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### **On-Line Sulfate Monitoring For Waterflood Projects**

Waterflood injection operations for offshore oil production can benefit from low-sulfate water. Removal of sulfate from the injected seawater prevents barium sulfate scaling that creates a loss of reservoir flow, and also eliminates the source of sulfur that is converted to hydrogen sulfide causing wells to turn sour. Current methods to monitor the injected water sulfate concentrations are typically conducted via traditional wet chemistry titration techniques around once or twice per shift. Even though the sulfate concentrations are critical, these measurement techniques are very time consuming requiring an hour or two for the result to be called in from the laboratory. A need exists for a reliable, in-situ method to continually monitor sulfate concentrations remain below 45 ppm in waterflood injection operations. Ideally, a non-contact sensor would be inserted into pretreated injected water in an appropriate location and allowed to communicate with a base instrument located remotely in the safe environment of a control room. Figure 1 illustrates the 19-inch rack-mounted, on-line, multiplexed, fiber-coupled Raman process analyzer that would be located in a control room.

Process Instruments Inc. has recently developed a fiber-coupled, Raman scattering instrumentation for this application that uses a long-life (~6-7 year) stabilized laser. We have developed similar technology for the monitoring of polymers, various industrial processes including gasoline blending, along with H<sub>2</sub>S and amine concentrations in aqueous amine streams used to remove H<sub>2</sub>S from hydrocarbon streams. Raman scattering is particularly well suited for this sulfate monitoring application because a unique Raman peaks associated with the sulfate can be detected. The Raman technique is often assumed to be similar to near-infrared and mid-infrared methods. Both approaches rely on measuring molecular vibrational frequencies (i.e. the peaks position) for chemical analysis and the strength of optical interactions (i.e. the magnitude of the peak) for determining molecular concentrations.

Some advantages with using Raman spectroscopy is that there is no sample preparation, no consumables are required for system maintenance, instrument calibration is automatic, and water does not interfere with the collection of Raman spectra. This technique can prevent any panic between titration measurements, so that operators would be less concerned about having excess sulfate concentrations injected into the well. An in-situ Raman sensor can also be used to provide instantaneous feedback on changes in the sulfate concentrations which can then lead to real time process control.

Figure 2 illustrates how the sulfate region of the Raman spectra changes with sulfate concentrations from 0 to 47 ppm. The Raman peak located at 982 cm<sup>-1</sup> is from sulfate (SO<sub>4</sub><sup>-2</sup>). The different concentrations were run through our in-line flow cell (Figure 3) for 8 hours with integration times of 10 minutes/spectrum to obtain good signal

strength. The in-line Raman probe and flow cell (Figure 3) is used to monitor a slip-stream sample line. The probe is intrinsically safe since it does not require any electrical connections, and only light is transmitted via fiber-optic cables to and from the probe. Since our instrument works in the NIR region, the fiber-optic cables can be >200 meters (660 ft) in length for sampling streams located at a remote location. The Raman probe is protected from the sample stream by a 1 mm thick sapphire window that is rated to 550 psi. To reduce corrosion from marine environments the flow cell and all tubing are 316 stainless steel. Typical flow rates are 20 to 50 cc/min. The sample cell has minimal dead space and can be easily cleaned if necessary. Conventional 316 stainless steel compression fittings allow quick connection with a sampling stream. The in-line probe is encased in a 316 SS, NEMA 4x enclosure.

A key advantage with the Raman effect is that it is a linear process. Therefore, the sulfate Raman band (Figure 2) will be twice as intense when the water sample contains twice as many sulfate molecules. Figure 4 demonstrates the linearity between the sulfate Raman band intensity and the actual concentration. The magnitudes from all of the spectra collected at each concentration are shown. The correlation coefficient of the linear fit was  $R^2=0.9992$ . Figure 5 shows the predicted sulfate concentrations obtained from the magnitude of the peak height vs. the actual concentrations of the solutions. The predicted values had a standard error of prediction (SEP) of 0.48 ppm when compared to the known concentrations. With increased sulfate concentrations the signal to background improves and one can notice that the Raman prediction become more robust with smaller errors of predictions.

# ON-LINE, MULTIPLEXED, FIBER COUPLED RAMAN PROCESS ANALYZER

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Figure 1. On-line 19-inch rack-mounted Raman process analyzer that would be located in a control room.

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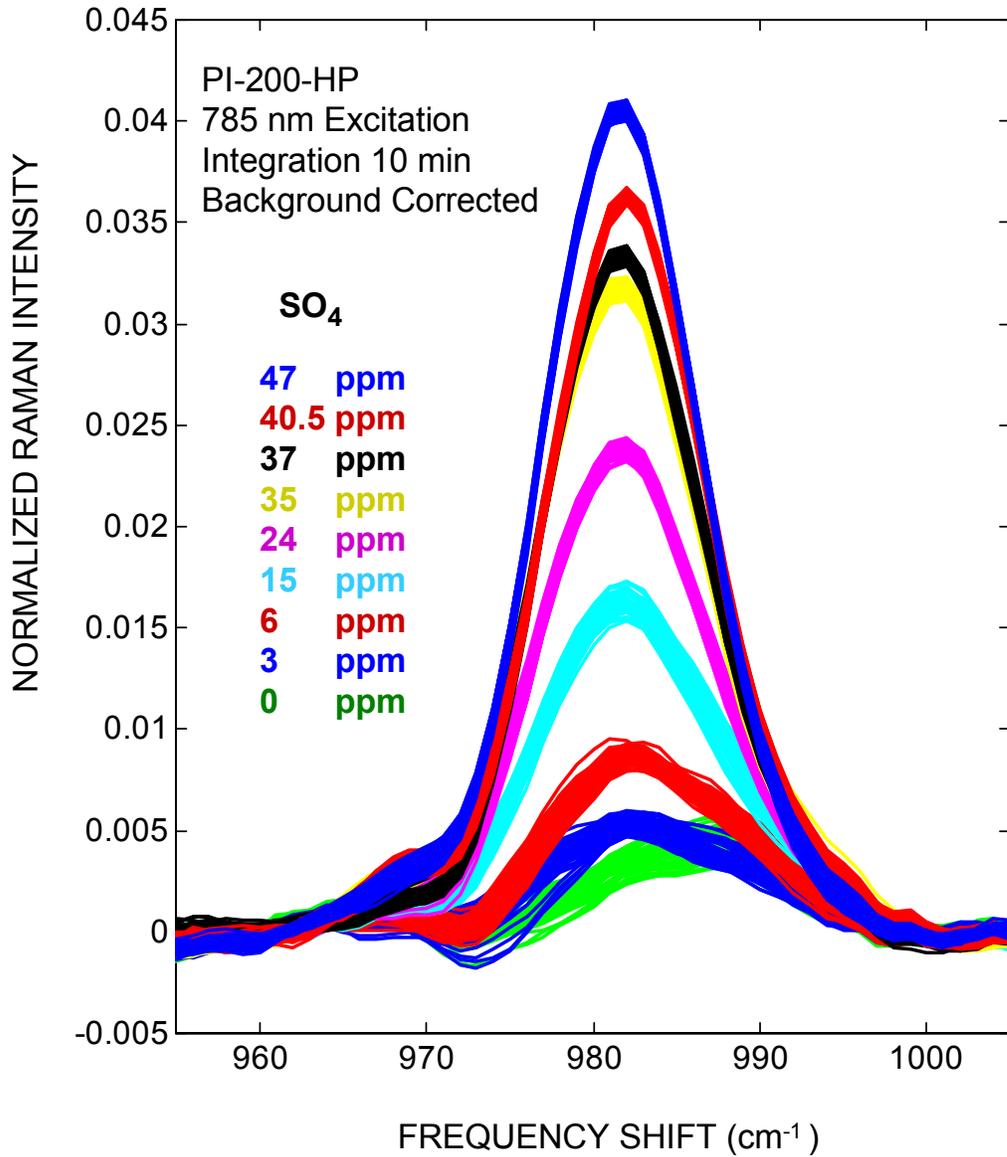


Figure 2. Sulfate region of the Raman spectra obtained from water samples containing 0 to 47 ppm sulfate concentrations.

## In-Line Raman Probe and Sample Flow Cell

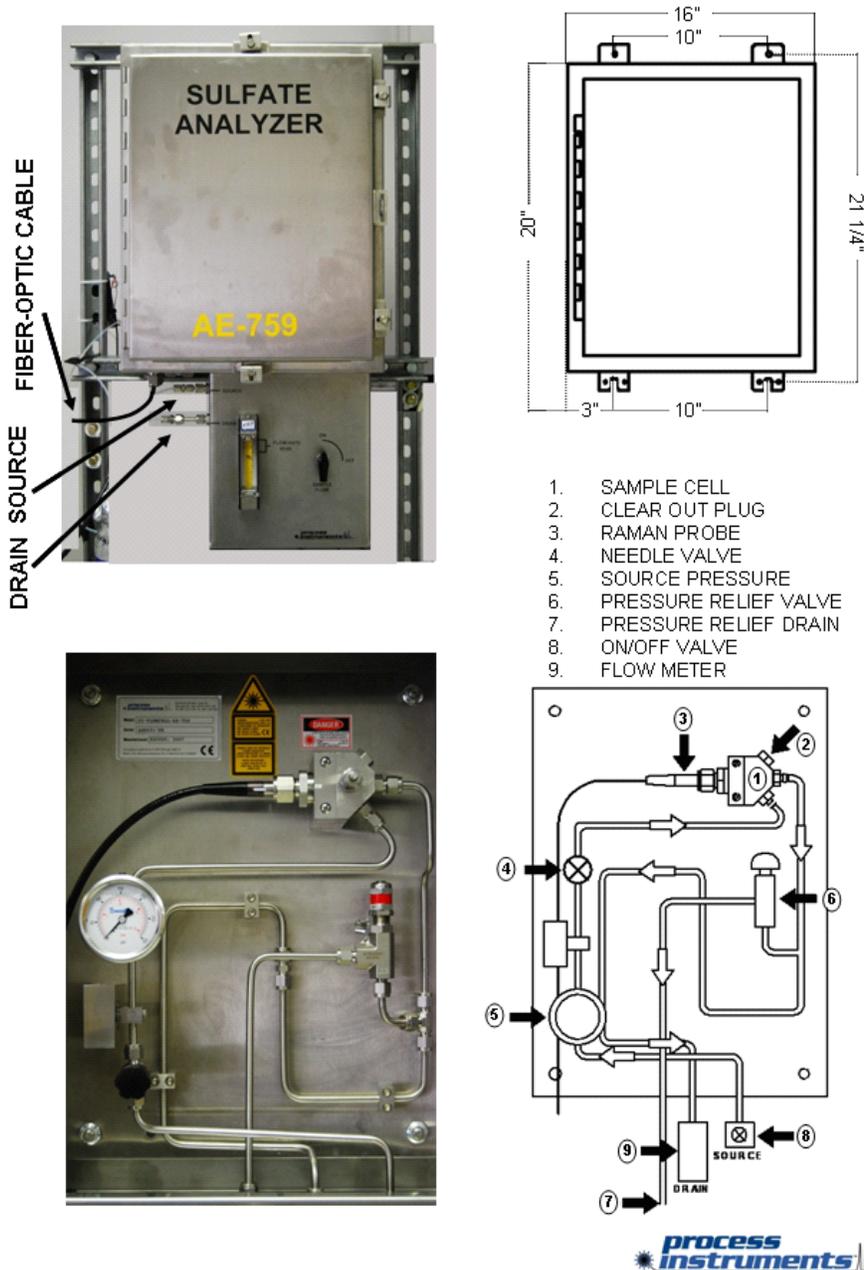


Figure 3. In-Line Raman probe and sample flow cell. All tubing and flow cell are 316 SS and encased in a NEMA 4x enclosure.

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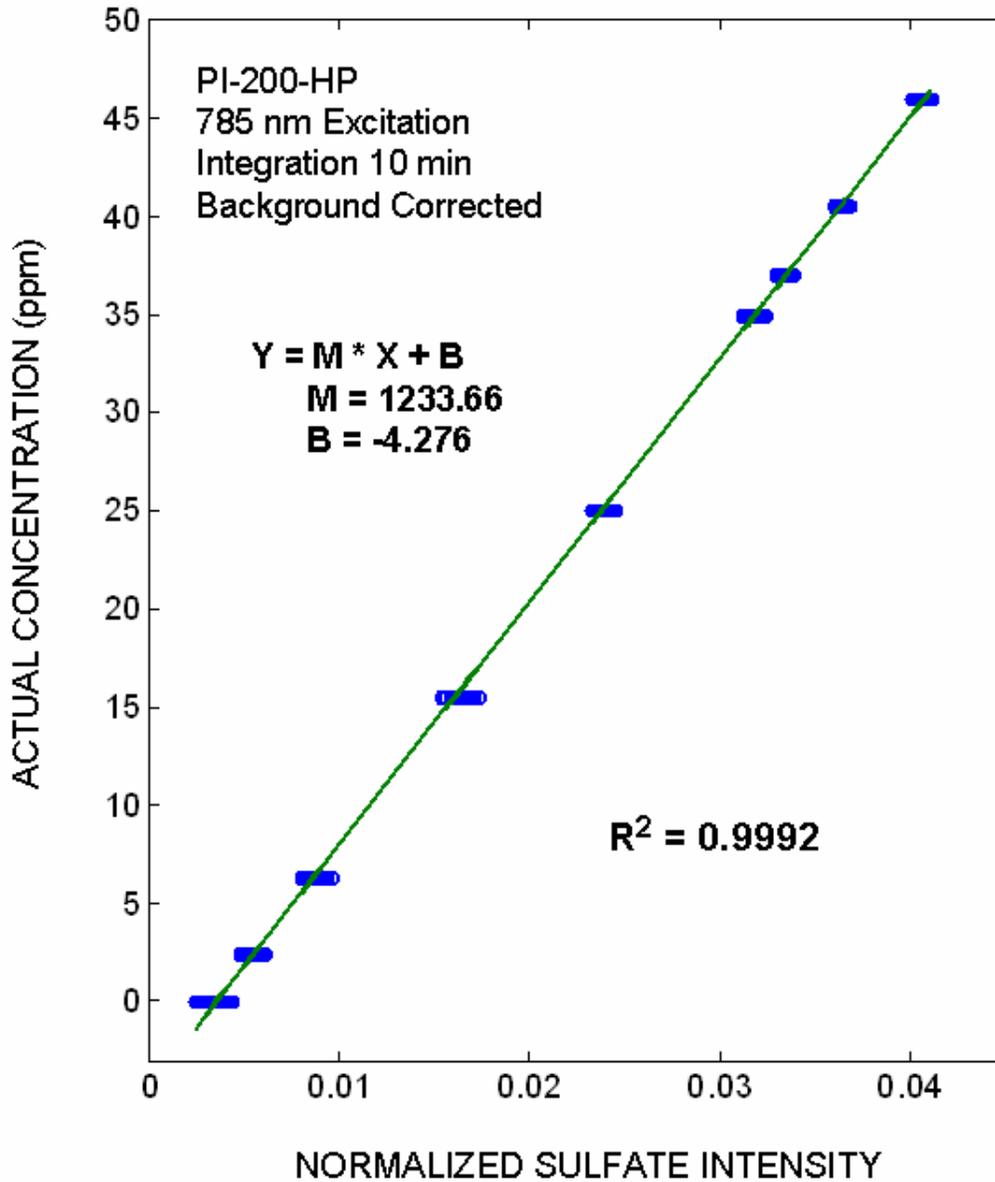


Figure 4. Linearity of the sulfate intensity (shown in Figure 2) with the actual concentration. Correlation coefficient  $R^2=0.9992$ .



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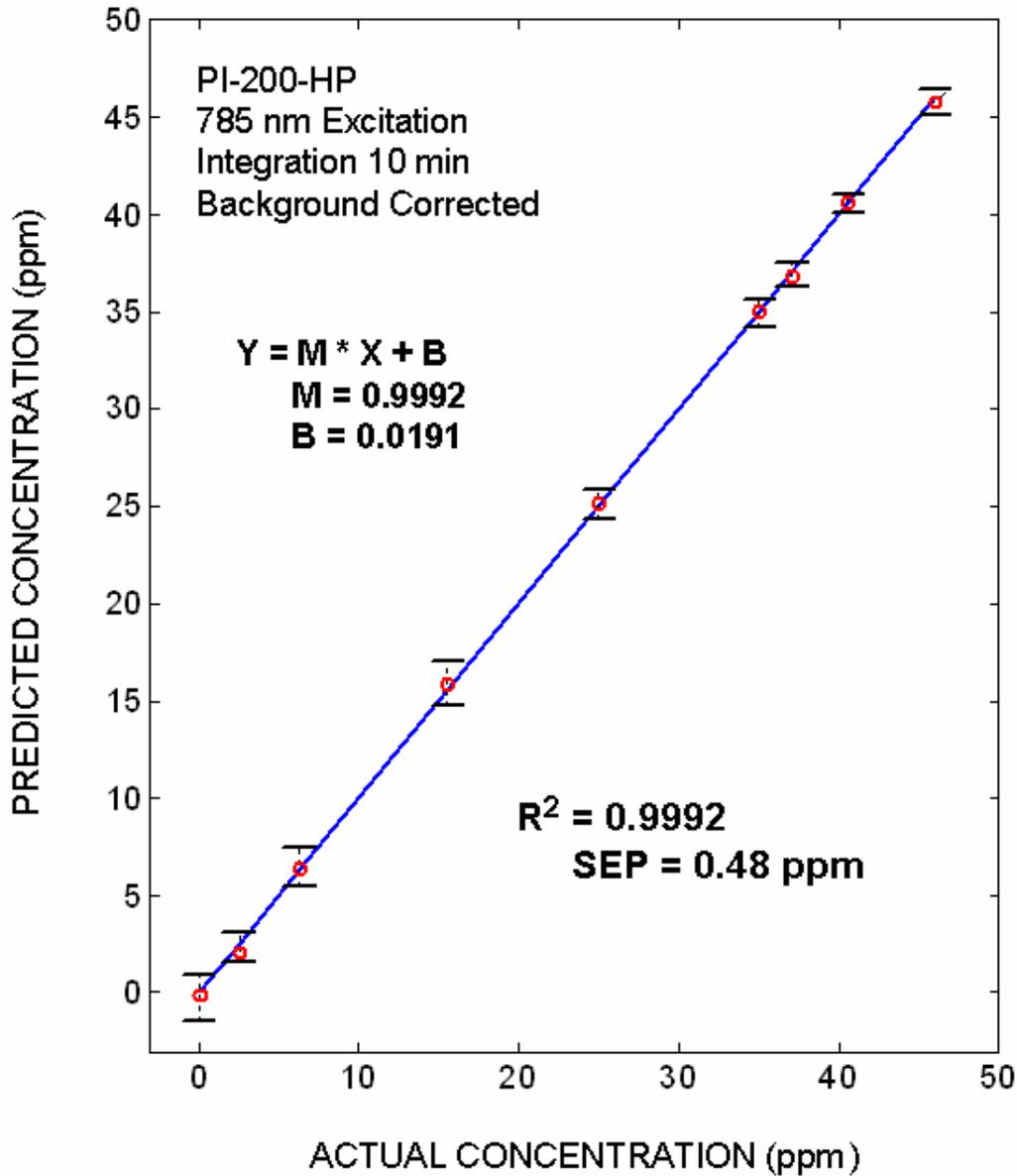


Figure 5. Raman predicted sulfate concentrations vs. the actual Concentrations. The standard error of prediction was 0.48 ppm.