE) of the nitrate regression results is 1.13% and the chloride regression results is 0.93% as one standard deviation of the error.

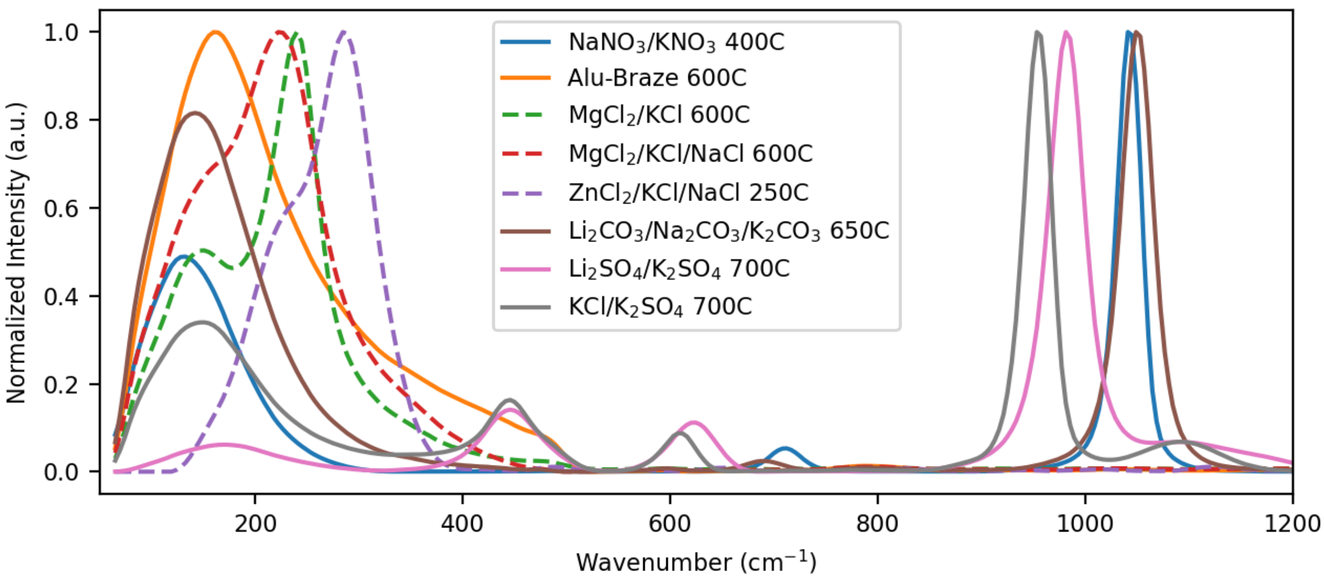

Figure 1: Raman spectra of molten salt mixtures measured at the high temperatures specified. Chloride salt spectra are shown in dashed lines for emphasis.

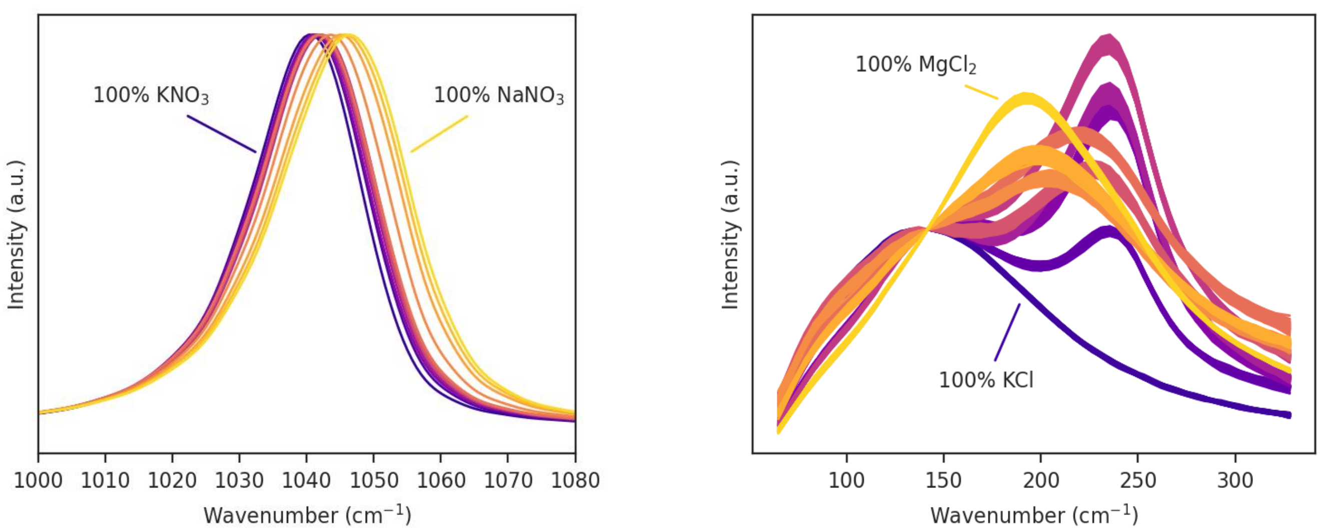

Figure 2: (left) Normalized Raman spectra of primary nitrate peak with a range of KNO_3/$NaNO_3$ mixtures. (right) Raman spectra of a range of $MgCl_2$/KCl mixtures, normalized to the KCl peak.

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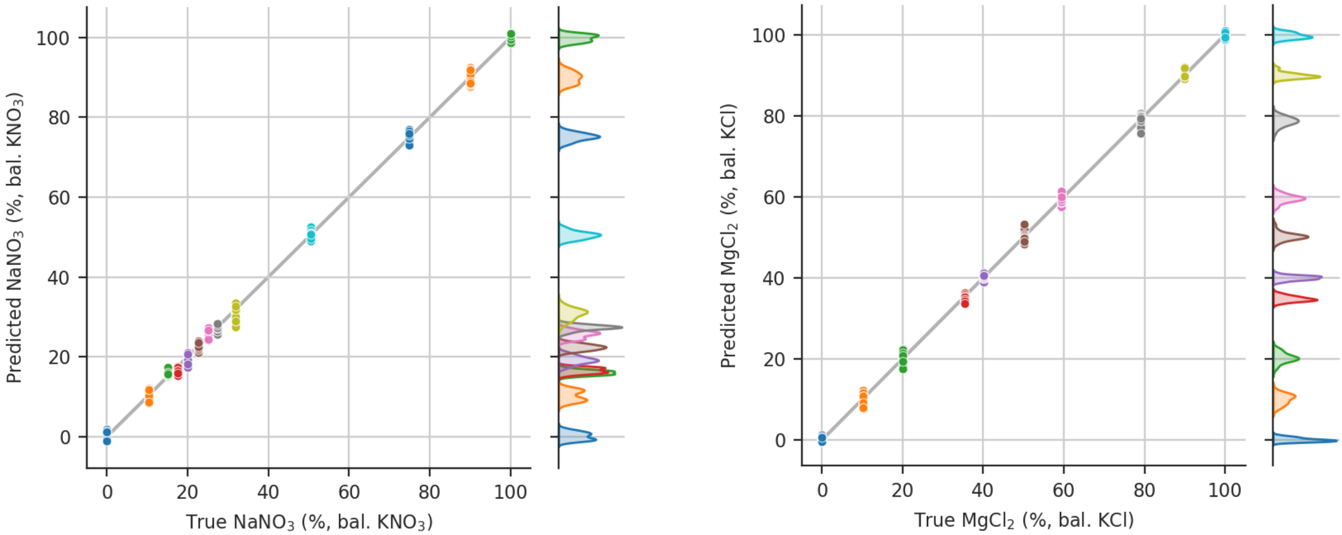

Figure 3: (left) Nitrate regression with RMSE =1.13% (right) $MgCl_2$/KCl regression with RMSE =0.93%

Conclusions

Molten salts make it challenging to be confident on precise chemical compositions. Sporian Microsystems SpecIQ™ High-Temperature Raman Fluid Composition Monitoring System is an effective tool to unambiguously monitor molten salt systems and provide constituent and contaminant classification and quantification. Instruments that are capable of continuous monitoring in harsh conditions and that allow for the use of machine-learning-based data processing are ideally suited for performing such measurements.

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[1] Turchi, C. S., Vidal, J. and Bauer, M. "Molten salt power towers operating at 600–650 °C: Salt selection and cost benefits." Solar Energy 164 (2018): 38-46.

[2] Beall, G. H., et al. "Ion-Exchange in Glass-Ceramics." Frontiers in Materials 3:41 (2016): 1-11.

[3] Janz, George J., et al. "Raman spectra and ionic interactions in molten nitrates." The Journal of Chemical Physics 35.2 (1961): 739-745.

[4] Bates, J. B. et al. "Raman Spectra of Molten Alkali Metal Carbonates." The Journal of Physical Chemistry 17.11 (1972): 1565–1571.

[5] Varghese, S., Subrahmanyam, A., and Hariharan, K. "Temperature-dependent Raman spectra of quenched lithium sulfate." AIP Conference Proceedings 2265 (2020): 030009.

[6] Brooker, M. H., and Huang, C.-H. "Raman spectroscopic studies of structural properties of solid and molten states of the magnesium chloride - alkali metal chloride system." Can J. Chem. 58. (1980): 168-179.

[7] Papatheodorou, G. N., Kalampounias, A. G., and Yannopoulos, S. N. "Raman Spectroscopy of High Temperature Melts. Molten Salts and Ionic Liquids," (2012): 301–340.

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