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FIBER OPTIC CONE PENETROMETER RAMAN PROBE FOR IN SITU CHEMICAL CHARACTERIZATION OF THE HANFORD UNDERGROUND WASTE TANKS

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ABSTRACT

A field hardened fiber optic Raman probe has been developed for cone penetrometer deployment in the Hanford underground chemical waste storage tanks. The corrosive chemical environment of the tanks, as well as Hanford specific deployment parameters, provide unique challenges for the design of an optical probe.

INTRODUCTION

There exist 177 underground storage tanks at the US Department of Energy (DOE) Hanford site that have been used by the DOE complex to process and store over 100 million gallons of chemical and mixed chemical/radioactive wastes generated from nuclear weapons and fuels production.(1,2) The DOE is currently in the process of retrieving, treating, and safely disposing of the wastes stored in underground tanks. Prior to retrieval and treatment, characterization is required of the wastes stored within the tanks to identify the chemical and radioactive composition to determine if waste transfer can occur within normal safety rules involving flammability, corrosiveness, and chemical compatibility.(3,4) Examination of both the basic physical and chemical parameters of the tank wastes are required to ensure continued operability during waste transfer and concentration/minimization. Current techniques of tank waste analysis involve the removal of core samples from the tanks, followed by costly and time consuming wet analytical laboratory testing.(5) Savings in both cost and time could be realized in techniques that involve in situ probes for direct analysis of tank materials in their native environment.

A powerful in-situ technique for tank waste characterization is the in-tank cone penetrometer, which brings interrogative methods to the tank waste matrix in its native environment, providing faster, safer, and more cost effective tank characterization both in terms of time and effort. The penetrometer provides a method of depth profiling of the tank waste in a few hours from surface to bottom. Applied Research Associates (ARA) was contracted by DOE Hanford to construct and deploy a 35 ton cone penetrometer and an associated instrument and control trailer for use in characterizing the properties of the slurries, sludges, and saltcakes of the tank farm. The sensors built into the penetrometer by ARA provide measurements of penetrometer tip pressure, sleeve friction, pore pressure, tip temperature, penetration depth, penetrometer inclination, and magnetic bottom detection. These sensors provide characterization of the *physical* properties of the tank wastes which impact operational considerations for tank waste retrieval as described in the Tank Farms Waste Compatibility Program Data Quality Objective (DQO).(3). Additionally, Science

Applications International Corp. (SAIC) was contracted to supply a neutron thermalization detection sensor to provide moisture content measurements of the tank wastes. The moisture measurements are used to satisfy operations and safety considerations outlined in the DQO. However, the penetrometer platform as described contains no methodology for in-situ chemical characterization. The need for chemical characterization of the tank wastes are driven by both DQO safety and operational considerations. Safety drivers include the monitoring of organic chemical and oxidizer levels to address energetics and flammability, nitrate and nitrite levels with regard to corrosion concerns, plutonium levels to address criticality prevention specification limits, and chemical detection of organic and inorganic species to identify chemical compatibility hazards, including ferrocyanides, nitrates, sulfates, carbonates, phosphates, and other oxyanions.(6) Operational concerns include the monitoring of phosphate levels, driven by the potential formation sodium phosphate crystals which will increase the viscosity of the waste by formation of a gelatinous matrix which will reduce the ability of pumps to transfer and retrieve waste. To address the chemical safety and operational DQO needs, LLNL was contracted to provide a fiber optic remote Raman chemical sensor system for incorporation in the ARA in-tank cone penetrometer.

Raman spectroscopy is a powerful tool for the characterization of unknown chemical constituents via their vibrational spectra. Being a laser based technique, Raman spectroscopy can advantageously use readily available laser light sources in the visible and near infrared to interrogate samples. These regions of the light spectrum, in particular the near infrared, are also very efficiently transmitted over long distances by fiber optics, making Raman a powerful tool in remote access spectroscopy, where it is inconvenient or unsafe for workers to make contact with the target sample. Being a vibrational technique, Raman spectroscopy is a nonspecific technique that can be used to identify and measure the large suite of inorganic and organic chemical species that are of great consequence in quantifying energetics in accordance with the safety DQO.(7,8) Such species include carbon hydrogen rich complexing agents like sodium succinate, acetate, citrate, EDTA, nitrilotriacetate (NTA), tributylphosphate, as well as inorganic oxidants and reducing agents such as sodium nitrate, nitrite, ammonium, uranyl, etc.(9)

The Hanford tank environment provides unique materials challenges in terms of chemical, radiation, and operational parameters.(10) Chemically, the typical tank waste matrix is an extremely complex heterogeneous mixture consisting of an alkaline ($8 \leq pH \leq 14$, up to 5 M NaOH) blend of solid and dissolved inorganic oxidizing agents such as sodium nitrate and sodium nitrite ($\leq$ 5M) and organic chelating agents and solvents. Radiation fluxes of up to 10,000 Rad/hour exist within the waste, primarily gamma and beta radiation from the decay of strontium, technetium, and cesium. Operationally, penetrometer push forces of up to 35 tons may be required to penetrate the concrete-like single shell tank saltcakes. Herein we describe a hardened fiber optic Raman probe designed specifically for incorporation in the Hanford in-tank cone penetrometer platform that provides in-situ characterization of the tank components of importance for safety and operational considerations in tank waste retrieval and remediation operations.

RESULTS AND DISCUSSION

General

The fiber optic Raman cone penetrometer probe system consists of a fiber optic filtered penetrometer probe designed and constructed by LLNL for use with the ARA penetrometer, a cone penetrometer Raman probe interface housing which includes a hermetically sealed sapphire window that provides a transparent viewing port that is chemically resistant to the corrosive tank waste matrix, up to 250 feet of radiation hardened fiber optic cable to interface the penetrometer probe to the ARA penetrometer instrumentation trailer, a high optical numerical aperture, high signal throughput Kaiser Optical f/1.8 HoloSpec holographic imaging monochromator for Raman spectral dispersion, a thermal electrically cooled charge coupled device (CCD) detector, a mode-stabilized SDL near-infrared semiconductor laser, and a portable computer and software to drive the system. These components have been successfully integrated with the ARA cone penetrometer platform at Hanford.

The fiber optic Raman probe for inclusion in the in-tank cone penetrometer is designed for collimated, colinear laser excitation and signal collection. The collinear probe was chosen both for the maximal overlap of the interrogated area with the collection area and its inherently compact design which facilitates emplacement in the limited space of the cone penetrometer. The probe sits within the cone penetrometer Raman probe interface along the penetrometer vertical axis. The penetrometer Raman probe interface is screwed directly into the penetrometer pipe, making it an integral portion of the penetrometer itself. Optical communication between the vertically seated Raman probe and the tank waste environment along the radial axis of the penetrometer interface is accomplished with a gimbal mounted silvered mirror, which connects the optical axis of the probe with the optical axis of the probe interface window train. The window train is terminated with an indium alloy hermetically sealed sapphire window which is designed to provide 1) optical access to the tank waste material, 2) a chemically resistive surface that is flush with the penetrometer pipe exterior surface, and 3) structural integrity under at least 45 tons of pressure. Laser input to the probe is provided by a single fiber optic cable. Collection of signal is performed by a seven fiber optic bundle. Seven collection fibers are used rather than one to both increase the collection area and therefore efficiency of the probe and to allow for a larger laser spot size (4 mm) to be used when interrogating the sample. A larger spot size results in increased signal to noise due to the larger area of coverage of the sample by minimizing the effect of inhomogeneous grain size. The collection fibers are filtered with a long pass filter to remove scattered laser light; the laser excitation fiber is filtered with a laser band pass filter to remove silica Raman generated in the optical fiber. The probe has demonstrated complete rejection of silica Raman and both refelcted and Rayleigh scattered laser line without compromising real signal. No silica Raman can be detected even when the target utilized is a flat aluminized mirror.

Cone Penetrometer Probe Housing and Window Assembly

The CPT Raman probe cone penetrometer interface housing consists of two major components, a probe housing and a window assembly (Figure 1). The parts are machined from 420 stainless steel, with a Rockwell Hardness of 50 after heat treating, a tensile strength of 260,000 psi, and a yield strength of 215,000 psi. The 420 SS is corrosion resistant, easily cleaned, and does not require chrome plating.

The probe housing is threaded directly into the cone penetrometer push rod on the uphole side, and a 2.00 inch O.D. cone mandrel on the down hole side. The housing is designed to be an integral unit of the cone penetrometer, supporting a load of a 35 ton vertical push. The housing provides space along its vertical axis for the fiber optic Raman probe, and a housing for the window assembly along its radial axis. A 0.875" diameter circular opening with an inner lip of 0.123" recessed 0.187" from the housing surface provides the mounting base for the window assembly. The housing incorporates electrical cable bypasses to allow the passage of wires to the ARA electronic sensor package located in the cone mandrel.

The window assembly provides optical communication between the vertically seated Raman probe and the tank waste environment along the radial axis of the housing. It consists of a hardened 420 SS insert that mates with the circular opening in the housing. The insert is locked down in the housing with an opposing screw and sealed with durometer 50 neoprene o-rings. The window assembly houses a sapphire window which is designed to provide optical access to the tank waste material without compromising mechanical strength or chemical resistance (Figure 2). The window is situated in the outer wall of window assembly centered about the optical axis of the assembly. Sapphire, also known as corundum, a form of alpha-aluminum oxide, has a Moh Hardness of 9, a tensile strength of 100,000 psi, a compression strength of 3.0×10^6 psi, and a Young's Modulus of 5.0×10^7 psi. The dimensions are 6.5 mm in diameter and 2 mm in thickness. The sapphire window resides within a milled flat on the outer surface of the window assembly which provides a surface flush with the window. The surface tolerance of the window relative to the outer wall of the window assembly is +0.002/-0.000". This tolerance was chosen to eliminate the possibility of contaminating the external surface of the window with tank waste during a push by removing the small dead space allowed by a recessed window. The sapphire window, which is edge metallized with a 0.005" layer of Ag, is hermetically sealed directly to the stainless steel body of the window assembly with an indium silver eutectic alloy. Sapphire windows have previously been utilized in geological applications of cone penetrometers. An indium silver alloy was selected for its corrosion resistance to sodium nitrate and sodium nitrite in the highly alkaline tank waste material.

Penetrometer push tests were performed to evaluate the integrity of the sapphire window assembly and the stainless steel housing under harsh deployment conditions. The part was subjected to 20 ton push testing through sand, hard gravel, and clay down to bedrock with no visible physical effects. The sapphire window was unmarred by pushing through heavy gravel, though the penetrometer pipe itself was deeply scratched. The Raman CPT probe assembly also qualified as leak proof during a 5 hour static internal vacuum test. The part was evacuated to 1 millitorr vacuum, then sealed off. There was no loss of vacuum during the duration of the test. The hardened stainless steel housing exhibited a slight compression of no more than 0.0015" around the window when subjected to up to 45 tons of force in a press. The compression was completely elastic. The maximum force the piece will experience during actual deployment is 35 tons.

The Raman CPT probe assembly and associated optics were subjected to chemical and radiation testing in a 600 Rad/hr gamma ray pit at Hanford.(11) The probe assembly was fielded within a vessel containing tank waste simulant. The key components of the simulant, 4 M NaOH, 2 M $NaNO_3$, and 4 M $NaNO_2$, represent the most reactive components of the tank matrix. The effects of radiation on the optics, the sapphire window, and the indium/silver alloy seal were investigated. The optics were visually inspected and exhibited no signs of darkening. The sapphire window and indium/silver seal were characterized by SEM and atomic force microscopy (AFM) measurements before and after a 17 day exposure. AFM is similar to conventional contact probe profilometry with a resolution on the order of an Angstrom. The sapphire window was completely unaffected by the caustic chemical solution and radiation. The total radiation dose over 17 days was approximately 350,000 Rad. Quartz optical components exhibited no optical darkening. BK-7 based optics darkened in the visible, but darkening was negligible in the near infrared. The integrity of the indium/silver eutectic alloy braze was not compromised. Radiographs of window samples were performed for characterization of pinholes or cracks in the indium/silver seal. None were detected, indicating a leak tight sealing of the window to the stainless steel body.

CPT Fiber Optic Raman Probe

The fiber optic Raman probe (Figures 3 & 4) is designed to lock into the window assembly within the assembled CPT Raman probe housing.(7) The locking feature provides self alignment of the optical axis of the probe with the optical axis of the window train. The collimated output/input of the Raman probe along the vertical axis of the CPT pipe is coupled to the CPT radial optical axis of the window assembly by an aluminized gimbal mounted mirror. A screw-driven gimbal mount is used to improve the accuracy and greatly simplify the probe beam alignment. Within the probe, the laser input and the Raman signal collection output are divided into two disparate channels (Figure 4). The laser input is introduced into the probe via a 320 µm optical fiber (PolyMicro Technologies, polyimide coated, low OH content, radiation hardened fiber). The f/2.27 output of the laser fiber is collimated with an f/2 lens. The collimated laser beam is passed through a CVI dielectric 785±5 nm band pass filter to remove silica Raman signal generated within the 250 feet of glass optical fiber between the probe and the laser within the CPT control trailer. The laser line (785 nm) is then turned 90° into the Raman signal collection channel by a Chroma dichroic mirror. The long pass dichroic mirror acts as a high reflector at the laser wavelength, but transmits residual glass Raman signal into a beam dump within the laser channel. The beam dump acts to reduce the passage of reflected silica Raman signal into the collection channel of the probe. The laser beam is finally turned 90° by a second Chroma dichroic mirror to exit the Raman probe along the optical axis of the Raman signal collection channel. A beam dump is associated with this dichroic serves as a final silica Raman reduction device. Figure 5 illustrates the rejection of silica Raman by this probe geometry. The raw spectra, with no background removal nor dark subtraction are shown. Figure 5a shows the spectrum of sodium nitrate recorded without removing the silica Raman generated over 250 feet of optical fiber. Figure 5b shows the Raman spectrum of the same sample recorded with complete optical removal of the silca signal. The reduction in laser intensity from the fiber input to the probe exit as measured outside of the sapphire window is 50%. Raman signal is collected along the same axis. Collimated tank waste Raman signal is turned 90° into the Raman signal collection channel by the gimbal mounted mirror. Scattered laser light at 785 nm is removed from the collected Raman signal by means of the laser turning dichroic. The scattered laser light is reflected back into the laser input channel, while tank waste Raman signal passes through the filter along the optical axis of the Raman signal collection channel. Further rejection of scattered laser light is performed by a Chroma dielectric long pass filter. Figure 5 illustrates the effectiveness of laser line removal by the probe. Neither the laser line itself (Figures 5a & 5b) nor silica Raman signal generated from collected laser light over 250 ft. of signal collection fiber (Figure 5b) are evident. The collimated tank waste Raman signal is focused by an f/2 lens onto a 900 µm optical fiber for transfer to the collection fiber optic bundle. The spectra of several tank chemical constituents are shown in Figures 6 and 7.

During tank deployment of the cone penetrometer, it is operationally necessary to withdraw the Raman probe and the electrical cabling associated with ARA's physical property sensors to provide clearance for SAIC's neutron thermalization moisture probe down the center bore of the penetrometer pipe once full push depth has been reached. The use of a removable Raman probe is precluded as safety considerations necessitate the potting of the penetrometer pipe uphole from the Raman probe to seal the pipe from potential contamination by hydrogen. To accommodate both the operational removal requirement and to meet safety standards, the probe utilizes removable Lemo 0B fiber optic connectors for both the laser input optical fiber and the Raman collection optical bundle. The output of the laser cable 200 µm fiber is coupled to a 320 µm fiber, while the input side of a six around one fiber bundle (individual fibers are 200 µm in core diameter) is coupled to a 900 µm core fiber. The two fibers (320 and 900 µm) are fed through four inches of epoxy potting to the body of the fiber optic probe via steel tubes. The entire probe, consisting of the optical body and transfer fiber optics, is mounted into the CPT Raman probe housing via screws which lock onto the uphole lip of the housing, sealing the space below the flange and mechanically locking the probe in place, as depicted in Figure 1.

The fiber optic cables that establish optical communication between the deployed Raman probe and the surface instrumentation are designed to be removable with a push/pull type locking mechanism. A survey of commercial fiber optic connector vendors yielded one vendor who manufactures such a connector, Lemo. The Lemo connector plug locks down when pushed into a receptacle. An upward force is required on an outer knurled collet on the plug to disengage it. Both the laser fiber and the collection fiber bundles are terminated in the CPT at the Raman probe with a Lemo connector. The Lemo connectors are attached to the ARA electrical cables by means of a 26 gauge wire loop, which in turn is connected to the Lemo fiber optic release collet. The connectors are released when the wires, terminated in a 30 wire Lemo friction fitted connector, are retrieved from the cone penetrometer pipe. Pull testing by ARA at a distance of 60 ft. demonstrated the ease of optical cable connector release, requiring no more than 2 N of pull force. The fiber cables are jacketed in 3.8 mm O.D. Hytrel composite material with Kevlar fiber reinforcement. This material is both durable and flexible, and can easily withstand the temperature requirements of the tank environment. The cables are 250 feet in total length to accommodate the length of a full CPT tank deployment and the required slack for threading the cable in the undeployed CPT pipe rack. The surface terminus of each fiber is equipped with an SMA 905 connector. The single laser fiber mounts in the output end of the diode laser source. The seven fiber collection bundle is arranged as a 1x7 slit array of fibers to match the input slit of the Kaiser monochromator.

In summary, we have described the design of a chemically hardened Raman probe for deployment in the complex chemical environment of the Hanford underground storage tanks. The probe exhibits excellent rejection of silica Raman signal generated over the 250 ft. lengths of optical fiber required by the cone penetrometer deployment without compromising laser and signal throughput.

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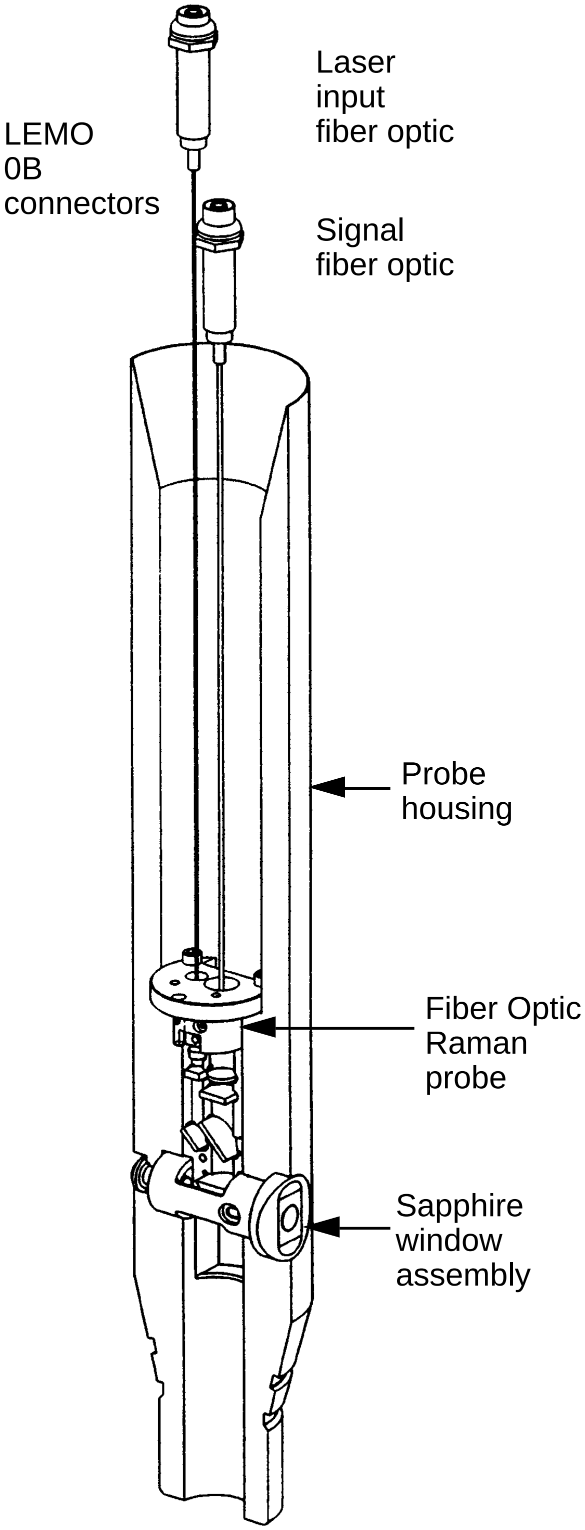

Figure 1. Cone penetrometer Raman probe, probe housing, and sapphire window assembly.

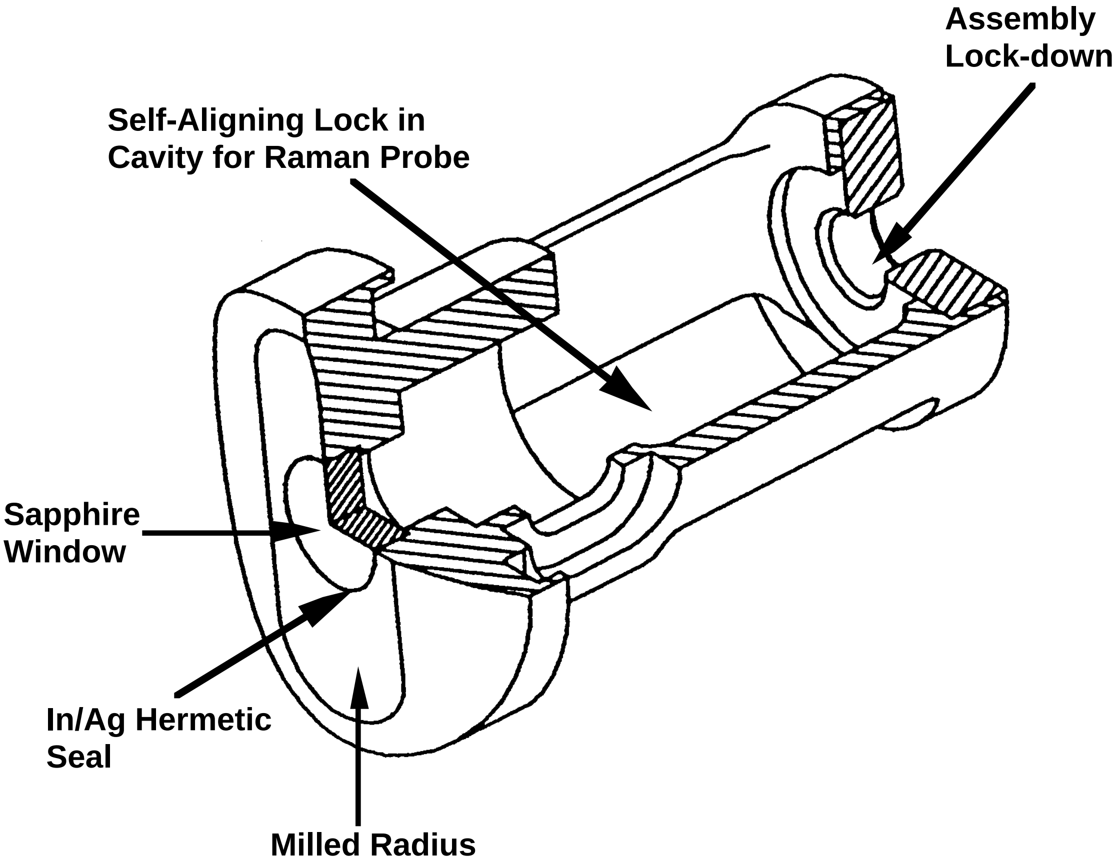

Figure 2. Sapphire window assembly.

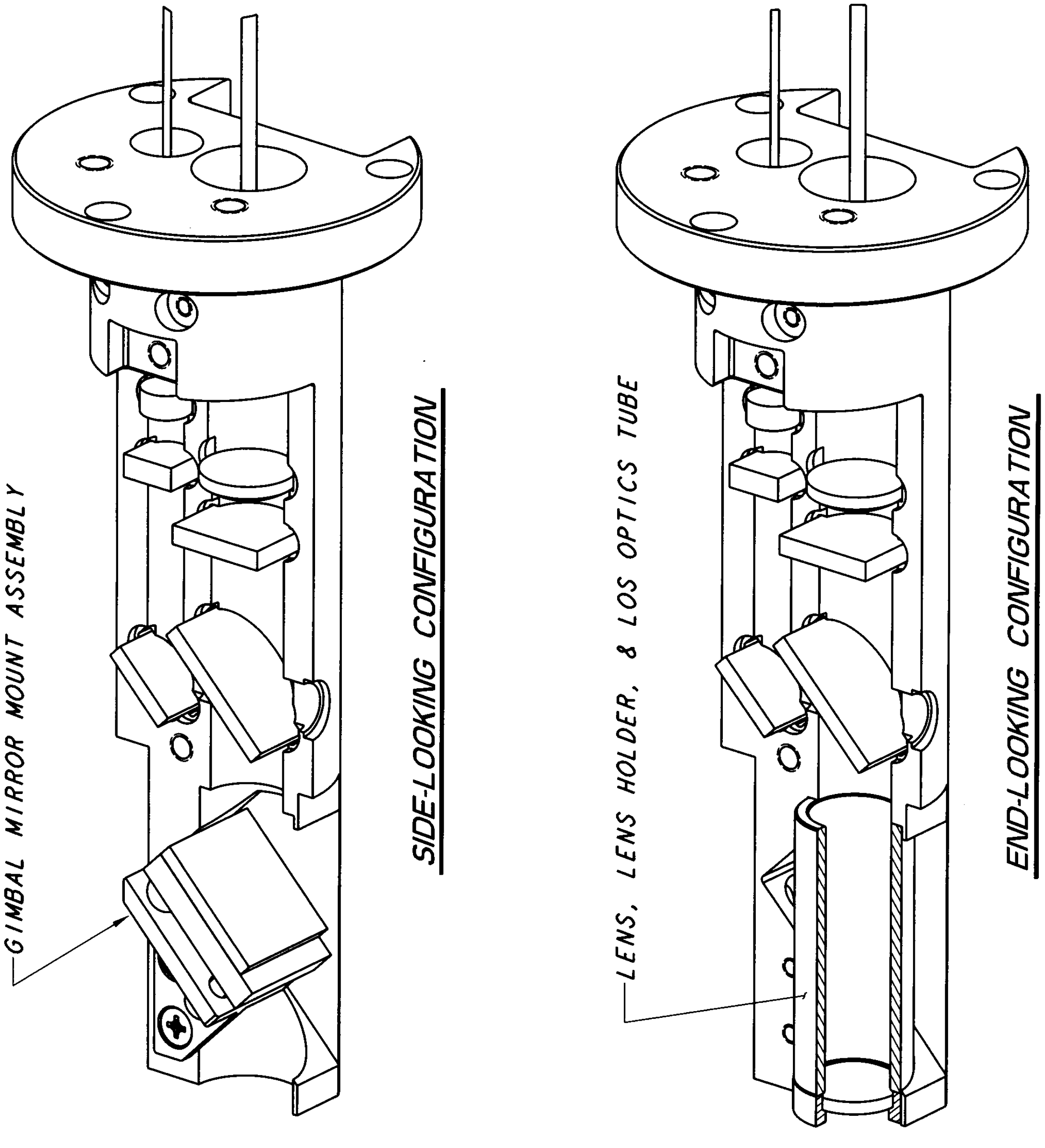

Figure 3. Fiber optic Raman probe. Side looking configuration is specific for the Hanford in-tank cone penetrometer.

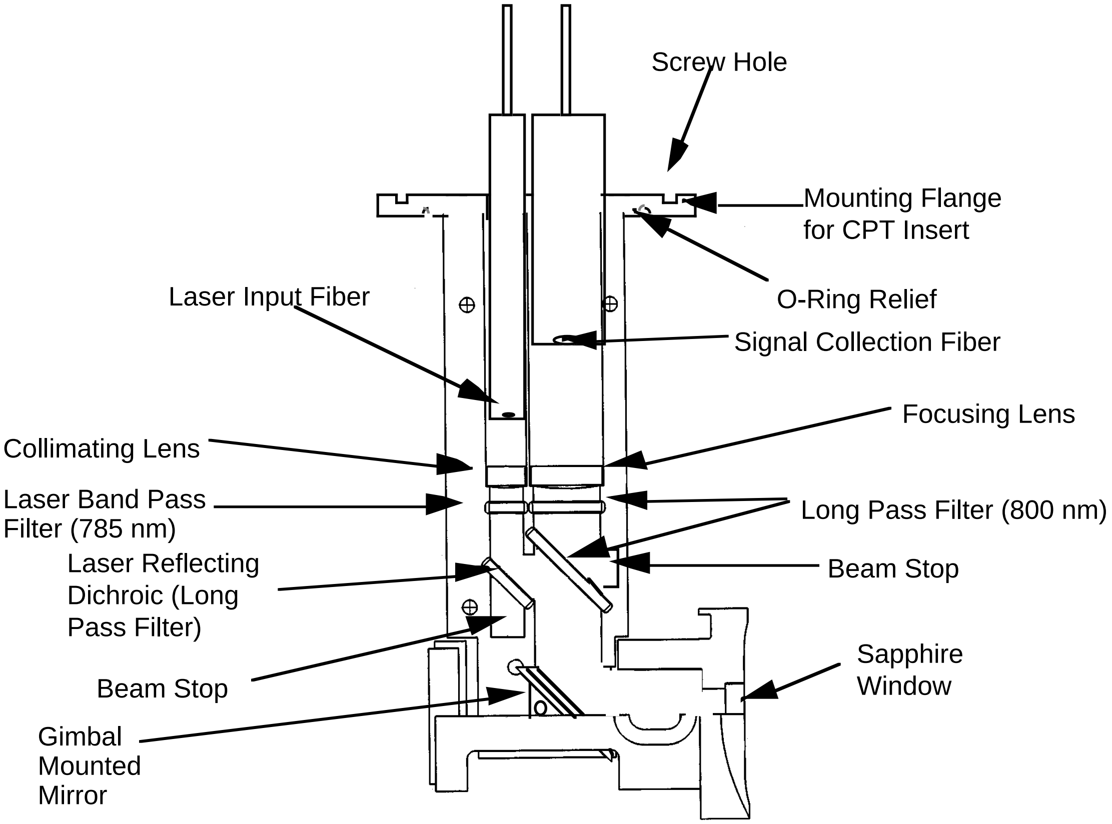

Figure 4. Raman probe optical components.

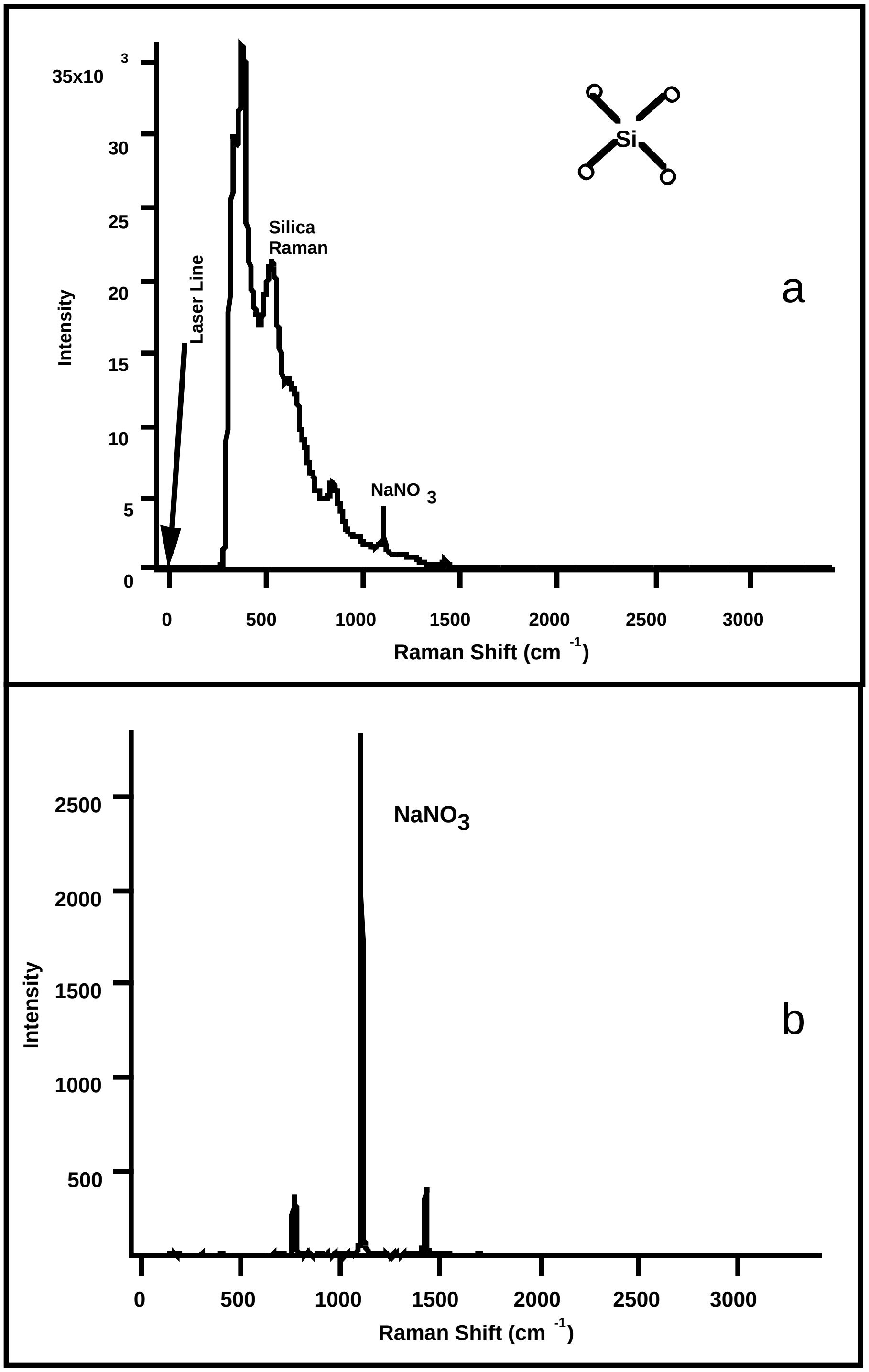

Figure 5. Raman probe silica response, sodium nitrate sample. a) unfiltered laser b) filtered laser. Exposure time is 1 sec.

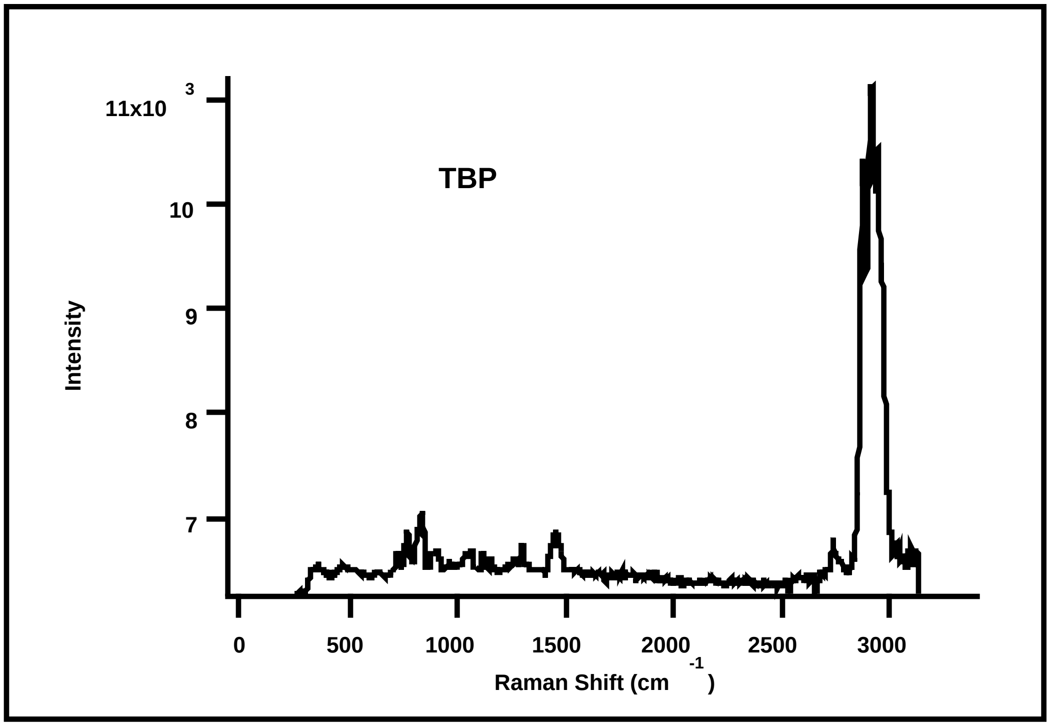

Figure 6. Raman spectrum of tributylphosphate. 20 wt. % TBP mixed with 20 wt. % aqueous NaOH.

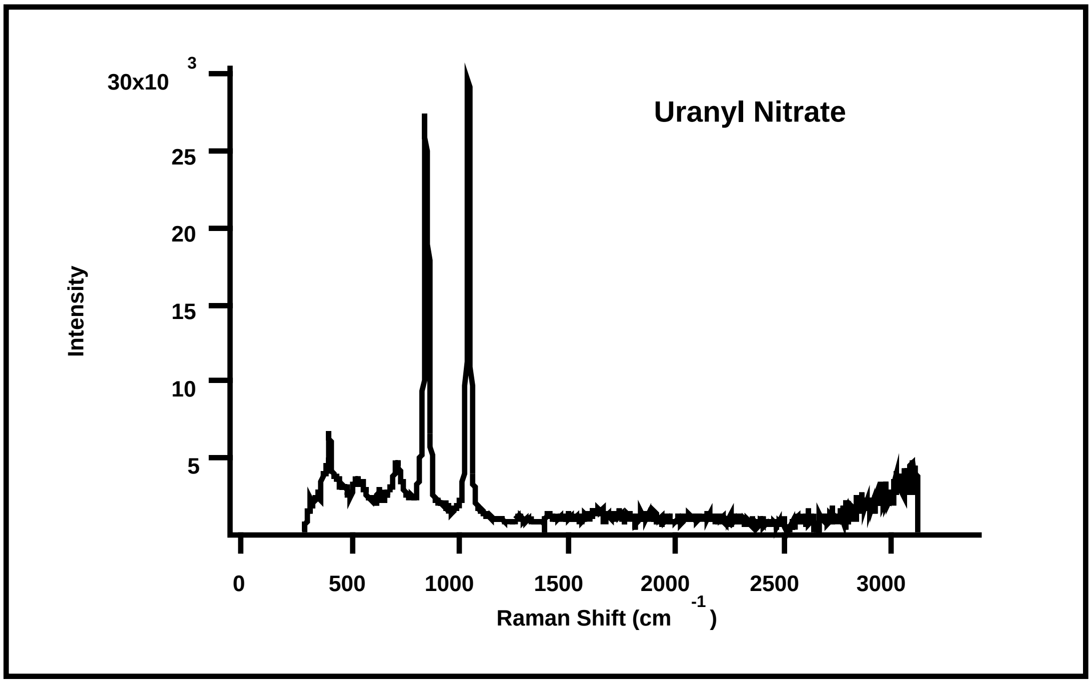

Figure 7. Raman spectrum of $UO_2(NO_3)$. 20 wt % mixed with 20 wt % aqueous NaOH.

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