SERDP Strategic Environmental Research and Development Program
Improving Mission Readiness Through Environmental Research

Real Time Neural Network Raman Signal Enhancement

Cleanup
CU-621

LEAD AGENCY: Department of Energy (DOE)

LAB: LLNL

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PROBLEM STATEMENT: There exists a great need for site investigation technologies that provide waste location and characterization in real time. Raman spectroscopy is a vibrational technique which can be used to identify molecular structure in solids, liquids, and on surfaces. It is relatively insensitive to water, making it an ideal technique for identifying molecular contaminants in aqueous solutions. While Raman is a powerful tool in chemical identification, some weak points exist. The first is inherent in the Raman experiment itself, where the efficiency of the Raman signal is only about 10-8 of that of the excitation light. This results in measurements where the signal to noise ratio can be quite low, often obscuring important spectral information. The second is in the processing of the vibrational data, which can involve large, time consuming multivariant analysis programs as the complexity of the mixture being monitored increases. Herein we propose the development of a real time multispectral analysis system based on hardware that is being developed by an industrial partner that can extract data from extremely high noise and identify individual components of complex mixtures.

PROJECT DESCRIPTION: A novel Raman spectrometer shall be developed that utilizes Neural Network (NN) signal processing to extract the chemical signatures of VOCs from spectra exhibiting extremely high noise levels. The Raman system shall be used to both identify and quantify DOE/DoD target contaminants in both solid samples and ground-water, with a secondary application being the location and identification of subsurface NAPLs. The system will utilize a Neural Network package that is being developed by Physical Optics Corporation (POC) for real-time signal extraction from high background noise in conjunction with a remote Raman spectrometer. The POC Neural Network is unique in that it is based on VLSI digital parallel processing HARDWARE rather than a software package. The advantage of the hardware approach is the greatly reduced processing time involved (30 milliseconds for complex spectral input). The NN shall be "trained" to recognize the spectral features of organic compounds such as aromatic and chlorinated hydrocarbons at concentration levels ranging from ppb in water to neat liquids, and inorganic complexes such as ferri- and ferrocyanide in aqueous and solid inorganic matrices. A field portable unit shall be delivered for deployment at new and existing DoD/DOE waste sites to identify and measure contaminants in situ. Preliminary OHER funded research has demonstrated the successful application of NN to Raman spectroscopic problems. The identification of individual components of complex chlorocarbon mixtures in the presence of signal to noise levels of less than 1:1 has been performed, as well as the observation of marked enhancement of the lower limit of concentration levels of organic contaminants detectable by Raman spectroscopy in solution (10000 ppm carbon tetrachloride by conventional Raman vs 100 ppm (V/V) using a thermal electrically cooled OMA and NN data extraction). These analyses were demonstrated in real time, with five component mixtures with a signal to noise level of less than 1:1 being fully identified in under 1 second per spectrum. Continued refinement of the NN package will yield enhancement of the sensitivity levels by potentially three orders of magnitude.

The tasks within this project can be summarized as follows:

Training Data Acquisition: In FY93, Raman data for preliminary work with POC (OHER funding) was obtained with a laboratory Raman system consisting of a water cooled argon ion laser, table mounted optics, a SPEX 0.75 meter monochromator, and a Princeton Instruments TE cooled Optical Multichannel Analyzer (OMA). The current proposal requires a new library of Raman spectra of target organic compounds to train the POC Neural Network shall be obtained utilizing a field deployable Raman system. One such system has been developed at LLNL for the DOE/OTD UST-ID(TTP 2112-03). This system consists of an air cooled Ar ion laser for Raman excitation, a compact Chromex 0.25 meter imaging monochromator with optics mounted directly to the monochromator, and fiber optics which couple the monochromator and the laser source to various geometries of Raman probes. The detector is a Princeton Instruments liquid N2 cooled CCD camera, which offers an improvement of S/N by a factor of 10-100 over the OMA. We shall also survey commercially available portable Raman systems to determine the best system to be utilized in this study. Once a system has been chosen, a library shall be constructed consisting of the Raman spectra organic and inorganic target compounds, particularly chlorocarbons including CCl4, CHCl3, CH2Cl2, TCE, PCE, and TCA, gasoline components (BETX), inorganics nitrates, nitrites, and cyanides. The matrix will include spectra of each compound at various aqueous and solid solution concentrations to train the Neural Network to recognize individual species quantitatively.

Optimization of Neural Network Designs and Algorithms: Building on algorithms and experience obtained in FY93, POC shall continue to improve the sensitivity of their Neural Network based Smart Optical Spectrum Analyzer (SOSA). Using the data from the field deployable fiber optic Raman system obtained as described above, POC shall investigate various algorithms, such as matched filtering, wavelet analysis and multichannel correlation, for optimizing S/N of the input/output signals. Neural Network models will be selected to train the system with large numbers of compounds to subsequently extract and emphasize special features of the Raman spectral signals. Different techniques will be compared and optimized combinations will be selected based on accuracy of spectral identification, rejection of noise, accuracy of compound quantification, and processing speed.

Real-time Testing of Neural Network With Remote Raman System: POC shall deliver the optimized Neural Network Spectrum Analyzer to LLNL for evaluation under laboratory conditions using the Fiber Optic Remote Raman Spectrometer. The ability of the Neural Network to accurately identify and quantify organics as neet liquids, mixtures, and aqueous solutions shall be analyzed. The Neural Network shall also be required to sense and characterize organics under various environmental conditions such as temperature, pH, turbidity, and different exposure times. Data obtained at this stage shall be used to further refine the Neural Network.

Llnl Field Demonstration: A field deployable version of the Neural Network shall be integrated with the field Raman system. The combined unit shall be tested at LLNL's site 300 for characterization of aqueous TCE levels and TCE NAPLs. Groundwater monitoring wells at LLNL main site will be used to demonstrate the utility of the system for TCE detection below 100 ppm.

DOE/DoD Site Demonstration: The Neural Network and Raman system shall be used at DOE/DoD sites for real-time identification and quantification of the components of the complex chlorocarbon contaminants in the groundwater. DNAPLs shall be mapped, if applicable. In addition, identification of inorganic components of UST core samples at the Westinghouse Hanford Site shall be performed in conjunction with the UST-ID Raman program Experience gathered at the test sites shall be used to define a practical instrument for real-time, ultrasensitive simultaneous detection, identification, and quantification of environmentally significant compounds at DOE/DoD hazardous waste and remediation sites.

EXPECTED PAYOFF: The success of this program shall result in a commercially available spectral analysis package to be manufactured and marketed by POC. While this proposal deals specifically with the application of the POC Neural Network to Raman Spectroscopy, the successful completion of this project will also serve as a proof of principal that the Neural Network can be universally applied to spectrographic techniques in general, eventually leading to the utilization of the spectrum analysis in Mass Spectrometry, Infra-red Spectroscopy, etc. The end deliverable to the DOE/DoD will be Raman instrumentation that can be used for qualitative and quantitative real time analysis of the components in environmental contamination sites.

TRANSITION PLAN: The original Neural Network technology was developed by POC under an SBIR to the army for target pattern recognition. The development continues as an in house program at POC, leading to eventual commercialization of the Neural Network for use in government, industrial, academic, and medical communities. The application of the Neural Network to environmental problems was a joint venture between LLNL and POC. The final transfer of technology from the laboratory to the field shall entail the purchase of the Neural Network system from POC as the commercial vendor.