

RAMAN MEASUREMENT OF SOLUTE CHEMISTRY IN BRINES FOR REMOTE ANALYSIS OF PLANETARY FLUIDS. M. E. Elwood Madden¹, C. M. Phillips-Lander¹, J. W. Burkhart¹, J. R. Johnson¹, C. R. Kosemund¹, A. L. Lewis¹, B. S. Turner¹, S. D. Williams¹, and J. M. Shaiman². ¹School of Geology and Geophysics, University of Oklahoma. 100 E Boyd, Norman, OK USA (melwood@ou.edu), ²Expository Writing Program, University of Oklahoma, Norman, OK USA (jshaiman@ou.edu).

Introduction: Seasonally active brines observed on Mars' surface [1] as well as the presence of salts in plume jets emanating from Enceladus [2] suggest that salty waters may be common throughout the solar system. The potential habitability of these solutions has been previously assessed based primarily on the aqueous activity/salinity of these solutions. However, microbial diversity and metabolic activity within groundwater, hot springs, and hypersaline lakes is influenced not only by salinity (and hence activity of water), but also by nutrient availability (N, P, S, C etc.) [3].

Traditional techniques devised to detect aqueous concentrations of nutrients and trace metals in planetary and terrestrial waters rely on direct sampling and analysis, which can lead to brine-induced clogging, corrosion, and/or sample cross-contamination. Raman spectroscopy provides an alternative analytical method for measuring covalently bonded solutes in aqueous solutions without physical contact with the sample. Therefore, the GeoWriting class at the University of Oklahoma set out to test the utility of Raman spectroscopy in measuring solute concentrations in high-salinity brines and to develop calibration curves which can be applied to unknown samples.

Methods: Standard solutions of NaNO_3 , Na_2SO_4 , NaBrO_3 , HBO_3 (at 0.1- 1.0M concentrations), and PO_4 (0.1-0.5M concentrations) were mixed with a stock saturated (33wt %) NaCl brine or 3.8wt % Na_2SO_4 brine at room temperature (1 ml of standard + 1 ml of brine). Methanol + water experiments were also conducted with 0-100% methanol mixtures (no salt was added in the methanol experiments). We placed the samples in a small cup and measured the Raman spectra of each sample produced by a 100 mW green (532 nm λ) diode laser at 100% power using a Renishaw InVia spectrometer in streamline mode. Raman scattering was collected with a 5x objective, 2400 l/cm grating, and CCD detector over 10-100 second intervals and then added to create the final spectrum representing 300s of data collection. We subtracted the background signal and then normalized the spectra based on the highest-intensity peak. Curve fits were obtained from the processed spectra using the Wire 4.1 spectral processing package. Based on the processed spectra collected at different solute concentrations, as well as

data from the literature, we determined the primary Raman peak for each of the solutes. By comparing the peak height for each of the solute curves to the primary water peak ($\sim 1640 \text{ cm}^{-1}$), we developed calibration curves for each solute in both NaCl and Na_2SO_4 brines.

Results and Discussion: We observed systematic changes in the Raman spectra with increasing solute concentration for each set of solute-brine samples.

NaCl brine analyses: All of the solutes produced a strong signal in NaCl brine samples, with no interference from the ionically-bonded salt in the brine. Calibration curves showed strong linear behavior in solute/water peak height ratios with increasing solute concentration. However, at high concentrations ($>0.75 \text{ M}$), the trend for nitrate became non-linear. Further experiments will constrain minimum detection limits at low solute concentrations in NaCl brine.

While some Raman peaks overlap (e.g. phosphate and bromate), these solutes produce multiple peaks which will allow deconvolution of multiple solute concentrations in more complex brines. Indeed, nitrate concentration was successfully measured and a calibration curve developed in mixed NaCl- Na_2SO_4 brine.

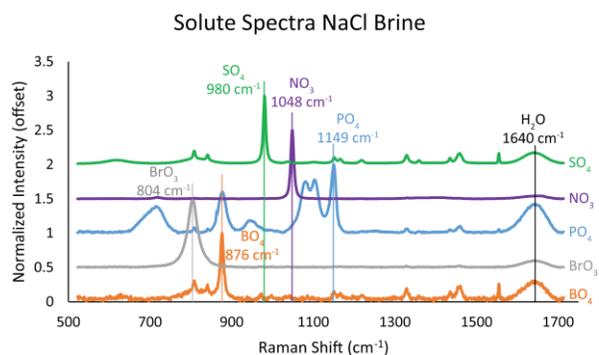


Figure 1. Characteristic Raman spectra of solutes in saturated NaCl brine. Concentrations are 0.5M, except phosphate (0.3 M). Note that each solute produces a clear signal in the NaCl solution, with little overlap between the peaks. Those solutes that produce peaks at similar wavenumbers (e.g. phosphate and bromate) produce other peaks as well which will allow unique identification of solutes in NaCl brine.

Na₂SO₄ brine analyses: All the solutes also produced a strong signal in the Na₂SO₄ brine. However, the sulfate ions in the brine matrix also produced an intense peak at 980 cm⁻¹, complicating the spectra. In high-salinity sulfate brines, the spectral window may need to be adjusted or truncated to avoid the sulfate peak, therefore allowing lower intensity signals to be measured with greater precision.

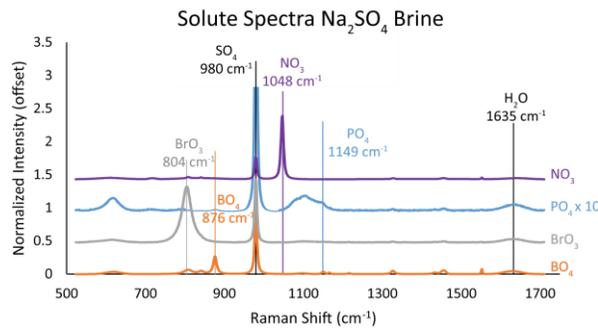


Figure 2. Characteristic Raman spectra of solutes in saturated Na₂SO₄ brine. Concentrations are 0.5M, except phosphate (0.3 M). Due to the strong Raman peak produced by the sulfate brine, the phosphate signal was multiplied by ten so that the phosphate peaks would be visible. The strong sulfate signal may influence the detection limit at low solute concentrations. Therefore, it may be advantageous to exclude the sulfate signal from future brine analyses.

Interestingly, the position of some peaks shift in the Na₂SO₄ brine compared to the NaCl brine (e.g. phosphate and H₂O), perhaps due to pH effects. For example, sulfate speciation is directly affected by pH conditions and therefore peak intensity ratios comparing HSO₄⁻ and SO₄²⁻ in NaCl brine have been used to determine the pH of fluids trapped in Permian red-bed deposits [3]. Likewise, phosphate and nitrate speciation is also directly affected by pH, which may lead to changes in the solute spectra at different pH conditions.

Methanol + water: Spectra produced by mixtures of methanol and water produced several strong peaks for methanol at 1032 and 1460-1465 cm⁻¹. Water peaks were observed at 995 and 1604 in addition to the water peak at 1640 cm⁻¹. This suggests that complexation within the mixture is likely affecting the Raman signal or the methanol may enhance the signal from the plastic sample container, leading to higher background signals. Further study is required to investigate these phenomenon.

Implications: Initial experiments demonstrate that Raman spectroscopy can be used to detect NO₃, SO₄, NaBrO₃, BO₃, and NaPO₄ in high-salinity NaCl and Na₂SO₄ brines. In addition, peak height ratios comparing indicative solute peaks to the main water peak (~1640 cm⁻¹) vary linearly with solute concentration, suggesting that Raman analyses can also be used to estimate solute concentrations in high-salinity brines. Methanol + water experiments yielded strong methanol and water peaks that can be used to discern the presence or absence of methanol in aqueous fluids on icy planetary bodies. This research demonstrates that Raman spectroscopy may be an important tool for assessing habitable conditions in high salinity brines without physical contact with liquid samples. This limits potential corrosion, clogging, and contamination risks while maintaining strict planetary protection protocols required for potentially habitable worlds, including Mars, Europa, and Enceladus.

Educational Impact: Undergraduate students in the University of Oklahoma's GeoWriting class collected and analyzed the Raman data presented in this study. Each student collected spectra from one solute-brine system, analyzed the spectra, developed curve fits, and compared peak height ratios to develop a calibration curve. Students then developed and practiced their technical writing skills to write a journal-style manuscript reporting their results and interpretations. Students also presented their work as a conference-style talk and poster to their School of Geology and Geophysics student and faculty colleagues. This research-driven course allows undergraduate geology and geophysics majors to actively participate in the scientific process and discourse, while learning and practicing science communication skills they will employ throughout their careers.

References: [1] Ojha L. et al. (2015) *Nat. Geosci.* 8, 82-83. [2] Postberg F. et al. (2009) *Nature*, 459, 1098-1101. [3] Benison K. et al. (1998). *Nature*, 392, 911-914.

Acknowledgements: Funding for the Raman spectrometer was provided by a recent NSF MRI grant EAR1428857 to the University of Oklahoma, with additional support from the OU Vice President for Research. Research support was also provided by grant NNX13AG75G from NASA's MFR program, as well as an undergraduate research grant from the School of Geology and Geophysics at OU.