Silica Fiberoptic Probe for Site Characterization

LEAD AGENCY: Department of Energy (DOE)

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PROBLEM STATEMENTS: This project is to develop improved techniques for locating, characterizing, and monitoring hazardous wastes in a timely, cost-effective manner as pointed out in the SERDP cleanup thrust. The innovative part of this project relies on the use of a unique all-silica fiberoptic spectral probe that we have initially developed for monitoring the soluble magnesium ion concentration in molten salts of interest to the electrochemical magnesium process industry. The probe is essentially a silica rod which maintains the characteristics of the individual optical fibers, from 2 to 7, of which it is composed. No glues, epoxy materials, or adhesives are used in the probe; such materials can result in stability problems, chemical or radiation, that are not shown by a pure silica material. This device has proven useful for spectral measurements in molten salts; it has the potential of many applications in the area of environmental analysis. In this project the probe will be coupled with commercially available components, in cooperation with EIC Laboratories, Inc., to make a portable instrument that will be field tested at various sites and process monitoring locations of interest to DOE, including the waste tanks of the Hanford site and in wells and locations on the Oak Ridge reservation. This probe should be very sensitive to heavy metals, various classes of organic compounds, biological contaminants and poisons. EIC Laboratories is already funded through the Morgantown Energy Technology Center of DOE under a project "Field Raman Spectrograph for Environmental Analysis." This new project involves applied research and an expanded technology demonstration.

PROJECT DESCRIPTION: We have developed an all-silica fiberoptic probe for use in monitoring the soluble magnesium concentration, as $MgCl_4^{-2}$, in molten $NaCl-KCl-CaCl_2-MgCl_2$ (35-35-15-15 mole%) at 700°C by Raman spectroscopy. We have also developed a normalization technique, based on comparing all spectra to the magnitude of the Rayleigh line scattering, to quantify this measurement. Because of the nature of the fabrication, this probe can be considered essentially a quartz rod that maintains the characteristics of the individual optical fibers of which it is composed. In preliminary studies the probe has been useful for obtaining Raman spectra over a temperature range of from 77 to 1200K, fluorescence spectra to 77K, reflectance spectra (of solids) from 77 to 1300K, and solution absorption spectra. The probe should be quite useful for characterizing and quantifying various inorganic and organic components on site in various environmental samples such as waste storage tanks, containers of unknown liquids, wells, soils, and groundwater. Normal Raman measurements would be applied to a high concentration of analytes; surface enhanced Raman spectroscopy (SERS) modified spectroelectrochemical SERS, fluorescence, and classical spectroelectrochemistry would be applied to trace concentrations of components. This probe will be quite useful for both the cleanup and compliance thrusts of SERDP.

The probe essentially has the physical properties of a pure silica glass rod so can be used over the temperature range of solid SiO_2, 0 to > 1500K; it is relatively inert to many chemical environments; it is made of very pure SiO_2 and has good stability to radiation effects. It is rugged, cheap to fabricate, and can be considered to be disposable if the need arises. In the case of our molten salt Raman application, it is slowly corroded by the melt, but continues to give reliable concentration information because of the normalization procedure that we developed. We wish to build on the above studies and develop applications of this probe to the identification and quantification of contaminants at locations of interest to DOE such as waste storage tanks, wells, containers of unknown liquids or solids, streams, groundwaters, or soils.

The probe will be applied to the characterization and quantification of solution and solid contents of the waste tanks at Hanford and INEL. The anion components of these tanks, CO3=, NO3-, NO2-, PO4=, ferri- or ferrocyanides, etc., have identifiable Raman peaks. The probe should be stable to the radiation fields in these tanks because it is essentially a quartz rod.

We have applied the probe to several different kinds of spectroscopies (i.e., Raman, fluorescence, absorption and reflectance) have fabricated and considered a number of different probe-head embodiments, and have demonstrated the usefulness of various coatings on the probe head to enhance its performance. Some of these studies have been published; some are as yet unpublished. Further characterization and development in these areas will maximize the usefulness of this probe as the analytical transducer for a portable field analytical instrument. For example, fluorescence measurements using the probe will be utilized to determine amenable organic and inorganic species at trace levels in various samples at DOE sites.

The fabrication of the probe head currently involves flame fusing the optical fibers into a quartz tube under vacuum conditions. The sealed end is cut and polished after fusing to make the probe head. The fusion process needs to be evaluated in terms of optimum conditions to provide a consistent method which produces proper sealing and minimal optical **?**cross-talk" across fibers in the head in order to guarantee quality control in preparing the head. There are various geometrical head configurations that will improve the probe efficiency. Some are uniquely possible because of the fused head design (invention disclosure ESID 947-X). Other embodiments will be developed (invention disclosure ESID 1389X) that will permit the capabilities of focusing exciting radiation and providing for the collection of a signal at a location away from the fiber head. One could therefore characterize the contents of bottles of unknown liquids at DOE sites.

We have demonstrated that a metal-coated optical fiber can be included in the bundles of fibers to be sealed in a probe. The metal coating on the fiber has served as an electrode to carry out spectroelectrochemistry. In this context, I am referring to studies in which a chromophore is generated or destroyed electrochemically at a location where it can be followed spectrophotometrically. These changes can be followed by fluorescence, Raman, or absorption spectroscopy depending on sample. The technique carried out in this fashion is very sensitive, and we wish to apply it to environmental samples. There are other spectroelectrochemical probes based on the principle that a silver surface can be electrochemically treated to yield, at least, generic selectivity to certain organic chloride compounds over other organic compounds. It is accomplished by placing a silver electrode close to the probe. A silver coated fused glass probe (probably with an inverted cone head) will be tested for such spectroelectrochemical SERS application. This design may greatly enhance the usefulness of an already useful environmental characterization device because the silver surface is immediately adjacent to the exciting and collection fibers.

We have carried out preliminary studies in which the all-silica fiberoptic probe head is coated with silica sol-gels. After curing the applied sol-gel, one has a porous surface on the probe head. Depending on the desired use, this surface can be clear or light scattering. Materials impregnated into the sol-gel are fixed in the sol-gel but able to interact with solutions surrounding the probe because the sol-gel surface remains porous. We have seen SERS effects by impregnating the sol-gel with silver, seen acid-base color changes by impregnated indicators, studied and published a spectral study of **?**buckyballs" impregnated in a sol-gel. These ideas will be further developed for their analytical usefulness.

The probe has been used to characterize, and quantify, amenable rare earth ions absorbed on the inorganic ion exchangers developed in the Chemical Technology Division at ORNL. We have done this by placing the probe in a bottle of either ZrO_2 or $Zr_3(PO_4)_4$ ion exchange beads on which Tb or Er have been absorbed. This approach is simple enough, and possibly not unique to our probe design. We want to extend the analytical usefulness of this technique so that it will be possible to analyze one or a few beads containing absorbed analytes of interest. Although we have no experience with this device for in-situ analysis, this would be possible and will be investigated. In either case this analytical approach would be applied to the identification and determination of amenable ions in bodies of water, tanks, waste streams, wells, etc.

We will collaborate with EIC Laboratories, Inc., Norwood, MA, in coupling our fiberoptic device to portable spectrometers and detectors they have developed. They have much site experience in environmental areas, and mutual interests will be served in a cooperative study. They are aware of our desires, and we have had much informal contact with them. To prepare for this collaborative effort, we require capital funds to purchase a research type spectrophotometer, CCD detector and associated computer controller to carry out laboratory studies that can be applied to their types of portable systems. One of our first demonstrations will be the use of an all-silica fiberoptic probe with EIC instrumentation for the Raman spectral characterization of components amenable to Raman spectral characterization at the Oak Ridge site.

EXPECTED PAYOFF: With successful completion of our project goals we will have a monitoring device that will have relatively excellent radiation and chemical stability and will be useful for many spectroscopic applications (Raman, fluorescence, SERS, absorption or reflectance). Compared with other probes which are used for such analysis, this probe should offer distinct advantages in harsh environments. It will also be simple, economical, and disposable if necessary. Already the probe is used for determining Mg ions in an industrial molten salt. After the developments described here, it shall find many other industrial applications, such as in areas of high pressure, low or high temperature, etc.

TRANSITION PLAN: As mentioned before, EIC Laboratories, Inc. will be an active collaborator in our studies. They have contractual obligations in place with many of the DOE problem sites. Implementation of our probes will be through this connection. We have had and continue to have additional informal contact with personnel at Hanford and at LANL for use of our probes. A prototype probe is already in use at LANL and will be used for Pu Raman studies in molten salts. By means of various programs within DoD and DOE, the end results of this project will be utilized. CRADA’s also will be developed for environmental and industrial users.