# Application Summary

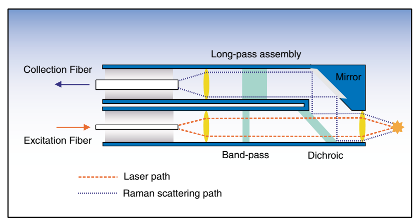
## A Raman Fiber Optic Probe to Monitor Hydrothermal Oxidation Processes

## Introduction

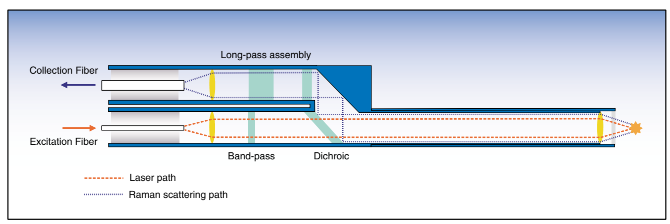
Hydrothermal oxidation (HTO) processes, such as supercritical water oxidation, are effective methods for the destruction of hazardous as well as nonhazardous aqueous wastes. Among the engineering tasks necessary in this technology is the ability to monitor *in situ* the process of chemical reactions, to identify constituents and products in the reaction vessel, and to monitor corrosion. Raman spectroscopy is ideal for HTO monitoring because Raman is a nondestructive method, requires no sample preparation, and can be integrated with fiber optics to provide remote analysis. The conditions inside an HTO reactor, however, pose a major challenge for Raman measurements because the reactor temperature and pressure is very high. Moreover, the corrosive nature of the materials inside the reactor further contributes to the difficulty in deploying analytical probes in these vessels.

EIC Laboratories has developed a Raman fiber optic probe for *in situ* monitoring of HTO reactors. The HTO Raman probe can be used in high temperature and high pressure environments, and is immune to corrosive conditions. This probe design, and variations based upon it, can be used for a variety of monitoring applications under extreme chemical and physical conditions.

body from the temperature source. This is achieved by removing the final focusing lens from the optical body and sending/receiving a collimated beam through an extension tube. The focusing lens is then placed at the end of the tube. An additional sleeve with a window is placed over the extension tube to seal the optics against pressure. The sleeve position is adjustable (i.e. the distance between the window and the lens can be adjusted) to select the probe's focal distance from the window. This enables optimization of the window position depending on the optical characteristics of the sample.




*Left:* Standard commercial probe with focused output. *Below:* Modified probe with extension tube and sleeve.




## Basic Probe Optics

The optical design of the HTO probe is based upon the commercial RamanProbe™ used for general laboratory analysis. The RamanProbe is a 0.5" cylindrical probehead that houses filtering and focusing optics for efficient signal collection and complete optical filtering of the Rayleigh line and silica background. Although rugged, the optical filters shift and lose throughput at elevated temperatures; the basic probe body is limited to about 200°C. For measurement of reactions at higher temperatures, an extension tube serves to displace the probe

The filtered probe is designed for use with a single excitation wavelength. For very high temperature work, blackbody emission from the sample may interfere with the Raman spectrum. The particular probe for this project was built for 633 nm excitation (HeNe laser).

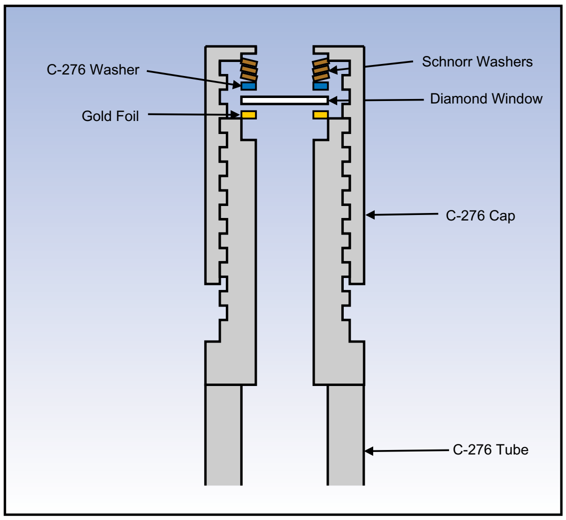
Raman fiber optic probe and extension sleeve.

[1]This project was funded by the Department of Commerce through an SBIR grant from the National Institute of Standards and Testing

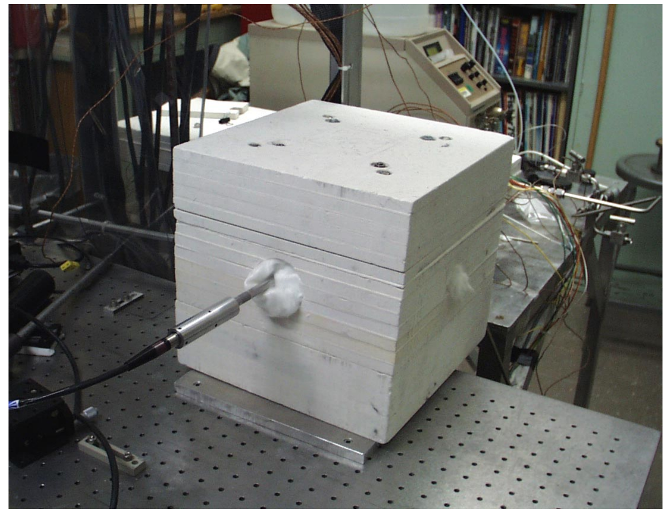
[2]Note: Raman instrumentation used and developed in this application are available from EIC's commercial affiliate, InPhotonics, Inc. Visit us on the web at www.inphotonics.com.

# HTO Probe Seal

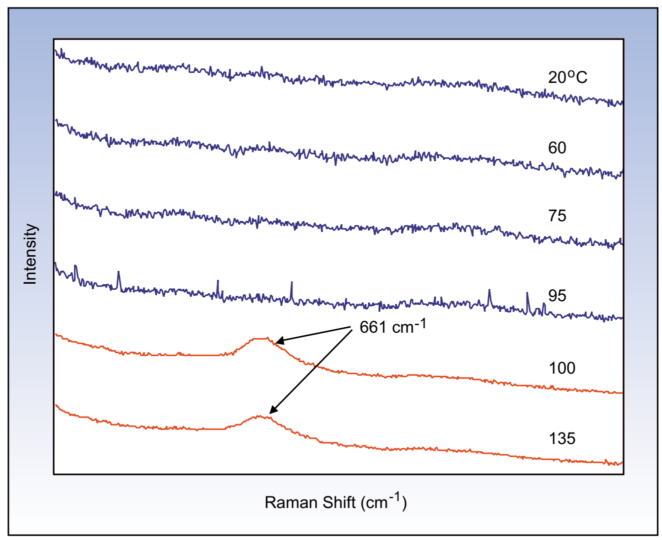
The seal of the extension sleeve was critical for the HTO monitoring application. To survive the corrosive environment, the probe would be made from Hastelloy C-276 with a diamond window at the tip. NIST designed a high pressure seal for the extension sleeve using a series of metal washers to load the window under pressure. The design was specified to at least 5000 psi.




High-pressure seal between Hastelloy C-276 and the diamond window.



The heater block surrounding the high pressure cell.

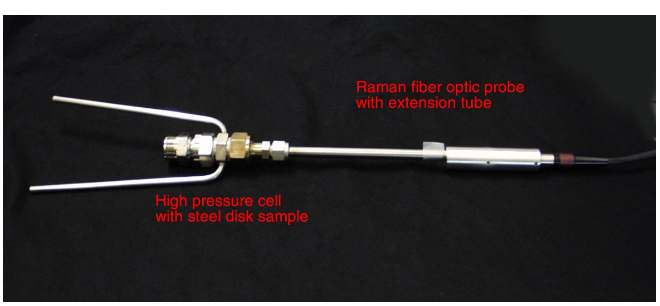



Raman spectra of a steel disk in superheated steam. The 661 $cm^{-1}$ peak shows the formation of $Fe_3O_4$.

# Testing

The probe was interfaced to a high pressure cell inside a heating block. A test sample (steel disk) was placed inside the cell such that its spectrum could be measured with the Raman fiber optic probe. Superheated steam was introduced into the cell, and spectra were measured at various temperatures.

The formation of $Fe_3O_4$ on the disk surface was observed at elevated temperatures and 3700-4000 psi.




The HTO Raman probe installed into the high pressure cell for testing.

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