DEVELOPMENT OF A RAPID, NONDESTRUCTIVE METHOD TO MEASURE AQUEOUS CARBONATE AND PERCHLORATE IN HIGH SALINITY BRINES USING RAMAN SPECTROSCOPY.
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Introduction: Brines have been discovered on or near the surface of planetary bodies, in particular in the recurring slope lineae on Mars [1] and plumes on Enceladus [2]. Measuring solutes within these, including carbonate and perchlorate, will yield information about internal processes, paleoclimate, chemical weathering, and the hydrologic cycle [3]. Studying solutes in near-surface aqueous systems will help in assessing habitability and the possibility of both past and current life by determining the availability of nutrients [4].

Raman spectroscopy is an promising technique for measuring solutes in high salinity brines. Since Raman uses a laser to induce vibrations in the molecular bonds, no part of the instrument touches the brine, preventing both instrument corrosion and/or clogging and sample contamination. Raman spectroscopy also requires little to no sample preparation, so it can be used remotely on landers or rovers.

Methods: We prepared the samples by mixing sodium carbonate or sodium perchlorate standards, ranging in concentration from 0 M to 1 M, with endmember brines at a volumetric ratio of 1 part standard + 1 part brine. Carbonate standards were mixed with 20 wt% NaClO₄ brine, 23 wt % NaCl brine, and 3.8 wt % Na₂SO₄ brine. Perchlorate standards were mixed with 23 wt % NaCl brine, and 3.8 wt % Na₂SO₄ brine. We collected a spectrum for each sample using a green 100 mW diode laser with a Renishaw InVia Reflex Raman mapping microscope in streamline mode. The 532 nm laser was focused through a Leica 5x objective lens into the liquid sample in a watch glass or ceramic plate. We used a grating with 2400 grooves per centimeter. Spectra were collected at 100% laser power for 100 seconds – 300 seconds through multiple accumulations. The high power, long collection time, and multiple accumulations reduced noise and produced a signal of sufficient strength to accurately measure solutes in all three brines.

Using the WiRE4.2 software package, we processed the spectra by subtracting the baseline, then normalizing and truncating each spectrum to aid in comparing the spectra and increase resolution. To determine the peak heights, we modeled the modified spectra using WiRE4.2’s curve-fitting tool. Ratios of the 1066 cm⁻¹ carbonate peak height or the 935 cm⁻¹ perchlorate peak height to the 1640 cm⁻¹ water peak height were calculated. We created the calibration curves by plotting the peak height ratios against either carbonate or perchlorate known concentrations.

Results and Discussion: Calibration curves developed for all solute-brine combinations exhibit strong linear trends, with R² values above 0.98, demonstrating that Raman is a viable technique for analyzing solutes in high salinity brines.

Carbonate in brine analyses: As carbonate concentration changes, the height of the carbonate peak (1066 cm⁻¹) varies. A strong perchlorate peak occurs at 935 cm⁻¹ with a secondary peak at 1110 cm⁻¹, a strong sulfate peak occurs at 980 cm⁻¹ [5], and a water peak occurs at 1640 cm⁻¹. Since NaCl contains no covalent bonds, it is not detected [5]. The carbonate, sulfate, perchlorate, and water peaks do not interfere with each other and therefore were easily modeled. A strong linear trend in peak height ratios with changing carbonate concentration appears to be valid at all carbonate concentrations, but future work will further investigate both the sensitivity and detections limits of this method in measuring carbonate content in chloride, sulfate, and perchlorate brines.

Given further experimentation and testing, it is a promising method for measuring aqueous carbonate concentrations in the field.

Figure 1. Processed spectra of 0.1 M carbonate standard in sodium perchlorate brine.

Perchlorate in NaCl and Na₂SO₄ brines analyses: The dominant perchlorate peak (935 cm⁻¹) varies directly with perchlorate concentration in the standards and does not interfere with the sulfate (980 cm⁻¹) or water (1640 cm⁻¹) peaks. Perchlorate calibration curves in both brines exhibit strong linear trends with R² values of 0.9893 for sodium sulfate and 0.9933 for sodium.
chloride. This trend appears to be valid for all perchlorate concentrations, but again, further work will investigate detection limits and the sensitivity of this method.

Figure 2. Characteristic Raman spectra of 1 M perchlorate in sodium sulfate brine

**Implications and Future Work:** Initial results suggest that both carbonate and perchlorate can be detected, and their concentrations measured in high salinity brines using the Raman spectroscopy. This technique may prove useful in both terrestrial field work and planetary missions. In the immediate future, this technique could be employed using the Raman spectrometer on the ExoMars 2018 mission or SHERLOC on the Mars 2020 rover if brines are observed. Future work includes testing more solute-brine combinations, as well as determining the detection limits and sensitivity for all solute-brine combinations. Analysis of natural terrestrial brines with also further test the technique.


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