

INTRODUCTION

Understanding what materials may be formed upon freezing of ocean fluids extruded to the surface of Ocean Worlds, and how they can be best detected and their abundances quantified, is a fundamental pre-requisite to the quantitative assessment of internal ocean composition and inference of habitability from measurements that would be conducted by a landed platform on the surface of Europa or on other Ocean Worlds. The primary goal of this research is to investigate the performance of a Raman instrument at detecting and quantifying the minerals formed.

The Europa Lander aims at finding evidence for life and/or habitable conditions on Europa. The Europa Lander Science Definition Team report suggested a strawman payload that would achieve these objectives; in particular, a “vibrational” spectrometer (Raman is the strawman payload instrument, infrared considered) is recommended to seek organic and inorganic traces of biological activity and characterize endogenic and exogenic non-ice constituents of the surface (including quantification of their abundances in the 0.1 to tens of percent range). Landed missions are also considered to other Ocean Worlds like Enceladus (Orbi-Lander PMCS study) and Ceres (Lander or Sample Return PMCS study). Although a body of literature exists on the Raman signature of relevant icy minerals (sulfates, chlorides, carbonates, sulfides, oxides, etc.), this literature does not investigate the minimum detection limit, accuracy of concentration determination, or most suitable instrument parameters. Filling these knowledge gaps is essential to constrain quantitatively what such an instrument may find, how well it can achieve its science objectives as function of configuration and parameters, and to prepare adequately for the analysis of scientific data.

EXPERIMENTAL METHODS

Sodium sulfate solutions were prepared by dissolution of sodium sulfate (Sigma Aldrich, $\geq 99\%$) into pure liquid water (Fisher Scientific, HPLC grade) at room temperature. The range of concentrations prepared spans 1 mM to 988 mM, the latter corresponding to the solubility limit of Na_2SO_4 in H_2O under ambient conditions.

Liquid solutions were deposited into the 200 μm well of cuvette microscope slides equipped with a thin fused silica cover (FireflySci), in order to prevent evaporation losses that could modify the concentration of the solutions, and subsequently analyzed by Raman spectroscopy.

Frozen brines were prepared by flash-freezing and grinding at cryogenic temperatures in order to obtain samples that were as homogenous as feasible, following the procedure described in Thomas et al. (2017). A droplet of solution was pipetted and deposited directly into a cryogenic mortar filled with liquid nitrogen. The frozen brines were then ground into a fine-grained powder while still immersed in liquid nitrogen. The powder was subsequently placed inside a Linkam LTS 350 optical cryostage pre-cooled to 100 K. The cryostage was then closed and placed under the objective turret of an Olympus BXFM microscope coupled to a Horiba Jobin-Yvon LabRAM HR spectrometer for Raman analysis. This experimental setup is further described in Vu et al. (2014).

Raman analysis of the liquid and frozen solutions was conducted with a 532-nm frequency-doubled solid-state Nd:YAG laser with 50 mW output power and no optical density filtering. An 1800 grooves/mm diffraction grating achieved a detector sampling around $0.5 \text{ cm}^{-1}/\text{px}$, and the spectrometer was calibrated before each experiment using the 520.7 cm^{-1} peak of a silicon chip. All Raman spectra used for quantification were obtained with a long working distance 50x Olympus objective, a confocal hole opening of 250 μm , a 30 s acquisition in each frequency range covered by the grating and detector, and three stacked accumulations to optimize signal-to-noise ratio and reject cosmic rays. Each spectrum was acquired over approximately 15 min.

RAMAN SPECTROSCOPY RESULTS

In this study we primarily focused on Raman peaks associated with the ν_1 vibrational mode of SO_4 and the bonded O-H region of H_2O (Figure 1).

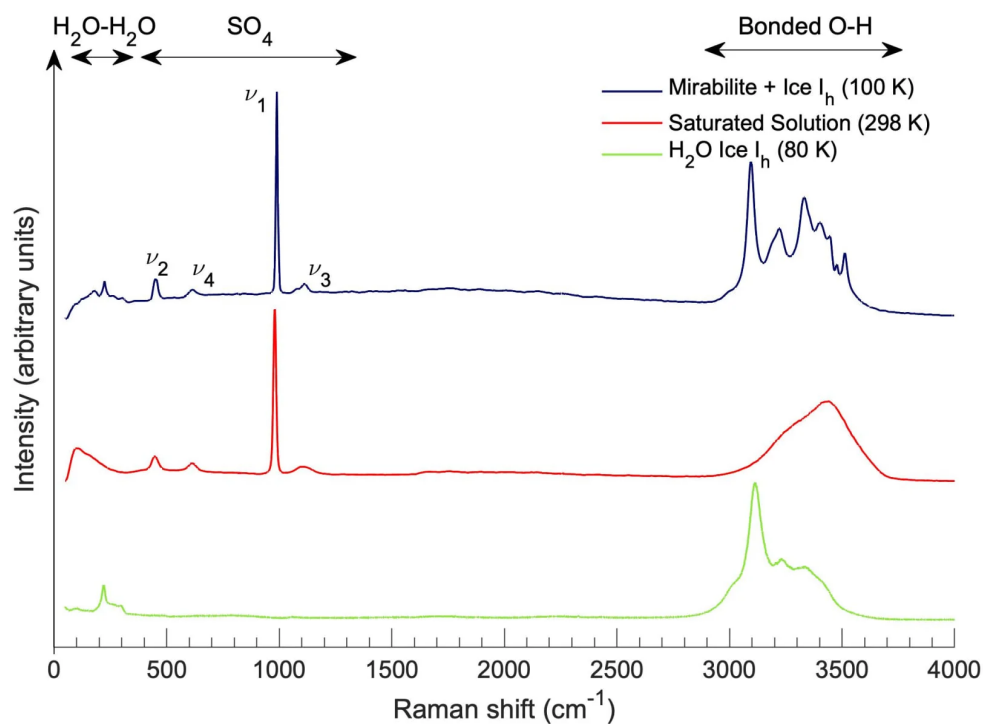


Figure 1. Raman spectra of ice I_h , saturated Na_2SO_4 solution, and frozen saturated Na_2SO_4 solution. Spectra are offset for clarity. “ $\text{H}_2\text{O}-\text{H}_2\text{O}$ ” and “Bonded O-H” indicate spectral regions of intermolecular H_2O lattice peaks and bonded O-H stretching modes, respectively.

In aqueous solutions, we found that as the Na_2SO_4 content decreases in more and more dilute aqueous solutions, the intensity of the sulfate peaks decreases (Figure 2).

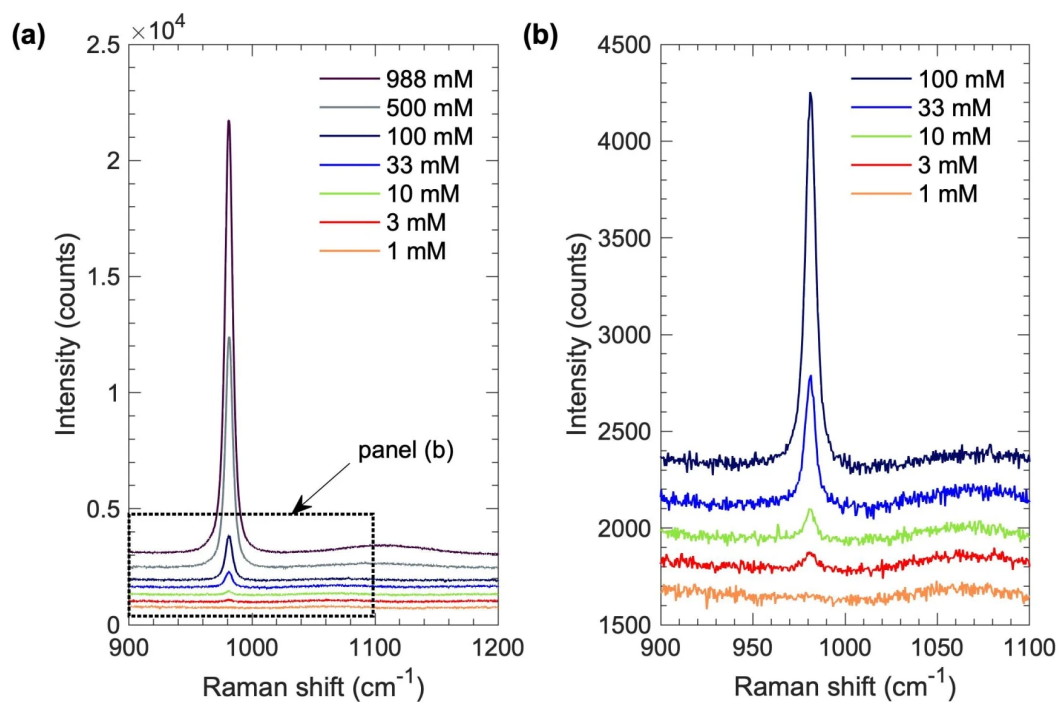


Figure 2. Dilution of Na_2SO_4 solutions results in a gradual decrease of the intensity of the SO_4 peaks. Spectra are slightly offset in intensity for clarity.

Conversely, in frozen brines, we found that the intensity of Raman peaks of Na_2SO_4 can vary largely within the same sample (Figure 3). Nevertheless, the ratio of peak intensities of $\text{Na}_2\text{SO}_4/\text{H}_2\text{O}$ appears to remain correlated with concentration.

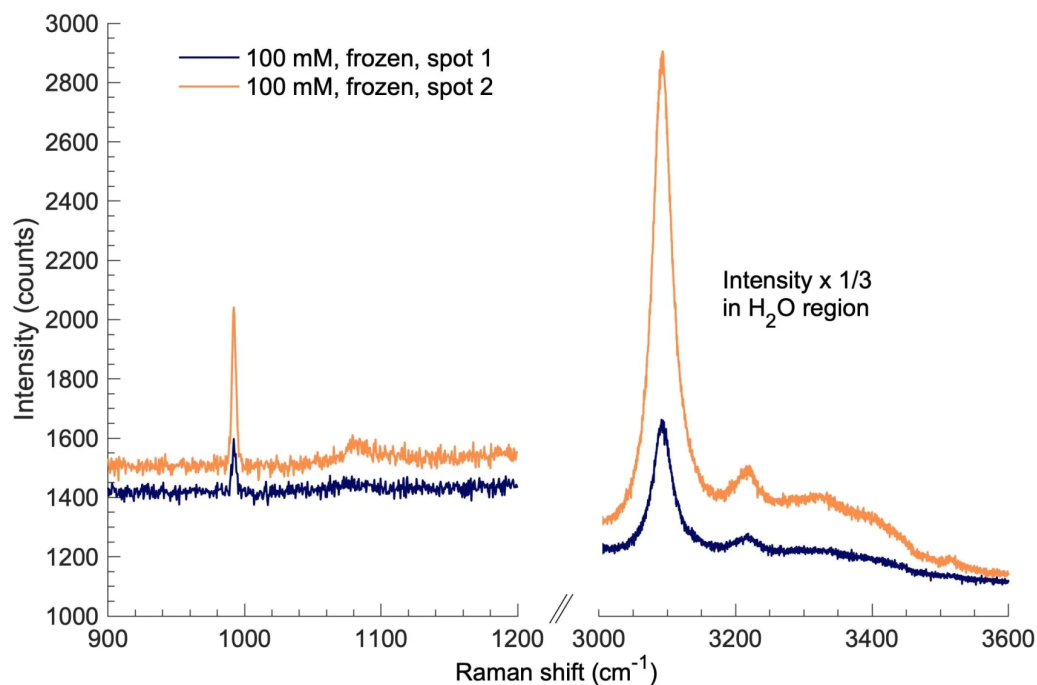


Figure 3. Raman spectra acquired at two different locations of a frozen 100 mM Na_2SO_4 solution illustrate

the large variability in intensity of peaks in each spectral region while peak area ratios are comparable (within 15%).

SULFATE QUANTIFICATION & UNCERTAINTY

A weighted linear regression of SO_4 peak area in liquid solutions and of $\text{SO}_4/\text{H}_2\text{O}$ peak area ratio in both liquid and frozen solutions, and $\text{SO}_4/\text{H}_2\text{O}$ peak area ratio in frozen solutions, yields very good fits to the datasets (Figure 4).

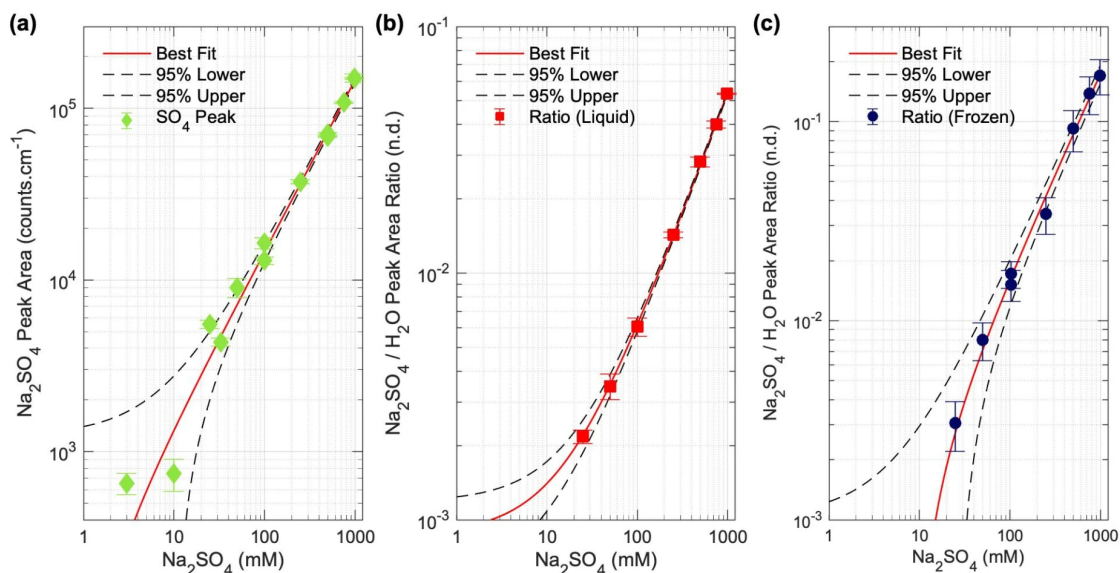


Figure 4: Log-log representations of linear regressions of the liquid and frozen solution datasets, including 95% confidence intervals.

We then evaluated the uncertainty of concentration estimates of an unknown Na_2SO_4 solution based on our results and the weighted fits (Figure 5).

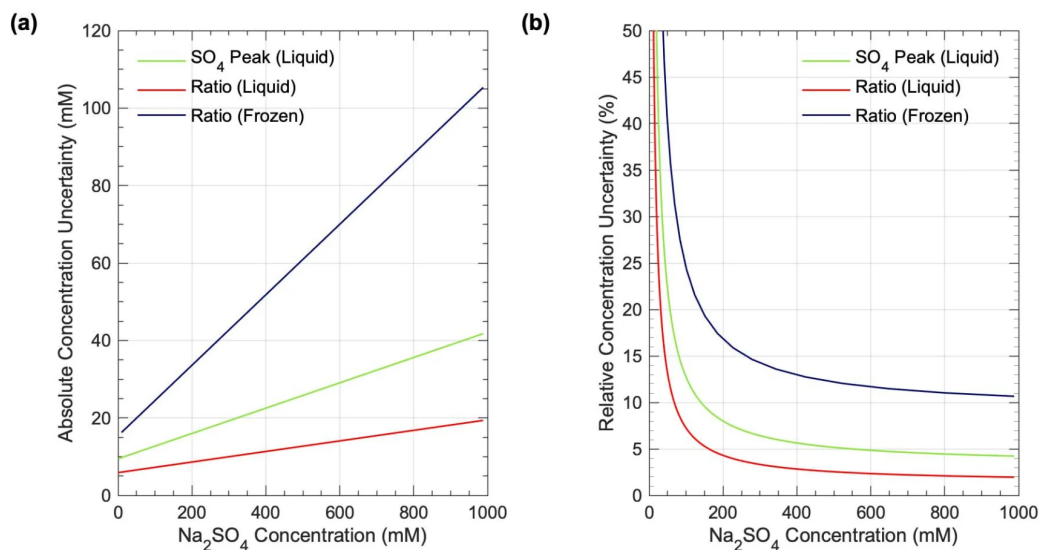


Figure 5. Estimated absolute (left) and relative (right) concentration estimate uncertainty at the 95% confidence level using the linear regressions from the datasets.

The uncertainty varies substantially with concentration. The relative uncertainty improves drastically as concentration in Na_2SO_4 increases, although the absolute uncertainty increases.

IMPLICATIONS

The most important result of this study is that the abundance of Na_2SO_4 in an icy sample can be quantified via Raman spectroscopy down to concentration levels equivalent to the salinity of highly saline terrestrial water environments and sea ice (~ 1 wt% salt), as well as oceanic water (~ 3.5 wt% salt).

The uncertainty in estimated concentration from calibration datasets would likely vary with concentration. This is consistent with signal-to-noise ratio considerations: the solute signal decreases as concentration decreases while the instrument noise remains constant.

With the method used here, the uncertainty of concentration estimates would be driven by the quality and precision of the calibration dataset, because confidence intervals of weighted fits are directly derived from the statistical dispersion of the dataset. These observations imply that calibration datasets need to be acquired on species of interest using realistic instrument acquisition parameters and span a wide range of concentrations. Such endeavors represent major laboratory efforts, and it would be valuable to conduct such research in advance of any in-situ Ocean Worlds mission equipped with an onboard Raman spectrometer in order to ensure that calibration studies would be readily available to support the analysis and interpretation of mission data.

CONCLUSIONS & ACKNOWLEDGEMENTS

Conclusions:

We assessed data precision and uncertainty of estimated concentration in liquid and frozen solutions. In liquid solutions, the precisions of sulfate peak areas and sulfate-to-water peak area ratios are comparable and they decrease with decreasing concentration. In frozen solutions, the precision and uncertainty of estimated concentration for the sulfate-to-water peak area ratio are substantially poorer than in liquid solutions, and they also decrease with decreasing concentration.

The overall poorer precision and uncertainty in frozen solutions likely originates from compositional heterogeneities that develop during freezing, since ice I_h does not incorporate impurities in its structure and expels them to grain boundaries. We anticipate that other systems would exhibit similar behaviors. This suggests that a multi-step analytical protocol, first in the frozen (native) state to assess the icy minerals present and preliminarily quantify them, then in the liquid state to refine estimated concentration of non-ice constituents to greater precision and lower uncertainty, would yield the best scientific return for an Ocean Worlds Raman instrument.

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DISCLOSURES

This work is presently under revisions for publication in the Planetary Science Journal.

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ABSTRACT

Raman spectroscopy is a promising analytical technique for *in situ* characterization of the icy mineral context on the surfaces of Ocean Worlds. This technique is highly sensitive to the molecular environment of ice and non-ice constituents, whereby non-destructive measurements can be conducted without any specific sample preparation. However, the application of Raman spectroscopy for space exploration remains in its infancy. Potential *in situ* Ocean Worlds mission concepts seek a quantitative assessment of the icy mineralogical context of samples that would be further analyzed for organic content and possible traces of biosignatures, which could be satisfied with a Raman spectrometer. To begin assessing this possibility, the current study aims to evaluate how well a laboratory Raman instrument can quantify non-ice constituents in icy materials. Here, we focused on the binary H_2O - Na_2SO_4 system because it is relevant to Europa, the materials that form upon freezing are well-understood, and the freezing behavior is predictable and devoid of metastable and/or glassy phases that could confound the analyses. We find that the sulfate-to-water peak area ratio shows a strong linear correlation with the salt concentration in the starting solution. Local heterogeneities in mineralogical abundances that likely developed during freezing of the solutions tend to degrade data precision and correspondingly increase the uncertainty of the estimated concentration from measurements conducted on frozen solutions. Future studies are needed to investigate other systems, include multiple components, and develop modeling approaches to account for textural and mineralogical variability in icy materials.

Part of this work has been conducted at the Jet Propulsion Laboratory, California Institute of Technology, under contract to NASA. Copyright 2021. All rights reserved.

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Thomas, E.C., Hodyss, R., Vu, T.H., Johnson, P.V. and Choukroun, M., 2017. Composition and evolution of frozen chloride brines under the surface conditions of Europa. *ACS Earth and Space Chemistry*, 1(1), pp.14-23.

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