

## ABSTRACT

Monwuba, Chukwukelue K. Ph.D., Purdue University, December, 2012. Study of Geoenvironmental Influences on Raman Spectroscopic Monitoring of Chlorinated Solvent Natural Attenuation Major Professor: Joseph V. Sinfield.

“Monitored natural attenuation” is presently deemed the most technically practicable and economical means of remediation for chlorinated solvents, and optical spectroscopic methods have gained attention as a potential means to enable long-term monitoring of this process. However the challenge of ensuring that effective remediation is occurring lies in obtaining high quality, representative field measurements in a complex hydrogeological environment. In particular, a number of factors inhibit acquisition of useful in-situ observations of these compounds such as the simultaneous presence of multiple compounds that can confound target analyte analysis, the low in-situ concentrations that pose health hazards, interference from both natural and anthropogenic in situ fluorophores, and the existence of suspended soil particles (turbidity) in subsurface pore water.

The purpose of this study was to evaluate and characterize the influence of these geoenvironmental parameters on the capability of a Time Resolved Raman Spectroscopy (TRRS) System to observe chlorinated solvents in simple aqueous samples and simulated degraded field samples via laboratory tests. The laboratory investigations were performed using a versatile low cost, compact, closed and open path laser TRRS configuration, designed and built to suit the requirements of the work.

The work led to the following findings:

The 20 $\mu$ J pulsed laser TRRS system was shown to enable direct detection of trichloroethylene (TCE) in aqueous solution at field relevant concentrations down to 150 ppm via monitoring of the TCE 450 $\text{cm}^{-1}$  ( $\sigma\text{CH}$ ) vibrational mode. In addition, observation of the effects of TCE-originated chlorine on the 3511 $\text{cm}^{-1}$  (OH) vibrational mode of water was shown to provide an indirect indication of TCE concentration with a 6.25-fold improvement in sensitivity relative to the direct measurements.

The capability of the TRRS system to obtain valid measurements ( $\text{SNR}>3$ ) of chlorinated samples in the presence of fluorophores with varying decay lifetimes (0.7-4.4ns) was also demonstrated. Experimental studies of humic acid, fluorescein, and rhodamine TCE mixtures

facilitated development of a model relating optimal TRRS photon collection counting time to fluorophore fluorescence lifetimes.

The influence of suspended particle size and turbidity on the TRRS measurement of target analytes in aqueous solution was also evaluated leading to a generalized turbidity correction model for aqueous samples containing compounds that do or do not influence the Raman vibrational modes of water.

Finally, validation of system sensitivity and developed corrective procedures was performed in the lab on samples that simulated the anaerobic degradation of chlorinated solvents. Test results demonstrated the potential for TRRS to mitigate the traditionally adverse effects of the aforementioned interfering geoenvironmental influences on target analyte Raman observations.

Overall, the results of this work highlight the fundamental impact of environment-related influences on Raman spectroscopic observations and have applicability in a broad range of fields involving analyses of materials in complex, turbid, and/or fluorescence limited settings such as water quality monitoring, precision agriculture, petroleum exploration, and assessment of homeland security threats. In addition, evolution of the design of the TRRS system enabled through this work has facilitated progress toward optical spectroscopic monitoring systems that can be deployed at low cost over large areas, and yet provide specific analyses of a broad range of chemical compounds in nearly real time.