

APPLICATION SUMMARY Detection of DNAPLs by Raman Spectroscopy

Introduction

The presence of dense non-aqueous phase liquids (DNAPLs) poses a threat to drinking water supplies. Because DNAPLs can "pool" in the subsurface, slow dissolution into large volumes of water results in a long-term source of contamination. Common DNAPLs are chlorinated solvents such as trichloroetyhylene (TCE), perchloroethylene (PCE), CCl₄ and CHCl₃. These chlorinated solvents have been used as degreasing agents for aircraft and are often located on and around military installations. DNAPLs can also be present where dry-cleaning facilities and other industrial corporations have been situated.

Locating and identifying DNAPLs is a challenging task, complicated by the non-stationary nature of the relatively thin layers. Accessing the buried contaminants is achieved with a cone penetrometer, which is essentially a very long tube with a pointed tip. The cone is hydraulically driven into the soil and can accommodate sensors for *in situ* detection of contaminants.



Above: A cone penetrometer truck (CPT) stabilized for cone deployment. Right: Cone tip and rod sections showing viewport for sensor implementation.



The Raman Sensor

EIC Laboratories has deployed a Raman fiber optic sensor in the cone penetrometer for accurate identification of DNAPLs. Modification of existing Raman technology enables a fully-filtered probe to be installed in the conventional cone rod. Protected by the environment with a quartz window, the probe is able to measure spectra periodically through the cone push; identification of DNAPLs is achieved by simple comparison with laboratory data.

The system consists of a mobile Raman spectrometer and a specialized side-viewing fiber optic probe. The spectrometer provides high quality spectra with no moving optical parts, offering rugged instrumentation necessary for mobile applications. The side-viewing fiber optic probe is a modified version of the "end on" probe used by EIC Laboratories in many other applications. Side-viewing optics enables the 0.5" diameter probe to be installed vertically inside the *ca.* 3" diameter cone rods. A quartz window protects the probe from the

environment during the deployment. Depths of over 300 feet are achievable with the Raman sensor, owing to the efficient optical filtering in the probe design.



The side-viewing RamanProbe™.

Deployment of the Sensor

The Raman sensor has been deployed at various sites since 1998. Spectral data shown are from a recent cone push at the Savannah River Site in Georgia.

As the cone continuously bores into the ground, survey Raman spectra were accumulated for approximately 10 seconds. When significant Raman bands are observed (or when another sensor detects the presence of DNAPLs), a longer Raman exposure is acquired. Identification of the contaminant is achieved by comparison with a spectral database of known DNAPL species compiled earlier in the laboratory.

The Raman cone penetrometer sensor continues to be deployed by an outside agency.



Inside the CPT: (Upper) The Raman spectrometer system, data station, and fiber optic cables.¹ (Lower) Cone rods with prestrung fiber cable await deployment.



Survey spectra measured while the cone is deployed.



Comparison of CPT data with a reference database provides positive DNAPL identification.

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¹Note: Raman instrumentation used and developed in this application are available from EIC's commercial subsidiary, InPhotonics, Inc. Visit us on the web at www.inphotonics.com.