2.4 Neural Network Raman Cone Penetrometer Signal Extraction and Enhancement

Technology Need

The need for in situ chemical characterization of the Hanford tank wastes are driven by both data quality objectives (DQO), and 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. Operational concerns include the monitoring of phosphate levels, driven by the potential formation of sodium phosphate crystals that will increase the viscosity of the waste by formation of a gelatinous matrix that will reduce the ability of pumps to transfer and retrieve waste. A fiber optic remote Raman chemical sensor system will be incorporated and deployed in the Applied Research Associates (ARA) in-tank cone penetrometer to address these chemical safety and operational DQO needs. While Raman is a powerful technique for characterizing chemical species based on their vibrational spectral signatures, it suffers from inherently weak signals and interferences from sources of spectral noise as shown in figure 2.4-1, including fluorescence, fiber optic silica Raman signals, and random charge coupled device (CCD) detector noise. Additionally, the tank analytes of interest are found in a complex chemical matrix that include overwhelming amounts of other materials. These materials may act as potential interferents in a measurement by giving rise to extraneous signals that yield complicated spectra that are difficult to interpret. The neural network (NN) package, jointly developed by Lawrence Livermore National Laboratory (LLNL) and an industry partner, Physical Optics Corporation (POC), will address these issues, providing on-line, real-time chemical identification and analysis to address DQO concerns. This approach uses on-line intelligence to overcome limitations in the signal to noise ratio of instrumentation, and to minimize the effect of interferents in the sample matrix without involving chemical or chromatographic preprocessing of samples.

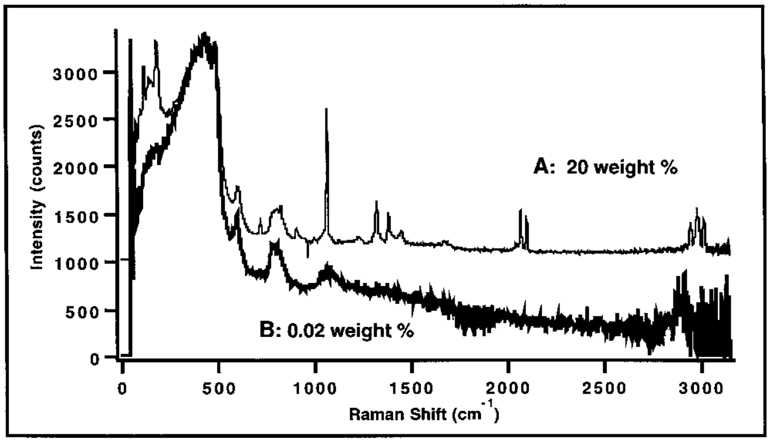

Figure 1: Raman spectra of tank waste simulant consisting of sodium nitrate, sodium nitrite, EDTA, sodium phosphate, and sodium ferrocyanide at 20 and 0.02 weight percent per component. The 20% spectrum exhibits multiple peaks due to the complex mixture. The 0.02% spectrum (bold) illustrates the obscuring of real Raman signal by system noise and silica fiber Raman (broad peaks).

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Figure 2.4-1 Raman spectra of tank waste simulant consisting of sodium nitrate, sodium nitrite, EDTA, sodium phosphate, and sodium ferrocyanide at 20 and 0.02 weight percent per component.

Technology Description

The goal of this effort is to produce and deliver a plug-in hardware module that enhances the capabilities of the Raman technique by performing signal extraction, automatic signal analysis, and feature identification on-line and in real time (one second or less per spectrum), in support of the in situ Raman cone penetrometer for chemical characterization of the Hanford underground storage tanks (USTs). The NN is utilized to identify and measure tank chemical constituents identified as safety and operational concerns to satisfy DQO that have been defined for UST waste retrieval and remediation efforts. The NN hardware is developed collaboratively with POC as a continuation of a project funded in FY94 by the Strategic Environmental Research and Development Program (SERDP) for the identification and enhancement of the Raman spectral signatures of chlorinated hydrocarbon solvents.

POC's NN system for the on-line analysis of tank waste component Raman spectral features is a pattern recognition system that combines conventional image processing and feature extraction methods with a proprietary hybrid NN. The neural network draws upon algorithms supplied by chemometrics, principal component analysis, cross correlation, acoustics, sonar, image processing, and oil exploration for a front end preprocessing package. These preprocessing algorithms are used to extract information from the complex raw spectral data, reducing large data sets to information on shapes, locations, intensities, ratios, and slopes of spectral features. The condensed features are fed into the input neurons of the NN for nonlinear processing and algorithms and NN architecture for identifying and measuring tank waste materials. LLNL is providing POC with the necessary Raman training spectral data for preprocessing algorithm and NN architecture development and optimization. These data consist of individual chemical components in concentrations ranging from 100 to 0.1 weight percent in both solid and aqueous matrices. These concentration ranges cover the concentrations of interest, as required by the waste tank retrieval and remediation DQOs. The tank constituents that are used for training the NN system for real time identification have been selected from the tank DQO lists and include, but are not limited to, sodium nitrate, sodium nitrite, bismuth phosphate, sodium carbonate, sodium sulfate, uranyl nitrate, sodium ferrocyanide, sodium nickel ferrocyanide, edta, tributylphosphate, acetone, sodium formate, dibutylphosphate, ammonium nitrate, sodium chromate, sodium dichromate, butanol, dimethylamine hydrochloride, formamide, sodium aluminate, sodium cyanate, and kerosene. POC is refining the NN package as needed to provide detection limits of tank constituents to necessary limits, greater than or equal to 0.1 weight percent.

Benefits

A cone penetrometer-deployed Raman probe offers the great advantage of in situ chemical analysis and depth profiling of tank wastes without the prior removal of waste materials. This greatly reduces the risk of contamination due to sample transportation and handling, minimizes exposure of personnel to radioactive contaminants, significantly reduces or eliminates sample waste generation, and provides significant cost savings. The current costs of obtaining and analyzing a single 18 inch core sample from a high level waste tank costs up to $750k per core. A data analysis package specifically designed for the analysis of concern for the safety and operational teams at Westinghouse Hanford Company (WHC), will add the benefit of greatly reduced data analysis time and cost. Operational data will be available as soon as it is recorded, rather than after a time delay to allow for post-collection processing analysis.

Collaboration/Technology Transfer

The original neural network technology was developed by POC under a previous contract to the Army for target pattern recognition, and to SERDP for chlorinated hydrocarbon solvent analysis. The application of the neural network to the Hanford tank farm environment will be a joint venture between LLNL and POC. POC will continue to hold the license to the neural network technology. The development will continue under this program as an in-house program at POC, leading to eventual commercialization of the hydrid neural network for use in government, industrial, academic, and medical communities.

Accomplishments

The NN was trained to identify the Raman spectra of individual volatile organic compounds such as CCl_4, $CHCl_3$, CH_2Cl_2, TCE, and TCA during FY95 under SERDP FY94 funding. The training of the NN was accomplished using single component Raman spectra with signal to noise ratios in the range of 5:1 to 35:1. Once the training was complete, the neural net was asked to identify approximately 75 low S/N (1:1 or less) spectra of individual chlorocarbons and four and five component chlorocarbon mixtures that represented complicated spectra with overlapping spectral features. The NN gave correct identifications with 93 percent accuracy, and gave 100 percent rejection of spectra consisting only of noise. Only 30 milliseconds were required to perform a complete deconvolution of 1024 spectral data points, including composition identification. The NN was also able to positively identify 2500 ppm (V/V) CCl_4 in methanol with 100 percent confidence, and 250 ppm (V/V) with 65 percent confidence. This represents an enhancement of the detection limits of CCl_4 by Raman spectroscopy by two orders of magnitude.

TTP Information

Neural Network Raman Cone Penetrometer Signal Extraction and Enhancement technology development activities are funded under the following Technical Task Plan (TTP):

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Bibliography of Key Publications

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