

PRELIMINARY INVESTIGATION INTO RAMAN SPECTROSCOPIC EVALUATION OF SULFATE IN FLUID FOR HYDRAULIC FRACTURING

APPLICATION NOTE RAMAN-005 (A4)

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Background

Hydraulic fracturing is a technique used to maximize production of oil and natural gas in unconventional reservoirs, such as shale, coal beds, and tight sands. During hydraulic fracturing, specially engineered fluids containing chemical additives and proppant are pumped under high pressure into the well to create and hold open fractures in the formation. These fractures increase the exposed surface area of the rock in the formation and, in turn, stimulate the flow of natural gas or oil to the wellbore.

Fracking fluids are water-based, and the sheer quantity of water involved, including acquisition, transport and disposal, makes this an increasing, and in some cases a dominant, share of the cost of operations. This, together with recent EPA rulings about disposal of waste water from Unconventional Oil and Gas Extraction is motivating the development of recycling methods for production and flow-back water from fracking operations.

Reuse of this fluid is contingent on chemical and physical properties, which in turn are related to the chemical composition of the water. Waste water from fracking wells generally has high total solids content often in concert with salts, organic chemicals, metals and naturally-occurring radioactive materials. Often, the water must undergo a cleaning or dilution step before reuse or discharge. An online monitor for high levels of sulfate could be one component of an on-line recycling system of water in hydraulic fracturing processes.

Methods

Samples of fracking fluid were analyzed using a TSI ChemLogix™ ProRaman-L unit with a wide spectral range (100–3300 cm⁻¹). Laser power utilized was between 200 mW (used to establish rough calibration curve) and 250 mW (used to test the cleaned and dried solids). Cuvettes were used to contain the liquids and slurries; a xyz positioner was used to focus the laser on the surface of the solids-only samples. Spectra were collected using the EZRaman Reader program, corrected for detector response and the background removed. The data were saved as .spc files, and then converted to ascii text files for import into spreadsheets for presentation and analysis.

Preliminarily, all slurry samples were analyzed after shaking. This resulted in a set of nearly identical spectra (not shown), dominated by scattering of the laser excitation beam by the particles in solution. Following this initial evaluation, the solution phase of the suspensions was then isolated for analysis by allowing the turbid samples to settle. In process control, this step would likely be performed with electrocoagulation and settling. Lastly, the solids were separated from the suspension, rinsed with water and dried to a film prior to analysis with Raman spectroscopy.

Results

Initial spectra of shaken and highly turbid samples showed no change in sulfate (SO_4^{2-}) features in this spectrum as a function of concentration. This observation provoked the use of simple sample preparation techniques, the first of which was to allow the suspensions to settle and test the liquid phase. Five independent samples were taken from each container, and submitted to Raman analysis at 200 mW (acquisition conditions 30s, 20x average). This approach yielded useful spectra, shown in figure 1. In these spectra, there is a clear increase in the sulfate feature at 980 cm^{-1} with increasing reported sulfate concentration.

When all of these samples are plotted as peak area of SO_4^{2-} feature at 980 cm^{-1} as a function of concentration and a linear fit performed, the R^2 of the fit is about 0.97. This is indicative of a quantitative relationship between the integrated peak area at 980 cm^{-1} and the concentration of dissolved sulfate in this concentration range. Use of this calibration function outside the bounds of this study must be evaluated, but the linear range of this relationship is likely to be wide. This calibration curve is presented in figure 2.

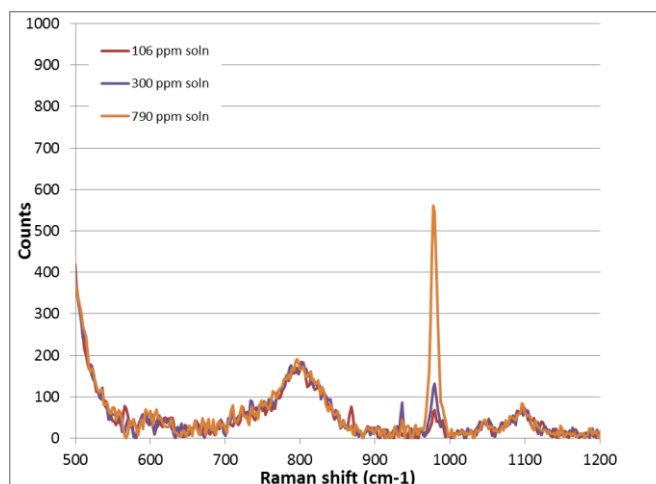


Figure 1. Background-corrected Raman spectra of settled fracking solution.

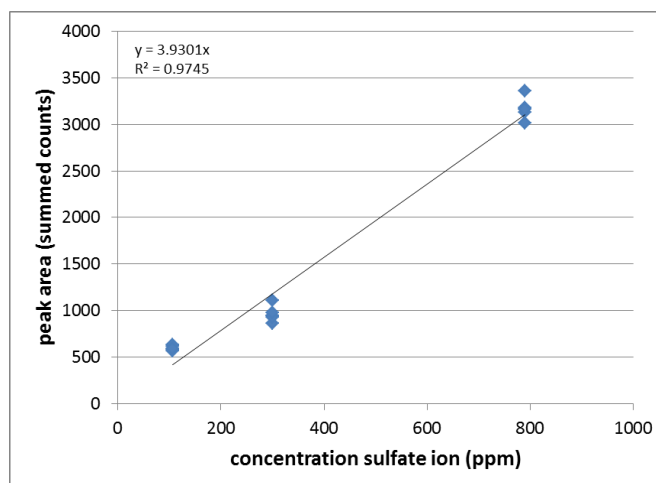


Figure 2. Calibration curve obtained from 5 samples each of the three submitted samples.

Summary

In this study, we were primarily interested in establishing the presence of the signal at 980 cm^{-1} , which is the location of a SO_4^{2-} feature (ν_1 , symmetric stretch of SO_4). This feature was present in the first set of spectra that were obtained on the shaken suspensions, but they did not vary as a function of sulfate in the sample. This is likely due to scattering of the laser beam by the suspended particulate material (which is moving on the timescale of the measurement). This observation indicates that it is likely that the removal of the solids may be necessary prior to application of an online Raman measurement.

A relationship between the sulfate feature and the reported concentration (it was not stated whether the reported concentrations in the samples were total sulfate concentrations or a soluble ones) was established with the dissolved portion of the sulfate samples, however, and lends confidence to the ultimate application of Raman spectroscopy to an online version of this measurement. The observation of sulfate in the solids portion of the samples indicates a need to understand the equilibrium of the sulfate between the liquid and solid phase before applying the measurement on a large scale. Further development of this application would involve this study.



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