Three-Dimensional Integrated Characterization and Archiving System (3D-ICAS) Phase I

Topical Report

July 1994

Work Performed Under Contract No.: DE-AC21-93MC30176

U.S. Department of Energy
Office of Environmental Management
Office of Technology Development
Washington, DC

For

U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By
Coleman Research Corporation
Springfield, Virginia

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1000 Independence Avenue
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July 1994

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1.0 INTRODUCTION

Coleman Research Corporation (CRC) provides this Final Topical Report for Phase I (of three planned phases) on the development of the 3 Dimensional Integrated Characterization and Archiving System (3D-ICAS) under contract number DE-AC21-93MC30176.

CRC is developing the 3D-ICAS to support Decontamination and Decommissioning (D&D) operations for the Department of Energy addressing Research Area 6 (characterization) of the Program Research and Development Announcement (PRDA).

The 3D-ICAS provides in situ 3 dimensional characterization of contaminated DOE facilities. Its multisensor probe contains a GC/MS sensor for organics, a molecular vibrational sensor for base material identification, and a radionuclide sensor for radioactive contaminants. This system development will have these advantages over existing technology:

- GC/MS chemical analysis uses non-contact infrared heating, advanced preconcentration techniques, and a high performance GC system which acquires a larger sample and achieves high performance GC separations. The result is a projected cycle time of under a minute with a projected detection limit in the low part per billion range. Conventional technology can range from hours to days for sampling, storage, transportation, and analysis at an off-site laboratory;
- chemical analysis costs are reduced because the process is automated and on-site;
- on-site, real-time analysis requires less time to respond to problems encountered during decontamination than is possible with conventional analysis;
- sample handling by data collectors and laboratory personnel is eliminated, thereby reducing health risks.

The positioning of the sample probe by the CLR 3D mapper relies upon the advantages of the CLR over other 3D mapping technologies as follows:

- the CLR 3D mapper is immune to ambient light and surface shading. Structured light or AM laser radar are not immune;
- each sample point is precisely located within 1mm. This is far more accurate than structured light or AM laser radar;
- computer recording of sample location removes human error;
- CLR is the only 3D mapping capability compatible with the GC/MS. Other 3D mappers would be overwhelmed by the sample illuminations of the GC/MS probe.

The 3D-ICAS consists of two mobile subsystems (the sensor platform and the mapper platform), which operate in contaminated areas, and the integrated workstation, which remains in a safe location. During characterization operations the mapper, using its coherent laser radar (CLR), maintains its precise location and supports and reports the positioning of the multisensor probe by the sensor platform. The operator at the integrated workstation, using displayed 3D map information, plans and directs the selection of surface areas to be characterized and the density of sampling to be employed. The 3D-ICAS then automatically samples these areas, archives 3D location, time, and levels of each contaminant, and provides map displays at the workstation showing contoured contaminated regions. The permanent measurement data archiving allow easy regulatory review of the characterization process and assures data integrity. The dense, uniform surface sampling allows the straight forward establishment of the contour bounds of regions exceeding regulatory limits.

The report is organized in four main sections:

1.0 Introduction

- states program objectives and scope and summarizes accomplishments

2.0 Technical Progress

- addresses technical accomplishments of each of the three major technologies (coherent laser radar 3D mapping and tracking, gas chromatography, and molecular vibrational spectrometry)

3.0 Phase I Demonstration

- discusses the demonstration of the 3D mapper and gas chromatograph with integrated 3D display

4.0 Conclusions, Recommendations and Revised Requirements for Phases II and III

1.1 Objectives

The overall objective of the proposed work is to develop a single 3D-integrated characterization and archiving system (3D-ICAS) and demonstrate Maturity Level V at a DOE site. 3D-ICAS will provide real-time quantitative measurements of volatile organics and radionuclides on bare materials consisting of concrete, asbestos, and transite; it will provide 3D display of the fusion of all measurements; and it will archive the measurements for regulatory documentation. 3D-ICAS consists of two robotic mobile platforms that operate in hazardous environments linked to an integrated workstation in a safe environment. Three distinct phases are proposed to achieve this objective.

The objective of Phase I was to verify and develop, where necessary, the component technologies of a 3D Characterization system and to assess their effectiveness as part of an integrated system and to demonstrate Maturity Level III. This phase showed the feasibility of high speed chemical analysis for identification and quantification of contaminants and demonstrated the capability for high speed 3D mapping of surfaces of base materials such as concrete and transite. This phase also verified, through laboratory studies and analysis, the utility

of a molecular vibrational spectrometry (MVS) sensor as a fiber optic component of a multi-sensor probe and determined the feasibility of remote spectroscopic analysis.

1.2 Program Approach and Progress Summary

Prior to this development program all basic subsystem components of 3D-ICAS had been demonstrated at least at the laboratory level. During the Phase I effort the CRC team accomplished the objective of verifying and developing the component technologies, assessing their effectiveness as part of an integrated system and demonstrating maturity level III. The scope of Phase I was to demonstrate the 3D Coherent Laser Radar (CLR) Mapper and gas chromatograph (GC) sensor for volatile organics and to evaluate molecular vibrational spectroscopic sensors for inorganic base materials and organics.

For the 3 Dimensional facilities mapping and sensor/end effector tracking and position location, the fiber optic CLR 3D Mapper has been implemented as a demonstration system under a separate NASA/DOE program. That system has been provided to this 3D-ICAS effort to allow implementation of sensor tracking and location software algorithms and to provide a 3D surface mapping and sensor location for the Phase I integrated demonstration. The separate NASA/DOE program is continuing forward with the development of a fieldable 3D mapper with substantially increased speed and accuracy which may be used to support Phases II and III of the 3D-ICAS development program. Under Phase I, the 3D Mapper demonstration system was capable of 3DOF location (3D location only) of a manually positioned GC sensor. In Phase II, using the NASA/DOE 3D mapping system now being completed with software enhancements, a robot arm borne multi-sensor package will be tracked in 6DOF (3D location and orientation) while performing 3D contamination mapping of surfaces. For contamination mapping, the 6DOF sensor tracking is essential to assure proper orientation of the sensor with respect to the facilities and equipment surfaces.

Subcontractor Thermedics Detection (TD) has modified its Gas Chromatograph system, originally developed for explosive detection, to detect hydrocarbon organic contaminants, notably PCBs and others of interest to DOE. This modification and subsequent experimentation has verified the ability of the system to perform successfully with a long transport tube between the collection head and the GC column, which will be required for the sensor head at the end of a long robot arm in the 3D-ICAS system. The system has shown a resolving power substantially exceeding the 100 lines/minute sought after to discriminate organic contaminants and promises, when integrated with a mass spectrometer in Phase II, to detect organic contaminants to regulatory levels (low parts per billion).

Finally, TD has developed a sensor which can desorb and collect contaminants directly from surfaces and convey them via a transport tube to the GC system. For DOE robotized contamination detection applications this is a significant development step, since it allows the elimination of the manual operation of conveying the separated collection head to GC system input as was required by the modified GC explosive detection system. This integrated sensor head was the front end of the GC system in the 3D integrated contamination mapping demonstration conducted at the conclusion of Phase I of the 3D-ICAS development program.

The University of Idaho (UI) has performed experiments to determine the most suitable remote molecular vibrational spectroscopic technique for the purpose of identifying surface materials as part of the D&D characterization effort performed by 3D-ICAS. The selected technique is a fusion of Near-Infrared (NIR) Raman Spectroscopy and Mid-Infrared (MIR) Reflectance Spectroscopy.

The NIR reflection spectra of many materials studied were featureless and unsuitable for identifying their chemical composition. MIR reflection spectra usually had high spectral contrast and high signal to noise ratio but the measured spectra were strongly dependent on the surface morphology of the sample: the ratio of diffuse reflection to specular reflection increased as the surface roughness increased. Both MIR reflection and Raman spectrometry yield relatively strong but variable spectra for concretes.

Raman spectra of most materials investigated, including asbestos, transite, woods, plastics and organic chemicals, could be measured with a 1064-nm neodymium-doped yttrium aluminum garnet (Nd^{3+} :YAG) laser source and an indium gallium arsenide (InGaAs) detector. The fact that these spectra can be measured through quartz or silica fibers is an added benefit. It has been shown that materials with Raman spectra as similar as those of hard and soft woods can be distinguished through the application of a feedforward neural network.

We have thus shown that a combination of MIR Reflectance and Raman spectroscopy show structured spectra for all of the basic materials of interest to DOE. We have applied pattern discrimination to distinguish similar classes of materials and have high confidence in accomplishing classification of the whole set of materials of interest to DOE with a fused MIR-Raman sensor approach.

Several tests have been made to determine the actual laser wavelength that should be used for the Raman sensor. The effect of fluorescence for many of the samples listed above has been tested at 632.8 nm [helium-neon (He-Ne) laser] and 1064 nm (Nd^{3+} :YAG laser), with illumination at the longer wavelength reducing fluorescence significantly. In the last 2 weeks of June, a trip was made to England by one of the UI team to obtain Raman spectra with a diode laser emitting at 780 nm on a monochromator equipped with a charge-couple device (CCD) array detector. Spectra of asbestos samples showed that fluorescence still presented a significant interference. Excitation with an 840 nm diode laser and measurement with a monochromator and CCD detection reduces fluorescence significantly, but for at least 10% of the samples, excitation with a 1064 nm Nd^{3+} :YAG laser and measurement using a Fourier transform Raman is necessary.

The strengths and weakness of various probe designs for Raman spectrometry have been investigated; several of these appear to have the properties required for remote measurements. A quartz confocal Raman spectroscopic probe such as the "Super-Head" probe marketed by Dylor appears to be the best design which is currently available to meet the DOE objectives.

2.0 PHASE I TECHNICAL PROGRESS

2.1 End Effector Tracking

CRC has developed an efficient approach for the CLR for tracking position and orientation of a robot end effector. Analysis, simulation, and laboratory experiments demonstrate the technique's effectiveness. The full 6 degrees of freedom capability of this approach will be implemented and demonstrated during Phase II. The full 6DOF system will measure three location coordinates (X, Y, and Z) and three orientation coordinates (Yaw, Pitch, and Roll). A simpler 3DOF system measuring the location coordinates was demonstrated at the end of Phase I.

The technique consists of scanning the CLR beam around a specific target on the end effector. The target is a wagon wheel consisting of reflective spokes on a non-reflective background (Figure 2-1). The wheel may be symmetric or asymmetric as discussed below. There may be one or several targets on the end effector as discussed below. The wheel diameter is nominally 2 inches for the 3D-ICAS project because of the assumed size of the sensor package to be used in Phase III.

The CLR is commanded to scan a circular pattern of radius approximately 1 inch on the target and centered somewhere on the target, within 1/2 inch of the center. Since the angular resolution in the scanner used in the Phase I demonstration is 0.01 degrees, a single scanner step produces a cross-range step of .07 inches at 10 meters therefore, generating a 1 inch radius circular scan is well within Phase I system capabilities.

The CLR returns range, signal amplitude, beam azimuth, and beam elevation data during the scan. The Phase I 3D-ICAS demonstration system is programmed so that the scanner sequentially steps to a succession of commanded beam positions, settles, and then measures signal strength and range during the observation period. Consequently, returned data consists of range signal amplitude pairs at a sequence of predetermined beam locations. The Phase II system will be modified so that the beam scans continuously while the CLR samples range, signal amplitude, and beam position at a specified sampling rate. This modification will increase operational speed so that a moving end effector may be tracked continuously.

The signal amplitude data are processed to estimate the horizontal and vertical cross-range coordinates of the target's center relative to the center of the circular scan. The signal amplitude is threshold-detected and median-filtered to produce a binary signal. The relative widths of successive on- and off-times are determined by the location of the scan axis relative to the target center. Figure 2-2 shows typical raw signal amplitude data and the binary signal from an experiment with a four spoke wagon wheel target, and the scan axis at the center of the target.

Amplitude data also provides the target's roll angle, i.e. rotation around the line of sight from CLR to target center. The phase of the binary signal relative to a reference binary signal is determined by the angular orientation of the target relative to the reference. Roll angle exhibits 4-fold ambiguity given a 4-spoke target. Consequently, unambiguous roll angle

Figure 2-1. Wagon Wheel Target

Figure 2-2. Signal Amplitude and Binary Signal

estimates are possible with the 4-spoke target as long as the roll angle is within ± 45 degrees (the practical range is somewhat smaller). Unambiguous roll angle estimates may be made by modifying the target so that the 4-fold symmetry is removed, e.g. by splitting one spoke into two segments to provide a vertical reference.

The range data are processed to provide estimates of range to the center of the target, and the two remaining orientation angles, pitch and yaw. Range varies through a single cycle of a sinusoid during a single circular beam scan. The peak-to-peak variation is directly related to the tilt of the target surface relative to the line of sight from laser to target. The phase of the sinusoid is linearly related to the orientation of tilt. The two measurements together provide yaw and pitch. The mean value of the range measurements is an estimator for the range to the point on the target surface intersected by the scan axis. The range to the center of the target may be computed from the two angles and the range estimate.

Pitch and yaw angle estimates deteriorate as the angles increase because the reflected light decreases and because the cross-range extent of the target decreases. A 2 inch diameter target presents a 1.4 inch cross-range extent at a 45 degree tilt angle; the 1 inch radius scan circle is not enclosed by the target. To remedy this, similar targets are provided on several surfaces so that the system may switch to another target that provides a larger cross section whenever necessary.

The discussion so far has concentrated on estimating the location and orientation coordinates of a stationary target during Phase I. The constraining factors are the existing CLR software, which was not designed for continuous tracking operation and the CLR processing hardware which limits the measurement speed. The software will be upgraded in Phase II to enable continuous tracking. The CLR hardware will be replaced with the next generation NASA/DOE CLR 3D Mapper system which will have at least 200X faster range and amplitude information to support the 6DOF tracking.

Continuous tracking is accomplished by continuously scanning the beam in a circular pattern with the focus and scan axis controlled by a Kalman state estimator filter. Estimates of the six coordinates are made once every complete circular scan. These estimates are inputs to the Kalman state estimator. The purpose of the Kalman filter is to provide instantaneous estimates of the end effector's location and orientation and to smooth effects of noisy measurements.

An enhancement to tracking accuracy is provided by occasionally sequentially stepping the beam to a series of retro-reflector spots and dwelling long enough for a high accuracy range measurement. These high accuracy range estimates are made using a quadrant detector so that vertical and horizontal errors as well as range are estimated. Since the location and orientation of the end effector are continuously updated by the Kalman filter, the beam may be pointed at the reference spots without searching, as long as the errors in the six coordinates are small. Consequently, the running error covariance matrix from the Kalman filter is used to determine when the high accuracy measurements must be made.

Coarse target acquisition is necessary to acquire tracking lock initially and whenever lock is lost. Rapid coarse acquisition may be achieved by conducting a raster scan over a large area with a relatively large spacing between measurement points. A rectangular target is more appropriate for coarse acquisition than the wagon wheel because the target's extent along the scan direction is constant regardless of what part of the target is scanned. The concept is that a raster scan is established so that two or more beam dwells would be on the rectangular target within a predetermined search volume. This establishes the target's location to within the raster dwell spacing. A second scan consisting of a single vertical sweep and a single horizontal sweep with much finer beam dwell spacing and centered on the rectangular target reduces the location estimate error so that the following circular scan may be centered within the wagon wheel target. For example, coarse acquisition of a 4"x4" square target within a 3'x3' search area requires 9 horizontal scans with 12 dwells per scan, or 108 beam dwells. The next raster consists of two scan lines about 8" long with .25" spacing, or 64 beam dwells. The center of the square may then be calculated to within .25" in each coordinate. The 108 beam dwells for the first search cover the entire search area. On average only half as many dwells will be needed because the target will be found before the end of the raster scan.

Selectable target shape is a definite benefit to acquisition and tracking. A rectangular target is optimum for coarse acquisition whereas a wagon wheel is optimum for high accuracy location and tracking. Active targets consisting of liquid crystal light switches in front of a reflective backing provide this capability. The targets would be switched to rectangular shape for acquisition and then switched to wagon wheel shape for tracking. A third configuration, an asymmetric wagon wheel, could be switched in to assist in determining roll orientation. Selectable targets provide an additional benefit during acquisition since several targets are needed on the end effector to ensure that at least one is visible to the tracker and properly oriented at all times. Selectively switching targets on and off would allow the tracker to identify the target being tracked. Although similar results could be obtained from multiple rectangular and wagon wheel targets with built-in unique identification coding, CRC feels that active targets provide a simple system solution to tracking with the minimum number of targets, all of which are identical.

2.1.1 Tracking for Phase I Demonstration

A robot arm is to be acquired in Phase II, and a moving platform for the arm in Phase III. Sensor movement in Phase I was done manually. The demonstration included mapping a small surface area and storing the 3D map before the demonstration. During the demonstration the GC was mounted on a manually positioned stage that could be moved along two axes, horizontal and vertical. Rotation was not allowed. In addition, the high speed CLR system required for automated 6DOF tracking will be developed in Phase II. Consequently, the Phase I demonstration consisted of manually moving the sensor head a short distance and letting the position estimation system determine vertical and horizontal position and range, in steps. The software will not be fully integrated until Phase II so that the operator must manually activate data acquisition, the location estimation processing, and contaminant measurement. Contaminant

measurements were plotted on the 3D map at the locations estimated for the sensor probe, i.e. the center of the stage carrying the sensor corrected for the location of the probe relative to the sensor stage.

2.1.2 Experimental Results

A simple experiment was run to demonstrate the feasibility of estimating the location of the center of a wagon wheel reflecting target using a circular scan on the coherent laser radar (CLR). A four spoke wagon wheel was made by hand, using a knife and straightedge. It was stuck on a piece of cardboard with scotch tape and positioned at roughly 4 meters from the CLR. A scan file of 256 range/azimuth/elevation triples was generated and passed to the scanner. The scan pattern file consisted of 256 range/azimuth/elevation triples defining a 1 inch radius circle range of 4 meters. Data files were acquired from several runs consisting of a single circular scan each with different horizontal and vertical positions. For the first run, the target was centered on the laser beam after the scanner was commanded to move to the null position. Thereafter, the target was moved horizontally and vertically for each run. Signal amplitude data files were processed as discussed above to estimate the horizontal and vertical position of the target. We stress that this experiment was run to determine the feasibility of the approach, and it was not tightly controlled. The target was made by hand. It was attached to the backing with tape and no attempt was made to ensure a flat target. The target was aligned by hand, and the tilt angles were not controlled. Better contrast between on and off signals would have been achieved if the backing had been painted with absorbing paint. Finally, position of the target at each run was estimated by eye.

The position of the center of the wagon wheel was estimated by searching on the center coordinates until the generated ideal intensity signal matches the thresholded and median-filtered data file. Results are shown below.

Data set	Estimated Center (inches)		Actual Center (inches)	
	El	Az	El	Az
WWHEEL	-.0023	-.0172	0	0
WWHEEL1	.0063	-.5206	0	-.5
WWHEEL2	-.1640	-.0340	-.2	0
WWHEEL3	-.1799	-.2678	-.2	-.3
WWHEEL4	-.1677	-.3112	-.2	-.3

The mean errors in vertical and horizontal coordinates were 0.0185 and -0.0102 inches respectively. The standard deviations were 0.0164 and 0.0251 inches respectively. Overall error standard deviation was 0.0251 inches (0.64 mm). If one assumes that the mean errors were due to errors in positioning the target originally then the standard deviation of less than 1 mm is representative of estimation accuracy using this method. Note that the positions of the target during each run were not tightly controlled, so that a major contributor to the estimation errors is uncertainty in the actual position of the target. However, the conclusion that the position estimation technique is feasible is inescapable.

The quality of the wagon wheel target and its orientation is shown in Figure 2-3. The low amplitude square wave is the simulated signal intensity signal using an ideal 4-spoke wagon wheel. The large amplitude signal is the detected, median-filtered data from the centered target. The figure clearly shows that the target's spokes were not ideal. It also shows that the target was quite well aligned, because the actual signal overlays the ideal signal quite well.

In conclusion, estimating the position of a wagon wheel target using a circular scan pattern is feasible. Accuracy will be improved by:

- Cutting a better target;
- Mounting the target better (alignment and flatness);
- Improving on/off contrast by painting the background with absorbing paint;

2.2 High Speed GC Detection of Organic Contaminants

2.2.1 Introduction

The function of the organic sensor system is to obtain samples from surfaces, and analyze the samples for the presence of polychlorinated biphenyls (PCBs) and other toxic organics. To obtain a sample, the surface is heated by infrared radiation, and thermally desorbed vapors are first entrained within an air stream and then extracted from the air stream onto a preconcentrator. The apparatus for thermal desorption and collection of vapors is mounted on the multisensor probe which is deployed by the robotic arm.

The preconcentrated sample is transferred to the analysis module, which is mounted in the mobile base station which supports the robotic arm. In the analysis module, trace level gas chromatography - mass spectroscopy (GC/MS) analysis is carried out using Thermedics Detection's novel high speed temperature programmed GC technology to perform GC separations in less than one minute.

GC/MS is widely recognized as the method of choice for definitive analysis of trace level organics in complex environmental samples. It is highly sensitive, and is applicable for a wide range of organics, including the PCBs. In GC/MS, the gas chromatograph separates the compounds present in a complex sample, and mass spectra analysis of each GC peak is used to identify the compounds. However, using conventional techniques, the GC separation takes 15

Figure 2-3. Wagon Wheel Quality

to 60 minutes, depending on the nature of the sample and the chromatographic resolution that is needed. This is far too slow for effective near-real-time mapping of contaminated structures.

Thermedics Detection has pioneered the development of surface sampling, preconcentration, and high speed temperature programmed GC, for ultratrace level detection in security screening applications. The EGIS explosives detector detects and identifies a wide variety of explosives in 18 seconds or less, and is deployed in 22 countries and 54 airports. This technology is well established for security screening applications. The present contract represents its first use for detection of toxic organics in the environment.

The high speed GC technology will be interfaced to a time of flight mass spectrometer, because quadrupole and other mass spectrometers cannot scan quickly enough for this application.

To summarize, the overall process requires the following steps:

1. Sample collection: Surface heating, air stream, preconcentration
2. Sample transfer from multisensor probe to analysis module
3. High speed GC separation
4. Mass Spectrometric analysis
5. Data collection and analysis

The starting point for this effort is Thermedics Detection's existing technology, which executes sample collection, sample transfer, and high speed GC separation.

The objective for Phase I was to use this technology to detect PCBs and other organic compounds on surfaces such as concrete. During Phase II of this program, the sample collection and GC system will be interfaced to a time of flight mass spectrometer and demonstrated in conjunction with the robotic arm and multisensor probe. For budgetary reasons, a flame ionization detector (FID) was used in Phase I to demonstrate the sample collection and chromatography.

2.2.2 Technical Approach

In Phase I, effort was required in each of the following areas: sample collection, sample transport, high speed chromatography, and detection. This section presents the pre-existing technology, and the technical approach used for each of these areas.

2.2.2.1 Sample Collection and Desorption

2.2.2.1.1 Pre-existing Technology

The pre-existing technology is configured as a hand-held probe and an analysis chassis. The operator uses the probe to collect a sample, and then inserts the probe into the analysis chassis, where the sample is desorbed and analyzed.

The sampling probe consists of a surface heating system, a collector element, and a suction

blower. The surface to be examined is rapidly heated, and sample vapors are entrained in an air stream that is pulled through the collector element.

Surface heating is done using a halogen lamp with closed loop control provided by an infrared thermometer.

The collector element is a coil of metal ribbon with a coating that enables it to collect and desorb organic vapors. During collection, the blower pulls 2 liters per second of air through the coil with efficient mass transfer and low pressure drop. During desorption, the coil is rapidly heated, and organics are desorbed into a small flow of carrier air, thus achieving a large factor of preconcentration.

The coil is rapidly heated by electric resistance heating, with closed loop temperature control using the coil resistance as a thermometer. The coil has a low mass and a high surface area, to permit rapid heating and cooling as well as efficient collection and desorption.

Typically, the blower is operated for about 10 seconds during collection. Desorption heating requires one second, and the desorption air flow requires several seconds. After desorption, the coil is cooled again after several seconds of air flow.

2.2.2.1.2 Current Effort

The existing sampling probe has been used successfully with explosives and narcotics, and engineering analysis at the beginning of this contract suggested that the fundamental design would be equally suitable for PCBs and other organics. Work was done to develop techniques and verify performance with these target compounds.

For a sampling probe mounted at the end of a robotic arm, it is necessary to desorb the collector and transport the sample to the analyzer without physically returning the sampling device to the analyzer chassis after each sample is collected. Work was done during Phase I to develop this capability.

In the pre-existing sampling probe, the front side of the coil is normally open to the environment and the back is ducted to the suction blower. When the sampling probe is inserted into the analyzer, this motion seals the front of the coil against the heated inlet port of the analyzer, and causes a spring-loaded plate to seal against the back of the coil, thereby providing a closed environment for desorption. The supply of pressurized desorption air is introduced through a port in the housing of the coil. During collection, the air flow goes from front side to back side. During desorption, the direction of air flow is reversed.

In the Phase I 3D-ICAS, the coil is mounted in a plate that shuttles laterally between collection and desorption positions. In the collection position, the front side of the coil is exposed to the environment, and the back side is coupled to the suction blower. In the desorption position, the front side is coupled to a heated receiving port and the back side is sealed with a plate. The lateral motion of about an inch is implemented using a rotary solenoid, and the seal for desorption is implemented using a linear solenoid. The relative direction of air flow is the same as in the pre-

existing device, but desorption is accomplished without physically moving the sampling probe.

After desorption, the sample must be transported to the analyzer. This is described in the next section.

2.2.2.2 Sample Transport

In the pre-existing instrument, the sampling probe must be physically inserted into the analyzer for desorption. The coil is sealed into a closed environment, and heated in a flow of carrier air, under pressure. The desorbed sample, in a flow of carrier air, is transported to the inlet of the GC system via a heated, deactivated line of length 30 cm.

In the Phase I 3D-ICAS, the sampling probe is left in place near the surface to be examined, and was not physically returned to the analyzer module with each analysis. Instead, the sample was transported along a flexible, heated deactivated line of total length 3 - 4 meters, to the inlet of the GC system.

For short transport lengths, desorption and transport can be carried out either under pressure or under vacuum, but pressure desorption is more effective. For the longer transport distance required in the 3D-ICAS, desorption under pressure is essential for sample transport.

The sample transport line is a heated, deactivated capillary GC tube. The transport time is significantly shorter than the time needed for chromatographic separation, because the sample remains in the vapor phase and does not adsorb to the walls of the tube. Transport velocities are 1 to 2 meters per second.

The transport line is implemented by placing a deactivated GC capillary inside a metal sheath that is heated resistively. This design provides flexibility and low mass.

2.2.2.3 High Speed Temperature Programmed GC

2.2.2.3.1 Pre-Existing Technology

Programmed temperature increases are used in GC separations to enhance resolution and address a broad range of sample compounds in the same analytical run. In conventional temperature programmed GC, the column is mounted inside an air oven, and the entire oven is heated in order to heat the GC column. The maximum rate of temperature rise is limited to about 10 C per minute by temperature gradients within the oven.

High speed temperature programmed GC was developed by Thermedics Detection for the EGIS explosives detector. In high speed temperature programmed GC, a capillary GC column is placed inside a specially designed thin-walled metallic sheath. Rapid, controlled temperature

programming is achieved by electric resistance heating of the metallic sheath under closed loop temperature control based on monitoring resistance changes as a function of temperature.

The high speed GC system consists of a focusing module and a chromatography module. The focusing module consists of a short length of GC column inside its metallic sheath, coupled to a cooling source. The focusing module is maintained at low temperature while the sample is introduced in a stream of air or carrier gas. At low temperature, the analytes are retained on the stationary phase of the GC column in the focusing module.

After sample focusing, the sample is injected by rapid heating of the focusing module. Sample injection is achieved with tight spatial coherence in less than 50 milliseconds, which helps to produce sharp chromatographic peaks. Two sequential focusing stages are used, to provide additional selectivity and tighter injection onto the chromatograph. After the sample is injected from the second focusing stage, the GC column is then heated through a rapid, tightly-controlled temperature program. Controlled heating rates in excess of 1000 C per second can be achieved. With this technology, the accessible heating rate is no longer a limitation to chromatographic performance. The speed and resolution of the chromatography is determined by processes such as carrier gas flow rate, and molecular diffusion over very short distances, which are inherently fast.

Samples are collected and analyzed without the need for additional sample pretreatment or clean-up prior to analysis. This is critically important for real-world operation - otherwise, the speed and ease of operation would be limited by the sample pretreatment process, and the final results would still be slow and skill-intensive. A series of physical separation steps are performed in the course of collecting the sample and presenting it to the GC column. The sample is extracted from environmental surfaces by thermal desorption and entrainment in an air stream. Then, the sample must adhere to the polymeric coating in the collector, and must be released into a second air stream when the collector is desorbed. The sample must then be collected and desorbed on two consecutive "cold spots". Any compounds that do not adhere to the collector or "cold spots", or adhere but do rapidly desorb again, are not presented to the chromatograph.

2.2.2.3.2 Current Effort

In the pre-existing system, the GC column length is about 1 meter, and a complete temperature programmed chromatogram takes about 10 seconds. The detector is chemically selective for the target compounds.

In the 3D-ICAS, PCBs and other toxic organics must be detected, using broad range detectors that respond to many different classes of compounds. This application may require greater chromatographic resolution, which can be achieved by increasing both the GC column length and the elution time.

An existing EGIS explosives detector was converted to a GC breadboard test system for the current effort. The EGIS system provided the cryofocusing elements ("cold spots"), sample switching valves, temperature controllers, and analog and digital electronics for high speed temperature programming. The breadboard system was constructed on a cart, and was equipped

with experimental GC columns and GC detectors.

The high speed temperature programming electronics were modified extensively to accommodate column lengths up to 7 meters, and chromatographic elution times up to 80 seconds.

2.2.2.4 Detectors

In gas chromatographic analysis, the constituent compounds in the sample mixture emerge from the chromatograph at different times, and are sensed by a detector that monitors the effluent stream of carrier gas. The mass spectrometer is the detector of choice for this application, but for budgetary reasons will not be introduced until Phase II of this program. In Phase I, other chromatographic detectors were needed in order to perform experiments in surface sampling and GC analysis.

Commonly used GC detectors for organic compounds include flame ionization (FID), photoionization (PID), thermal conductivity (TCD), and electron capture (ECD). For high speed GC, fast time response is essential.

Ability to operate under vacuum may also be important. Both the pre-existing high speed GC system and the mass spectrometer operate under vacuum. Vacuum operation may have a significant effect, because the linear velocity of the carrier gas and the diffusion rate in the gas phase are important parameters that vary inversely with pressure.

For this work, an FID was initially selected based on response time and the possibility of vacuum operation. Because of procurement delays, an existing gas phase fluorescence detector was also interfaced to the GC and used for initial chromatographic experiments.

2.2.3 Experimental Results

Experiments were carried out using the GC breadboard test station to optimize GC performance characteristics and demonstrate sampling from surfaces.

For GC performance experiments, microliter quantities of test solutions were deposited onto the collector coil of the pre-existing sampling probe, using a microliter syringe. The probe was then inserted into the inlet of the test station, and the analytical cycle was run.

For surface sampling experiments, microliter quantities of test solutions were deposited onto a brick and allowed to soak in. After the solvent evaporated, the sampling probe was used to heat the surface of the brick and collect a vapor sample. The probe was then inserted into the inlet of the test station, and the analytical cycle was run.

The results of a typical experiment are shown in Figure 2-4. The test solution contained 0.2 microgram per microliter of Aroclors 1221, 1248, and 1254, for a total of 0.6 microgram of PCB per microliter, in methanol.

The solid trace was obtained by injecting 0.3 microgram of PCB directly onto the collector coil. The dotted trace was obtained by placing 30 microliters of solution, containing 18 micrograms total of PCB, onto a brick, in a spot of diameter 3 cm. The solution was allowed to soak in and dry. The EGIS sampling probe was then used to heat the surface of the brick and collect a vapor sample for 20 seconds.

The chromatographic conditions were as follows: 1 meter DB-5 column, FID, hydrogen carrier gas. FID operated normally, exhausting into ambient pressure. Carrier gas flow rate 2.5 ml per minute. Temperature program: Hold at 35°C for 3 seconds, then increase 10.65°C per second until 280°C, then hold at 280°C for 10 seconds.

About 15 peaks are resolved, with close correlation between the two chromatograms. All of the peaks eluted in less than 30 seconds. Calculated recovery of PCB from the brick is about 7%, which is close to the collector's theoretical collection efficiency of 10%. When the same spot on the brick was sampled a second time, the signal strength was reduced by a factor of 5, which confirms the effectiveness of the sampling process.

The data in Figure 2-4 were obtained using a 20-second surface sampling time and operating the surface heating system at the standard temperature set-point. We have also obtained equivalent results using 10 seconds of sampling time, with more careful attention to the alignment of the sample head with the target location on the brick. Because of the strong dependence of vapor pressure on temperature, we expect to further enhance sampling effectiveness by increasing the temperature set-point of the surface heating system.

The recovery of several volatile organic compounds (e.g., EPA method 8240) is shown in Figure 2-5. This test solution contained a total of 2 micrograms per microliter, in methanol. The dotted trace was obtained by injecting a 0.2 microliter sample placed directly onto the collector coil. The solid trace was obtained by placing 2 microliters of the same solution onto a brick, in a 1 cm diameter spot. The solution was allowed to soak and dry. The remote sampling head was then used to extract (3 seconds) and transport (6 seconds) the sample to the GC analysis unit.

The chromatographic conditions were as follows: 6 meter DB-5 column, FID with 5 ml per minute hydrogen gas flow rate and a 10°C per second to 275 C temperature program.

In both chromatograms all the peaks are present and well resolved. The elution time is still within 30 seconds even for the 6 meter column. From this test the recovery of eight different compounds was determined to be about 5% for 3 seconds of surface sampling. A second sampling of the brick indicated the signal strength had been reduced by a factor of 5 or greater for the eight different compounds confirming the effectiveness of the sampling technique for these volatile compounds.

Figure 2-4. Results of a Typical Experiment - PCBs - 1 Meter FID

Figure 2-5. Method 8240 VOE's Analyzed on 6 Meter Column

Shown in Figure 2-6 are the chromatograms of direct and surface sampled analyses of PCBs from galvanized pipe measured under similar conditions as those outlined above. The calculated recovery is about 5% for 3 seconds of sampling which is similar for that for other compounds and for brick surface materials. This test indicates that the surface sampling technique can be used to sample other types of materials as well as different geometries, e.g., curved surface versus flat.

In the robotic system, it is important to avoid touching the surface to be sampled. Experiments were conducted to determine the effect of stand-off distance, and equivalent results were obtained when the sampling probe gasket was either in contact with the brick, or held 1, 2, or 4 mm above the surface of the brick. Thus, positioning of the sampling head should be well within the capabilities of the robotic arm.

Figures 2-7 and 2-8 show chromatograms obtained using a faster temperature program: 25°C to 280°C at 37.3°C per second, then hold at 280°C. All of the peaks elute within 10 seconds. The Phase I success criterion for chromatographic resolution is chromatographic resolution of 1.6 peaks per second, equivalent to resolving 100 peaks per minute. In Figure 2-7, 14 PCB peaks elute within a four-second interval, for a resolution of 3.5 peaks per second. In Figure 2-8, 8 diesel range organics are extremely well resolved in about 5 seconds, for a resolution of 1.6 peaks per second.

Comparable results were also obtained for polynuclear aromatic hydrocarbons.

Experimental work continues with longer GC columns. Figure 2-9 shows chromatograms of the same PCB mixture on 1 meter and 2 meter GC columns, using the same temperature program in each case. Fifteen peaks are resolved for the 1 meter column; in almost the same elution time, 24 peaks are resolved using the 2 meter column.

The experimental work on longer chromatographic column indicates a increase in resolution with the sacrifice of very little analysis time. Figure 2-10 shows chromatograms for the same PCBs mixture analyzed on both a 2 and 6 meter length of DB-5 column under identical conditions of carrier gas flow and temperature program. The longer column does not appreciably widen the individual peaks nor does the analysis time greatly increase. The number of peaks in the chromatogram has increased from 27 for the 2 meter column to 47 for the 6 meter column.

Figure 2-11 shows chromatograms of gasoline compounds also analyzed on the 2 and 6 meter columns under similar conditions to those for the data presented in Figure 2-10. Again the vast improvement in resolution is evident in comparing the solid (2 meter) and dotted (6 meter) traces. The separation between adjacent peaks and the occurrence of new peaks separated from shoulders shows the improvement in resolution is not limited to a particular class of compounds.

This ability to separate the components of a complex mixture in a short time (seconds) demonstrates the strong advantages of high speed GC separation. Applicable to a wide number of analytical applications, high-speed GC separation combined with MS detection will provide

Figure 2-6. PCBs Analyzed on 6 Meter Column

Figure 2-7. High Speed Temperature Programmed GC-FID, Aroclors 1221, 1248, and 1254

Figure 2-8. Modified Diesel Range Organics (1 Meter Column)

Figure 2-9. Chromatograms of the Same PCB Mixture on 1 Meter and 2 Meter GC Columns

Figure 2-10. PCBs Analyzed on 2 and 6 Meter Column Lengths

Figure 2-11. Gasoline Analyzed on 2 and 6 Meter Column Lengths

high-resolution, trace-level organic chemical detection and quantification in a small fraction of the time that is currently required for typical GC-MS analyses.

Experimental work in the chromatographic separation of target compounds of widely varying volatility with the same run is shown in Figure 2-12. In this case the separation and detection of TCEs and PCBs are performed in the same analysis run. The chromatographic conditions were as follows: 6 meter DB-5 column, FID, hydrogen carrier gas flow rate at 5 ml/min and temperature program was 10°C/sec to 280 C and hold for 40 seconds. In Figure 2-12 the solid trace is from a test solution containing 2 and 6 micrograms of trichloro ethylenes (TCE) and PCBs, respectively, which was applied to the brick and sampled for 5 seconds. Also in Figure 2-12, the dotted trace is a direct injection of the same solution containing 0.2 and 0.6 micrograms of TCEs and PCBs, respectively. The recovery is approximately 5%. This data indicates that both TCEs and PCBs can be effectively sampled, transported, separated and detected in under one minute using the technology incorporated in the Organic Sensor.

The PCBs are a mixture of biphenyl congeners containing from 1 to 10 chlorine atoms per molecule, with many position isomers for each chlorine number. The chromatograms shown above all resolve the chlorine number congeners of the PCBs, with varying degrees of resolution of the positional isomers. In mass spectrometric analysis, separation of positional isomers is not required, because all positional isomers of the same chlorine number have the same mass spectrum. Chlorine occurs as a 3:1 mixture of stable isotopes of mass 35 and 37. The isotopic signature creates recognizable patterns in the mass spectra, and greatly simplifies interpretation. All of the chromatograms shown above are more than adequate for identification of PCBs by GC/MS. The higher chromatographic resolution is especially useful for analyzing very complex samples that may contain diesel range alkanes and polynuclear aromatics in addition to PCBs.

The experimental results presented in Phase I were obtained using a flame ionization detector, which is non-selective. In Phase II, GC/MS will be used to enhance selectivity and provide definitive identification of compounds. Figure 2-13 illustrates the two-dimensional information available from GC/MS. A typical chromatogram of PCBs is shown on the time axis. The mass axis shows the mass spectrum of one of the congeners, tetrachlorobiphenyl. Identification is based on both the chromatographic elution time and the mass spectrum.

In the experimental data shown in Figures 2-4, 2-7, 2-8, and 2-9 the sampling probe was operated by hand. In the 3D-ICAS, it will be necessary to process samples without physically returning the sampling probe to the analyzer module. A sample transport system was developed under this phase where the preconcentrated sample is desorbed from the collector and rapidly transported to the analyzer module without loss of sample. Data shown in Figures 2-5, 2-6, 2-10, 2-11, and 2-12 are from samples extracted from surfaces, preconcentrated, and automatically transported to the analyzer for a distance of 3 meters. Currently, the entire process of sample extraction and transport to the GC analyzer requires less than fifteen seconds. The sample transport velocity is on the order of 1 to 2 meter per second using filtered, dry air. The transport is accomplished using resistively heated, narrow bore tubes encased in protective, insulating wrap. This design is a low mass, flexible system with a minimum bend radius of 6 inches. The

Figure 2-12. TCEs and PCBs Analyzed in Same Run

Figure 2-13. Conceptual Illustration of Two-Dimensional Information from GC/MS

transport system design fits well into the requirements for a flexible, low loss transport system to enable remote, robotically deployed sampling in less than 15 seconds.

2.2.4 System Timing Diagram

Figure 2-14 shows the projected timing diagram for operation of the sensor on the robotic arm, in scanning mode. Cycle times of individual steps are based on the experimental results and engineering analysis presented above. Five seconds are required for repositioning the sampling probe. Surface sampling and preconcentration is done in 10 seconds, and the sample is then desorbed and transported to the analyzer in 5 seconds. Twenty seconds are used for chromatography, and 5 seconds are allowed for cooling the GC column before chromatographing the next sample.

The sample probe can be repositioned any time after the surface is sampled, and the probe is ready to collect a new sample any time after desorption has been completed. As shown, a new sampling cycle is started every 25 seconds, and analytical results are available 45 seconds after each cycle begins.

For quicker surveys, the chromatography can also be done in less than 10 seconds, at lower resolution. This would result in a new sampling cycle every 15 seconds, with analytical results available 35 seconds after each cycle begins.

2.2.5 Detection Sensitivity

In the surface desorption experiments described above, 18 micrograms of PCB was deposited on a brick. The estimated mass of the affected volume of brick was 3 grams. The detection limit was about 350 nanograms per gram of brick. This includes a sampling efficiency of 7% and an instrumental detection limit of 24 nanograms.

In the EPA contract laboratory program (CLP), the required quantitation limit for various Aroclors in soil is 33 nanograms per gram of soil. Assuming a similar quantitation limit for brick, a factor of 10 improvement is needed, or an instrumental detection limit of about 2.5 nanograms of total PCB. Since about 15 GC peaks were present, this corresponds to a detection limit goal of 160 picograms per GC peak.

The FID has not yet been tuned to achieve its full sensitivity, since detection sensitivity is not a program goal until Phase II, when the FID will no longer be used. In Phase I, the FID was used primarily as a detector to achieve the program goals related to surface sampling and GC separation.

Meeting the EPA CLP quantitation limits for PCBs, volatile organic compounds (VOC), and semi-volatile organic compounds (SVOC) is an important goal for both Phase II and for the eventual commercialization of the technology and we are confident that this will be achieved. Detection limits for mass spectrometers are on the order of one picogram. Thus, with proper engineering and tuning, the target detection limit of 160 picograms per GC peak should be readily

Figure 2-14. Projected Timing Diagram for Operation of the Sensor on the Robotic Arm

attainable. If necessary, the effective sensitivity can also be increased by modifying the sampling process. A larger sample can be acquired, either by enlarging the size of the heated zone on the surface to be examined, or by combining a number of contiguous samples prior to analysis. In addition, the mass transfer efficiency of the collector element can be increased by decreasing the air flow rate. These operational details will be worked out as the experimental work proceeds.

2.2.6 Summary of Accomplishment of Phase I Tasks

The objectives of Phase I were to determine equipment and procedures needed for high speed GC separation of toxic organics, develop the necessary sampling probe for sampling surfaces for the presence of toxic organics, and better define the requirements for Phase II.

GC Separation: The Phase I objective was to determine equipment and procedures needed for high speed GC separation of toxic organics, using analog compounds similar to PCBs. High speed GC separation has been demonstrated, using the actual PCB target compounds rather than analogs. Chromatographic elution times ranging from 10 to 30 seconds have been demonstrated, compared to conventional GC that requires 15 to 60 minutes. The chromatographic resolution satisfied both the success criteria for Phase I and the practical requirements for effective GC/MS analysis.

Sample Probe: Effective sampling has been demonstrated using both hand deployed and automated, long transport sampling probes. PCBs, VOCs, unleaded gasoline and diesel oil have been thermally desorbed from bricks, concrete, wood and iron pipe materials. Effective sampling and preconcentration within the sampling probe has been demonstrated for as short as 3 seconds sampling time. The transport time for the concentrated sample is as short as 6 seconds for 3 meters length between the sampling probe and the GC unit. All of the Phase I performance requirements for the sampling probe have been met or exceeded.

Requirements for Phase II: The requirements for Phase II are essentially unchanged, but are understood in greater detail. For example, the sensitivity requirements for the mass spectrometer are defined by the measured effectiveness of the surface sampling process. Chromatographic peak widths on the order of 100 milliseconds confirm the need for a time-of-flight mass analyzer. The overall cycle time and repetition rate for the chemical sensor system are defined by the measured surface sampling time and GC separation time. Based on the experimental results to date, the chemical sensor system can be used for simultaneous detection of a wide variety of organics, such as solvents, diesel range alkanes, and polynuclear aromatics, as well as PCBs.

2.3 Molecular Vibrational Spectroscopy Classification of Surface Materials

2.3.1 Background

In Phase I of this project the optimum technique was to be determined for the remote vibrational spectroscopic sensing of processing products and other items of contaminated waste to allow both qualitative and potential quantitative information to be obtained. For the decontamination and dismantlement (D&D) of these areas there is a need to be able to fully characterize the materials remotely. The molecular vibrational spectrometry (MVS) sensor should allow the characterization of the solid surface matrix materials (concrete, asbestos, transite, organic polymers, etc.) and moderate levels (parts per thousand) of organic contaminant (e.g. fuel oils). The MVS sensor probe should give further information to the other instrumental sensors such that the fused sensor has enhanced detection capabilities.

The exact type of spectroscopy, whether it be infrared/reflectance or Raman, was not apparent at the start of this project and evaluation of these techniques for the job in hand was the starting point for the project. Three methods have been investigated, namely mid-infrared reflectance, near-infrared reflectance, and Raman spectroscopy.

2.3.1.1 Mid-Infrared (MIR) Reflectance Spectroscopy

In this method both specular and diffuse reflectance may be observed with the fraction of each depending on the surface morphology and optical constants of the sample. For weakly absorbing, smooth media the effect of specular reflectance will be minimal and can be approximated as a pseudo flat baseline. When the surface materials roughen, however, the diffuse reflectance component of the spectrum is greatly increased. It should be noted here that the signal-to-noise ratio (SNR) degrades with respect to the concentration by $C^{1/2}$. Thus at low concentration, spectral features of minor components should be observable. MIR reflectance spectra measured between 3000 and 4000 cm^{-1} should allow the observation of concretes, clays and asbestos from silanol (Si-OH) groups (3800 and 3500 cm^{-1}), and trace organics from their carbon-hydrogen (C-H) vibrations. Any fiber probe systems for this spectral region would be based on fluoride fibers such as lanthanum fluoride (LaF_3). A review of fibers used for MIR and NIR analysis has been recently made [1].

For the spectral region below 2000 cm^{-1} there are a number of fibers which could be used. These included silver halides and chalcogenide glasses [1]. The chalcogenide fibers and the silver halide fibers both have associated disadvantages. The silver halide fibers are prone to damage by water, sunlight, and higher energy radiation. The chalcogenide glass fibers have very low transmission over long fiber lengths and are very susceptible to mechanical damage.

2.3.1.2 Raman Spectroscopy

Raman spectroscopy is suited to remote-sensing problems due to the high efficiency of quartz fibers and optical clarity of glass or quartz containers [2-5]. As the Raman effect can, in principle, be observed using any radiation in the electromagnetic spectrum [6], a choice of the correct wavelength to use is important here. The main factors determining the appropriate excitation wavelengths are the ν^4 dependence of the Raman effect (suggesting that UV and visible lasers are

desirable), the effect of fluorescence and thermal emission (suggesting that near-infrared lasers are preferable for real-world samples of the type being investigated in this project). In practice, the later factor is more important. Thus the major instrumental alternatives for this program appear to be;

- (a) A monochromator operating with a diode laser emitting at around 800 nm and charge-coupled device (CCD) device detection [7-10];
- (b) A Fourier transform (FT)-Raman system with a 1064 nm Nd³⁺:YAG laser and germanium or indium gallium arsenide detector [4, 11-16].

Alternatives to these NIR Raman spectrometers are conventional systems based on argon-ion $\{\lambda = 457.9, 488.0, 514.5 \text{ nm}\}$ [17] or helium-neon laser [17] $\{632.5 \text{ nm}\}$ excitation sources. But in those cases the problems of fluorescence would be expected to be the greatest although signal intensity and detector sensitivity [related to the ν^4 expression] will be at their maximum [4-6,17]. Fluorescence masking has been observed for thorium and uranium compounds from nuclear processing plants when using excitation in the visible {argon-ion excitation $\lambda = 488.0 \text{ nm}$ } but the use of excitation at $\lambda = 1064 \text{ nm}$ has given good quality spectra [18]. Further alternatives are the Hadamard transform systems [19,20] (which are still not commercially available and will not be further discussed) or a UV-excited system [21,22]. For UV excitation, the Raman signal intensity will be at its largest but sample degradation and fiber damage could be large. UV-Resonance Raman enhancement of selected samples would aid identification in very low concentrations [23,24]. The final alternative is an FT-Raman system operating at a different wavelength than the 1064 nm norm. FT-Raman spectrometry with excitation for operation at 780 nm, 850 nm and 910 nm is currently being evaluated by Hendra's group in the UK [25]. A stand-alone FT-Raman spectrometer which is permanently operational with both 780 nm and 1064 nm lasers and single mirror switching to determine which laser, filter, detector combination is used is commercially available from Bruker, but would have to be significantly modified for field use [26]. Results from Hendra's group suggest that approximately 50% of real world samples are ruled out due to fluorescence masking when using an excitation wavelength of 780 nm [27]. Chase [28] has reported that about 90% of the samples that fluoresce when illuminated at 780 nm give acceptable Raman spectra using the 1064 nm line of a Nd³⁺:YAG laser and most of the remaining samples can be studied with the 1300 nm line of the same laser.

Several designs for fiber-optic probes have appeared over the last fifteen years for use in a number of areas of Raman spectroscopic analysis from surface enhanced Raman spectroscopy (SERS) [29,30], and waveguide [31] and remote sensing measurements [32-35]. The principal designs which have been optimized for the excitation wavelength and instrument configuration are summarized below;

- 1. Two separate fibers mounted with various angles between the collection and input fiber; this type of probe was originally used for the study of liquids [35-38].
- 2. The so-called "Y-shaped" fiber-probe [39-43] in which the input fiber is mounted with the beam focused onto the fiber using a standard microscope objective and the input fiber held in a micrometer positioner. The output of the collection fiber is mounted at the entrance of the instrument, be it a Jacquinot stop or a slit. The

sampling end or probe-head has the single input fiber mounted in the center of a bundle of collection fibers. The number of fibers in the bundle has been a subject studied by many different authors [16,39] and no optimum number of fibers has been suggested. Early FT-Raman spectroscopic studies centered around using six collecting fibers but more recently Williams et al. have had success with 18 fibers arranged in two layers, the first of six and the second of twelve fibers [12,16,44]. This arrangement is the basis of the commercial fiber-optic Raman spectrometer-probe available from Chromex Inc. This "Y-shaped" probe has the advantage of being able to collect the scattered radiation in a 180° degree back-scattering geometry [5,6].

3. Other types of fiber-optic probes have included dual bundle arrangements for excitation and collection [13].

The material from which the fiber bundle should be made is also important. Early studies used silica fibers that had a fair degree of water content. This caused Raman scattering to occur along the fiber. The effect was weak but on a fiber of long length the effect was potentially significant. Corning low-water silica glass have been reported as being the best material for Raman fiber-optic probes and for some near-infrared process analysis probes [44,45]. One use of a Raman fiber-optic probe has been as a control quantitation device used in the study of the co-polymerization of methyl methacrylate and styrene [44]. A 150-meter long probe using fibers of internal diameter (i.d.) 200 μm was run from the FT-Raman spectrometer equipped with a Nd^{3+} :YAG laser, and germanium (Ge) detector maintained at 77K into a probe head of a nuclear magnetic resonance (NMR) spectrometer and spectra were obtained simultaneously from the two spectroscopic techniques [46]. In almost all cases, the probe head does not have incorporated any focussing devices. The divergent nature of the beam helps reduce the potential problem of photolytic degradation and heating of the sample [34].

2.3.1.3 Near-Infrared (NIR) Reflectance Spectroscopy

The NIR spectrum has been shown to be useful for detecting C-H, nitrogen-hydrogen (N-H), and oxygen-hydrogen (O-H) combination bands and overtones [50]. The NIR spectrum can be used to detect subtle differences in the sample due to chemical or structural changes or chemically different environments. The signal-to-noise ratio that can be obtained for spectra in the NIR region is particularly good, but the information that may be obtained from NIR spectra usually requires chemometrical analysis or pattern recognition methods to be applied to extract quantitative or qualitative information [51-54].

Initial reports of the coupling of fibers to NIR spectrometers was for the purpose of using a NIR spectrometer to test fiber quality [55,56]. There have also been several reports of the coupling fiber-optics with a NIR spectrometer [51,57]. Initial reports concerned the application of dispersive NIR spectrometers [54,57,58] the use of which is still widespread in the NIR field. The use of highly sensitive FT-NIR instruments has been slower to expand due to the relatively high signal-to-noise ratio (SNR) observed in dispersive NIR spectrometers while the SNR of FT-NIR spectra may be limited by the dynamic range of the analog-to-digital converter (ADC).

In recent years several newer types of fibers, such as zirconium fluoride (ZrF_3) and LaF_3 , have been reported. These fibers extend the observation range into the mid-infrared region to approximately 2000cm^{-1} . Commercial reflectance fluoride fiber probes are currently available from Bruker Spectrospin. [59] or Graseby Specac [60]. These types of fibers also suffer from the fact that small crystallites can form on preparation which intensify Rayleigh scattering. The crystallite scattering can become particularly severe if the fiber length is long [54,60]. The final drawback of the fluoride fibers is that their cost can make lengths of 50 meters prohibitively expensive.

Thus the most popular fiber material has been established as silica. One problem of silica fibers is that silica absorption bands, from hydroxy groups, cause the fibers to have a large absorption background. Comparisons between normal-hydroxy silica fibers and low-hydroxy silica fibers have shown that the background can be significantly reduced for low-hydroxy fibers. Two separate authors have stated that Anhydroguide G [61] and Corning type 1508 [54] are particularly useful for NIR spectroscopy. The Corning 1508 fiber has also been used successfully for FT-Raman spectroscopic studies [16].

An important factor to consider for all types of spectroscopy is the choice of detectors and many authors have experimented with different NIR detectors, Archibald et al. [51,61] used indium antimonide (InSb), InGaAs and Ge , while Mackinson [54] used indium arsenide (InAs). The disadvantage of an InGaAs detector is that the wavenumber range is less than for the other detectors [51]. A consideration for all these detectors is that the signal reaching the detector must be below a certain level to prevent detector saturation and non-linearity in response [51,54]. An energy transmission of approximately 2% has been found to be ideal by Mackinson et al. [54].

Recently fiber-optic lengths in NIR have reached a length of two kilometers which should allow fiber probes to be used for remote sensing and process control measurements [45,53,61,62]. For such measurements fiber-optic multiplexers that could allow a number of probe devices to be interfaced to one spectrometer would be useful [53].

Several systems have been developed using a dual-fiber probe, in which the radiation input and collection fibers are separated opposite to each other. By altering the separation of the two fibers, depth profile information about the samples can be made [51,52].

2.3.1.4 Neural Networks for Pattern Recognition of Raman Spectra

A number of computer-based pattern recognition and automated learning methods have been developed for the classification and spectral feature extraction of compounds from their vibrational spectra [63-69]. Since 1986 a variety of advanced information processing technologies known as artificial neural networks have been developed to solve difficult pattern classification problems that were almost unsolvable by standard linear pattern recognition methods [70-73]. A class of artificial neural networks called mapping or feed-forward neural networks has been shown to perform as nearly ideal pattern recognition systems [74,75].

Mapping neural networks designed for pattern recognition use some type of supervised learning algorithm and are usually constructed as layers of many simple interconnected numerical processors called processing elements and use some type of supervised learning algorithm where

each connection has an associated weight or gain [71,72]. The layer that receives the input pattern is called the input layer, while the layer producing the classification results is called the output layer. Mapping neural networks may also have one or more layers positioned between the input and output layers which are termed hidden (or middle) layers because they have no direct connections to the input/output interface. The hidden layers and output layers are known as processing layers since these layers perform numerical operations on the input patterns. The processing elements of the hidden layers perform feature extraction operations on the input patterns to produce appropriate output classifications [71]. Figure 2-15 is a diagram of a 3-layer feed-forward neural network. In this work, the input patterns will be the Raman spectra of various matrices, the output layer will provide the appropriate classification while the hidden layer performs feature extraction of the spectral bands characteristic of the particular compound class. The most common supervised learning algorithm used by mapping neural networks is the generalized delta rule, also known as error backpropagation [71,73]. Error backpropagation is an iterative gradient descent procedure which minimizes the mean squared error between the desired output and the actual output. Two parameters, a learning and momentum coefficient, are commonly used to control the rate of convergence of error backpropagation. Each neural network processing layer may be assigned a learning and momentum coefficient, which controls the accuracy and rate of convergence of the neural network [71-73]. These coefficients are usually real values between zero and 1. Simple pattern recognition tasks can use large values close to 1, while difficult classification tasks require small values close to zero [73].

Spectra may need to be preprocessed before being presented to an artificial neural network for spectral interpretation and classification. Preprocessing of spectral data provides the necessary scale invariance and correct baseline references for optimum neural network classification performance. Preprocessing includes numerical operations such as baseline correction, scaling, or spectral truncation. Figure 2-16 is a flow diagram of the procedure for the classification of Raman spectra described in section 2.3.2.1.2 of this report.

2.3.2 Methodology, Results, and Discussion

2.3.2.1 Comparison of MIR, NIR, and NIR FT-Raman for the Sensing of Solids

2.3.2.1.1 Experimental Procedures

A number of samples including wood, brick, concrete, asphalt, asbestos, transite, plastics, and pure chemicals were collected from various locations. The samples were examined either without sample preparation or after grinding to a fine powder. The larger samples were held in a continuous solids holder while the powdered samples were packed into a cup.

Figure 2-15. Feed-Forward Mapping Neural Net

Figure 2-16. Schematic Showing the Role of Preprocessing in the Coupling of Neural Networks for Raman Spectral Pattern Recognition

The samples for FT-Raman spectroscopic analysis were studied using a Perkin-Elmer System 2000 Fourier Transform spectrometer fitted with the standard Perkin-Elmer Raman attachment and a modified Spectron 301 Nd³⁺:YAG laser ($\lambda = 1064$ nm). Spectra from the Perkin-Elmer System 2000 were corrected for instrument response using a white light correction system. Spectra were collected using an accumulation of 100 (15 mins) or 500 (80 mins) scans, 4 cm⁻¹ resolution and a variety of laser powers from 2 mW to 750 mW at 1064 nm.

MIR and NIR spectra at 4 cm⁻¹ resolution were measured with an on-axis diffuse reflection attachment (Spectra-Tech) using the same FT-IR spectrometer equipped with a deuterated triglycerine sulphate (DTGS) and an InSb detector, respectively, by collecting 32 scans for MIR and 16 scans for NIR.

2.3.2.1.2 Results and Discussions

Figures 2-17 thru 2-19 present high-contrast spectral data of cement, brick, and asbestos by MIR diffuse reflectance (DR) and Raman spectroscopies. There have been a number of spectroscopic studies of cement [76-78], and asbestos [79,80]. The interpretation of MIR DR spectra of these materials is complicated by changes in the surface texture of the sample. There is difficulty in differentiating between the diffusely scattered radiation and the specularly reflected component. This phenomenon is highlighted in Figures 2-17, 2-18a, 2-18b, and 2-19. In Figure 2-18a in the wavenumber ranges 1350-1050 and 850-700 cm⁻¹ the effect of specular reflectance can clearly be seen. The strongest band in the MIR DR spectrum of all the samples is the broad silicon-oxygen (Si-O) stretching band centered near 1100 cm⁻¹. The exceptionally strong specular reflectance maximum in this region offsets the diffuse reflectance minimum, however, making it appear as if no absorption features occur between about 1000 and 1300 cm⁻¹. The changes in the spectra of Figure 2-18a over these ranges indicate the varying degrees of specular reflectance observed in MIR reflectance spectra of these samples. In cases where there is combined diffuse and specular reflectance, the ratio of specular to diffuse reflectance varies from sample to sample and from analysis to analysis. Thus a simple library search for the identification of neat materials from their MIR reflection spectra is not going to be reliable. In the laboratory, the sample morphology may be changed to obtain almost pure diffuse reflection spectra but when the system is coupled with a fiber-optic probe and hazardous samples this would not be possible. Therefore, while it can be concluded that MIR diffuse reflection has given the best combination of spectral contrast and signal-to-noise ratio, the diffuse component of the reflected radiation is unfortunately compounded with a specular component and as a stand alone analysis technique, MIR reflectance based materials recognition will be complicated.

From Figure 2-18b it can be seen that although the Raman spectra of bricks ($\Delta v = 200$ -2000 cm⁻¹) are relatively weak, the spectrum of brick is reproducible. Thus a standard brick spectrum could be included in a library of expected materials. In previous FT-Raman spectroscopic studies of cement minerals [78] it was stated that an excitation wavelength of 1064 nm has little potential for analytical success. This study has shown that Raman spectra of cement materials are

Figure 2-17. MIR Diffuse Reflectance Spectra of Several Cement Samples

Figure 2-18a. MIR Diffuse Reflectance Spectra of Several Brick Samples

Figure 2-18b. Raman Spectra of the Bricks Studied Previously by MIR Reflectance Spectroscopy

Figure 2-19. MIR Diffuse Reflectance Spectra of Friable Asbestos Demonstrating the Effect of Compounded Diffuse and Specular Reflectance from ν - 4000 to 450 cm^{-1}

susceptible to sample heating, suffer from fluorescence, and have a low Raman scattering cross-section. Most cement types contain silicates and aluminate materials which have low scattering cross-sections and thus very weak intensity Raman peaks. Therefore the Raman spectra of these types of matrix materials are of very low intensity. An alternative excitation source at $\lambda = 1300$ nm may offer potential for cement analysis but these type of samples are only marginally readily amenable to any form of Raman spectroscopic analysis. The relatively weak Raman intensity of the cement matrix material will, however, aid in the analysis of materials embedded in cement such as polymers or fuel oils.

The situation for asbestos is much more positive. Both previous work [79,80] and the NIR and Raman spectra measured to date indicate that both techniques yield spectra of sufficiently high quality for identification. A number of NIR and Raman spectra of asbestos samples have been obtained. The most common morphological form, *crysotile*, can be distinguished from the other crystalline forms of asbestos and the presence of *crysotile* in *transite* can be readily detected.

Raman spectra of a number of polymers (Table 2-1) and 200 organic liquids have been measured. The spectra of these compounds are being analyzed on the basis that they might be found as organic matrices, the contents of transparent or translucent containers, or trace organics in an inorganic matrix, as outlined in the contract proposal. Preliminary conclusions are encouraging, but detailed results will not be known until the first few months of Phase II.

The majority of organic liquids studied gave intense Raman spectra. Example spectra are provided in Figures 2-20 (aliphatic) and 2-21 (aromatic compounds). Organic polymers also are medium to strong Raman scatterers [81-83]. A number of polymer spectra are displayed in Figure 2-22 obtained at two laser wavelengths, $\lambda = 488.0$ and 1064 nm, which demonstrate the ability of Raman spectroscopy to study polymeric species [84]. Raman spectroscopic studies of polymers and organic compounds and an investigation of the suitability of Raman spectroscopy and neural networks for polymer analysis are currently underway.

Supervised training of neural networks for Raman spectral pattern recognition is complicated by the presence of: (a) outlier spectra and (b) similarities between spectra of materials in different classes [70-73]. Without *a priori* knowledge of the statistical characteristics of the training set or test set spectra, supervised training may lead to slow learning, over-training, or non-robust performance. Neural networks which perform unsupervised learning, such as Kohonen's self-organizing map (SOM), are susceptible to coarse classification performance and slow learning [71-73]. A neural network paradigm which includes the most desirable features of both supervised and unsupervised learning would allow rapid, robust and fine grain classification of Raman spectra.

A novel self-supervised feed-forward neural network has been developed which performs optimal mappings from the Raman spectral domain into a reduced dimensional projection domain. The application of the self-supervised network to the mapping of Raman spectra of woods is shown in Figure 2-23. The performance of the network indicates that Raman spectra of complex matrices with similar features can be well resolved in the mapping domain. Coupled with other types of neural networks, the novel network could form a hybrid neural network which would function as a high performance pattern classification system.

Table 2-1.
List of Polymers Which have been Studied Utilizing Raman
Spectroscopy

Polybutadiene (PBD)
Polybutadiene-co-acrylonitrile (PBD-co-AN)
Polychloroprene (PC)
Polyethylene (PE) {low density}
Polyethylene (PE) {high density}
Polyethylene terephthalate (PET)
Polyisoprene (PI)
Polyisoprene-co-methyl methacrylate (PI-co-MMA)
Polymethyl methacrylate (PMMA)
Polypropylene (PP)
Polystyrene (PS)
Polytetrafluoroethylene (PTFE) {Teflon}
Polyvinyl chloride (PVC)

Figure 2-20. The Raman Spectra of Several Aliphatic Organic Liquids; (a) Cyclohexane, (b) Hexane, (c) Acetone, (d) Ethyl Acetate, (e) Carbon Tetrachloride, and (f) Chloroform $\Delta\nu = 200 - 3500 \text{ cm}^{-1}$

Figure 2-21. The Raman Spectra of Several Aromatic Organic Liquids; (a) Benzene, (b) Toluene, (c) Benzaldehyde, (d) Benzonitrile, (e) P-tolyl Acetate, and (f) Pyridine $\Delta\nu = 200 - 3500 \text{ cm}^{-1}$

Figure 2-22. The Raman Spectra of a Number of Polymers; (a) High Trans-1,4 Polybutadiene, (b) Polybutadiene-co-acrylonitrile copolymer {50/50} mix, (c) High Trans-1,4 Poly-Isoprene, (d) High Cis-1,4 Polyisoprene (e) High Poly-3,4-isoprene, and (f) Polyisoprene-co-methyl methacrylate copolymer {50 / 50 mix} $\Delta\nu = 200 - 3500 \text{ cm}^{-1}$

Figure 2-23. Results of Applying a Self-supervising Neural Network to the Mapping of the Raman Spectra of Woods

An initial study involved obtaining the spectra of water pressure treated and untreated woods with representative spectra of treated and untreated Douglas Fir being shown in Figure 2-24. It can be seen that there is no appreciable difference in the spectra for the two wood samples. This is important since water pressure treatment of woods has become more popular in recent years and any spectral difference attributed to water treatment could seriously affect the identification of the wood by neural computing.

Surface roughness also did not appear to cause any band shifts that could detrimentally alter the wood analysis by changing the extracted spectral features. This result is not altogether unexpected as the laser incident radiation used in these experiments has a penetration depth of about 2 mm [85]. Sample positioning (analogous to gross sample roughness) has been reported as causing band shifts of up to 2 cm^{-1} [86] which is not expected to adversely affect neural network classifications. For remote analysis the use of a fiber-optic probe for sample illumination and collection of the Raman scattered radiation would minimize penetration of the excitation beam because of the divergent nature of the beam on leaving the fiber [87] and would cause surface scattering to be the origin of the majority of the Raman signal. Thus it was necessary to study the effect of sample roughness on the observed spectrum. Sample roughness has been shown to seriously effect the application of mid-infrared diffuse reflectance spectroscopy for sample study. This is because the signal observed is a combination of diffusely and specularly reflected radiation [88]. The lack of major variations in the Raman spectrum caused by changes in the surface morphology is a unique advantage inherent to Raman spectroscopy over its infrared counterpart.

The Raman spectrum of Lodgepole Pine recorded at two different laser powers, 750 mW and 400 mW is presented in Figure 2-25. From these spectra it can be seen that appropriate care must be taken when illuminating the sample since a thermal emission profile [89] may be superimposed upon the spectrum of the wood. This might cause confusion for the neural network by changing the intensity of both the aliphatic C-H and unsaturated C-H stretching bands ($\Delta\nu = 2800\text{--}3200\text{ cm}^{-1}$) relative to that of the 1600 cm^{-1} ring stretching band, since these relative intensity ratios are characteristic of hard or softwood ring [90]. The bands around 3300 cm^{-1} , in Figure 2-25 plot a, are assigned to OH stretching modes however their intensity is artificially enhanced by thermal emission of the sample under high laser power. A detailed description of these results was submitted to *Spectrochimica Acta* and is now in press. This paper is enclosed as Appendix A.

A summary of the results of this survey in terms of spectral quality, i.e. the combination of spectral contrast and signal-to-noise ratio, is given in Table 2-2a. It can be seen that the majority of the samples analyzed were not amenable to good spectral quality NIR analysis. Both MIR and Raman spectroscopy also have other inherent disadvantages. Raman spectroscopy can suffer from the well known problems of sample heating, fluorescence and sensitivity; alleviation of such problems by changing laser wavelength and detection mode is currently being investigated. Nevertheless only asphalts tended to give no Raman signal as the spectra were always masked by fluorescence. Tables 2-2b and 2-2c show a further comparison of MIR and Raman spectroscopy signal quality, including also the effects of fluorescence and spectrum variability. These tables indicate the complementing nature of the two techniques.

Figure 2-24. The Raman Spectrum of (a) Water-treated and (b) Untreated Douglas Fir

Figure 2-25. Raman Spectra of Lodgepole Pine Showing the Effect of Excessive Laser Power on the Raman Spectrum; (a) 750 mW and (b) 400 mW

Both MIR and Raman spectroscopic techniques may be interfaced to fiber-optic assemblies. A summary of the types of fibers that may be used is given in Table 2-3. The optimum material for NIR Raman is silica, allowing the use of relatively inexpensive fiber optics common for communication applications.

2.3.3 Raman Spectroscopic Probe Designs

Recently a new probe design commercially available from Dylor (EG&G instruments) has shown promise as the Raman spectrometry sensor of choice [1]. This probe design has a number of advantages over the initial fiber-optic probes used for Raman spectroscopy [3-7]:

1. Focusing lenses which increase the intensity of the Raman signal observed by increasing the laser irradiance per the unit volume of the sample. Thereby increasing the Raman signal intensity;
2. Rayleigh filters which prevent the Rayleigh radiation from entering the collection fiber. This will minimize the effect of Raman signal from the fibers themselves obscuring Raman signal from the samples being investigated;
3. Probe head protection by sealing the probe head behind a protective window;
4. Interchangeable lenses for varying the focussed laser beam depth. Useful for homogeneity checks on colorless samples.

<p>Table 2-2a. Summary of Spectral Quality for a Number of Representative Samples from the Three Spectroscopic Methods Studied</p>			
Sample	Mid-IR	Near-IR	Raman
Concretes	G	P	P
Bricks	G	P	M
Woods	G	G	VG
Asphalt	M	P	VP
Asbestos	G	P	M
Porcelain	G	P	G
Polymers	M	P	VG
Organics	G	P	VG

VG = Very good
 G = Good
 M = Medium
 P = Poor
 VP = Very poor

Table 2-2b. Mid-Infrared Reflection Spectroscopy		
Material	Intersample Variability	Useful Signal-to-Noise*
Concretes	5	VG
Bricks	3	VG
Woods	2	P
Asphalt	1	VP
Asbestos	3	VG
Porcelain	2	G
Polymers	3	M
Organics	2	G
Transite	3	G

5 = Very High	VG = Very Good
4 = High	G = Good
3 = Medium	M = Medium
2 = Low	P = Very Poor
1 = Very Low	VP = Very Poor

* The actual signal-to-noise ratio is often effectively degraded by the complex nature of specular/diffuse reflection information mixing.

Table 2-2c. NIR Raman Spectroscopy		
Material	Intersample Variability	Useful Signal-to-Noise Ratio (degraded by fluorescence and sample heating)
Concrete	1	VP
Bricks	3	G
Woods	1	VG
Asphalt	1	VP
Asbestos	3	M
Porcelain	2	G
Polymers	2	G
Organics	1	G
Transite	3	M

Variability

5 = VERY HIGH	VG = VERY GOOD
4 = HIGH	G = GOOD
3 = MEDIUM	M = MEDIUM
2 = LOW	P = POOR
1 = VERY LOW	VP = VERY POOR

Useful Signal-to-Noise ratio for FT-Raman spectra recorded at 1064 nm (in terms of spectral interpretability)

Table 2-3. Comparison of Available Wavenumber Range and Problems Associated with Fiber-Optics When Coupled to a Vibrational Spectrometer		
Fiber Type	Wavenumber Range	Problems Observed
Chalcogenide	5000-900 cm^{-1}	High attenuation; glasses limit length to under 2m
Heavy Metal	10000-2200 cm^{-1}	Length limited by Fluoride Fibers attenuation to 10m; high cost
Quartz	15000-2200 cm^{-1}	If high OH content, Raman signal can be obscured

The only disadvantage of this probe design is that it is exciting laser specific and would require a rebuild if the exciting laser wavelength was to be changed.

The MIR probe should be designed to maximize the signal and be optimized for the spectrometer of choice. This probe design is currently under development from Galileo Optics. A version is available for NIR studies but the MIR probe is still being optimized. A commercial version should be available by August 1994 at the latest.

There exists no one probe which will provide optimal results for both Raman and infrared spectroscopy. This is due to the fact that to optimize the probes different materials are used as the required transmission characteristics are different for the two techniques.

The fiber optic probe for Raman spectroscopy from Dylor is currently available and when coupled with its associated spectrometer/detector can be optimized for use with any exciting laser over the wavelength range 600-1064 nm.

In Phase II a fused MIR/NIR Raman probe will be implemented for laboratory use which combines these commercially available instruments. This use of commercial instrumentation will minimize development risk and allow the Phase II MVS sensor development effort to focus on the complex fused NIR Raman-MIR spectroscopic pattern discrimination problem.

2.3.4 Conclusion

The expected results of this phase of the MVS sensor development for 3D-ICAS can be summarized as follows;

1. Both MIR and Raman spectroscopies have distinct advantages for a number of samples whereas NIR spectroscopy produced good quality spectra only for woods.
2. MIR reflection spectra contain the greatest spectral contrast but separation of the diffuse and specular components is complicated. FT-Raman spectrometry also has the advantage of being able to study the low wavenumber region ($\Delta\nu < 450 \text{ cm}^{-1}$) not available to MIR studies.
3. From the results obtained it is recommended that a fused MIR reflectance and Raman spectroscopy be used with a combined fiber-optic probe. The neural net-based spectrum recognition techniques investigated under Phase I for Raman spectroscopy will be extended to a combined Raman-MIR approach in Phase II.

3.0 PHASE I DEMONSTRATION: 3D Contamination Mapping with a CLR Tracked GC Sensor

The purpose of task 4.1 was to demonstrate the accomplishment of the critical Phase I goals (success criteria) and show the readiness of the CRC team to proceed to Phase II of the 3D-ICAS development. To this end, a GC sensor capable of resolving well in excess of the 100 gas chromatographic lines per minute has been developed and, therefore, as part of a GC/MS subsystem will be able to detect and discriminate organic contaminants down to the low parts per billion regulatory levels. A demonstration model of the fiber optic based CLR 3D mapper has been developed under a separate program and shown to be capable of surface mapping accuracy of ± 0.5 mm sought for the 3D-ICAS. Under the Phase I effort of this program, six degree of freedom (6DOF) tracking algorithms have been developed and implemented at the 3DOF level (3D sensor location) to support the integrated demonstration. The integrated demonstration system successfully determined the position of the GC sensor head in three dimensions as the GC measured the level of organic contaminants. It also displayed a spatial map of the contamination level. As a simulated remediation effort alters surface geometry and the level of contamination, the surface map shows both the new surface elevation and new measured contamination levels as a function of position. For the demonstration, the GC sensor head was manually positioned, rather than robotically positioned as it will be in Phases II and III of the 3D-ICAS development, and was spaced and kept in proper orientation with respect to the surface by means of mechanical support points whereas that function will be automatically performed by the robotic and proximity sensor/CLR tracking closed-loop control in Phases II and III. Thus, the second half of 6DOF sensor head tracking, providing orientation, was not necessary for the Phase I demonstration.

The demonstration consisted of five parts focusing on 3D mapping, GC, the integrated 3D-ICAS system, scarifying, and tracking. Figure 3-1 is a schematic representation of the demonstration equipment and configuration.

The GC was demonstrated by itself to show the capability to detect complex organic compounds at high and low contamination concentrations on cement blocks. Capability to detect and recognize complex compounds and to quantify their concentrations was demonstrated by displaying calibrated chromatograms on a PC.

Mapping in three dimensions was demonstrated by mapping a complex surface of different concrete materials of varying thicknesses (contours) and displaying the 3D contour map. The surfaces consisted of a concrete wall board with two square concrete patio blocks (each approximately 3 inches thick and 2 feet square) positioned side-by-side on the wall board and with a 3mm thick strip of quick set concrete approximately 4 inches wide placed on one of the concrete patio blocks (Figure 3-2 is a picture of the setup showing the concrete wall with the GC probe, the light colored box on the right side with the cables connected to it, positioned against the concrete surface). For the purpose of the demonstration, surface geometry and areas of contamination were altered by positioning these multiple layers of various thickness and types of material having the bulk properties (see Figure 3-1) of interest for the DOE EM programs. This replaced the surface scarifying operation suggested in the proposal to maintain cleanliness of the CRC optics laboratory without compromising the demonstration of accomplishments of

Figure 3-1. 3D-ICAS Phase I Integrated Demonstration Configuration

Figure 3-2. Setup of the Concrete Wall with the GC Probe (Photograph)

Phase I 3D-ICAS development objectives. The CLR system used for the demonstration was not optimized for speed, and obtaining high resolution spatial maps with the current system is time consuming. Thus, the density of measurement points for the demonstration was adjusted to decrease the overall measurement time while still providing a representative contour map of the surface but without resolution to the levels of precision of which the system is capable. Several high resolution 3D maps obtained by the current system prior to the demonstration were available for review. Figures 3-3a, 3-4a, and 3-5a are copies of these maps with corresponding photographs (Figures 3-3b, 3-4b, and 3-5b) of the objects to provide a basis of comparison.

Contaminant mapping was demonstrated by a manual process because acquiring a robot arm and developing system software are part of Phase II. Three small regions of the examination area were contaminated with organic materials at known concentrations. A spatial map was obtained by the CLR mapper. Once the spatial map was obtained and displayed, the contaminant mapping process was started. The GC was positioned by hand for each measurement. Once in position, the GC measurement was activated. Each measurement took 15 to 25 seconds. While the GC was working, the CLR mapper searched in coarse acquisition mode to locate the center of the GC to within 0.25". Since the brassboard GC measures contaminants over a circular area 1.5" in diameter, the specified mapping accuracy was adequate and allowed reasonably fast location determination. When the GC completed its analysis, the chromatogram was displayed on the GC monitor. The data was simultaneously transferred automatically to the simulated workstation where it was integrated by the resident software and displayed at the workstation monitor on the 3D contour map indicating location on the mapped surface, the type of contaminant, and the relative concentration. Figure 3-6 is a print of the screen of the workstation indicating the 3D surface contour map with the location, identification, and relative concentration of three detected spots of contamination on the surface.

To demonstrate the success criteria of a measurement accuracy of 1mm or less for the CLR, one of the strips of concrete material was approximately 3mm thick. Its thickness was repeatedly measured with the CLR, and the data was displayed as a histogram with standard deviations of the measurements identified. The result demonstrated was an accuracy within less than 1mm (0.6mm) (see Figure 3-7).

Figures 3-8 through 3-10 are pictures of the overall demonstration set up. Figure 3-8 shows the CLR scanner on the rear-end of the optic bench looking toward the concrete surfaces. The GC probe is shown positioned over the right patio block. The GC and its monitor are on the right side of the optics bench, and the CLR and its monitor are on the left side. Figure 3-9 is a full view of the GC brassboard system. Figure 3-10 includes the workstation monitor with the integrated graphic display on the monitor (see Figure 3-6).

Under Phase I, the University of Idaho has determined that a fusion of NIR Raman and Mid IR reflectance spectroscopy is the most attractive molecular vibrational spectroscopy (MVC) technique for 3D-ICAS surface materials identification, has developed algorithms, which discriminate closely similar materials and thus, at this point projects the capability to discriminate surface materials of interest for DOE D&D operations. UI has identified commercially available

Figure 3-3a. 3D Map - Cylinder and Cone

Figure 3-3b. Photograph - Cylinder and Cone

Figure 3-4a. 3D Map - Tools

Figure 3-4b. Photograph - Tools

Figure 3-5a. 3D Map - Ceiling Foam

Figure 3-5b. Photograph - Ceiling Foam

A graphical display from the live Phase I 3D-ICAS demonstration. Coherent laser radar (CLR) 3D mapping data and high speed gas chromatograph (GC) data are fused. The CLR was used to measure (map) the varying concrete surface in three dimensions and to locate the successive positions of the GC probe on that concrete surface. The 3D mapping was not disturbed by the bright light of the simultaneously operating GC desorption probe. The fused graphical display shows the concentration of three selected chemical compounds at each of the three probe positions. Further measurement and analysis could be used to 3D contour map the concentration of any selected compound on the mapped 3D surface.

Label	Contaminant	Color	Concentration
X	C18 (n-Octadecane)	Red	High
+	C20 (n-Eicosane)	Yellow	Medium
0	C22 (n-Dodecane)	Green	Low
		Black	None

Figure 3-6. 3D Surface Contour Map

Figure 3-7: CLR Measurement Accuracy

Figure 3-8. Demonstration Setup

Figure 3-9. GC Brassboard Analysis Unit

Figure 3-10. Workstation Monitor

fiber optic probe components which can be incorporated into a multi sensor head for 3D-ICAS. As per the 3D-ICAS proposed development plan and contract statement of work the MVS surface materials identification were not a part of the Phase I integrated demonstration.

4.0 CONCLUSIONS, RECOMMENDATIONS AND REVISED REQUIREMENTS FOR PHASES II AND III

The objectives of the 3D-ICAS development Phase I tasks have been accomplished, the specific success criteria have been met, and all subsystems have been developed at least to level III maturity. The CRC team is now ready to proceed to Phase II and subsequently Phase III of the development with little remaining risk. The program task objectives and their completion status are given in Table 4-1. Table 4-2 shows the Phase I success criteria and shows that in each case, these criteria clearly have been satisfied. Only in the area of the mobile platform which carries the sensor arm is there potential for a significant change in approach as will be discussed. This will not affect Phase II of the proposed 3D-ICAS development program.

The impact of the Phase I effort on Phase II and Phase II task requirements is shown in Table 4-3.

The fiber optic CLR demonstration system development on a separate NASA/DOE program has produced a system which supports 3D mapping for the Phase I demonstration and, under this program, the 3D sensor head location algorithms have been developed, implemented in software and demonstrated. The separate NASA/DOE program is developing an even more accurate, 200 times faster CLR 3D Mapping system, suitable for industrial use, which will be available for high speed Phase II 3D mapping and sensor end effector 6DOF tracking developments. There is no risk proceeding forward in the areas of 3D facilities mapping and sensor positioning for 3D contamination mapping. In the original 3D-ICAS proposal, CLR-based end effector location (3DOF) tracking had been proposed. With the CRC developments of this Phase I effort we are now confident that we can provide efficient CLR-based location and orientation (6DOF) sensor end effector tracking in Phase II, yielding improved sensor guidance, at a somewhat reduced Phase II effort.

The adaptation of Thermedics Detection's high speed Gas Chromatograph technology to the quantitative detection and classification of organic contaminants has proceeded as planned. The modified GC system with its newly developed sensor head and transport tube exceeds the proposed detection resolution and speed requirements so that, when combined with an available commercial mass spectrometer detection system, it will be able to detect organic contaminants at the low parts per billion level at high speed. Thus, with the proven GC detection capability in its new configuration which does not require human manual coupling of the collection head to the GC system, we may proceed at low risk in Phase II to a robot arm borne sensor system for remotely directed automatic contamination mapping.

The University of Idaho has determined under Phase I that fused NIR Raman-Mid IR reflectance is the best vibrational spectroscopic approach for non contact identification of base materials of surfaces in DOE facilities. Commercial off-the-shelf fiber optic-coupled probes have been identified for both spectroscopic techniques which are suitable for inclusion in the 3D-ICAS multi sensor probe. Neural net-based discrimination algorithms have been implemented in software for FT Raman spectra which can distinguish similar materials such as different species of wood. When extended to fused MIR and Raman spectra, these techniques will easily distinguish the major surface types of interest for DOE D&D operations. Finally, the fused MVS sensor probe is

projected to be effective in surface materials identification at a range of 1mm, thus imposing no extra requirement for 3D-ICAS sensor positioning. The net impact of the Phase I MVS development effort on Phase II requirements is the identification of a fused rather than a single spectroscopic probe approach as the best MVS technical approach.

The dimensions of facilities such as the K-25 plant at Oak Ridge may require a different transport mechanism for the sensor platform than the small robot vehicle of the originally proposed system configuration. Such facilities may have a vertical dimension of 50 feet or greater, thus requiring a gantry or a larger vehicle with a tall erectable mast to carry the sensor platform with its sensor probe, robot arm, and GC/MS analyzer hardware. The gantry with more than adequate capacity for the 3D-ICAS sensor platform is available as on site equipment. Also, CRC has evaluated the stability of commercial erectable masts as stable platforms for 3D mapping of airplane structures to support manufacturing operations. Thus, the sensor platform choice is not a development issue or area of significant program risk. The principal new determination is that it is not reasonable to cover the full vertical dimension of facilities targeted for D&D using the vertical reach of the robot arm alone. Therefore, the robot arm needs only to be capable of mapping out a local region, with major position changes accomplished by a gantry or mast platform. Thus a robot arm of modest reach, as originally proposed for the Phase II demonstration, will be adequate for the Phase III field demonstration and eventual field development.

The ability of commercial robot arms to satisfy 3D-ICAS requirements for load handling, reach, speed, and stability has been corroborated. One example is the FANUC ARC Mate 100.

**Table 4-1. 3D-ICAS Development Phase I Task Accomplishments
(Per Contract SOW Tasks)**

TASK OBJECTIVE	TASK ACCOMPLISHMENT
<p>Task 1.1 GC Sensor Use high speed GC technology to develop a system to detect volatile hydrocarbons.</p>	<p>High speed GC system developed and demonstrated with hydrocarbons of high interest (PCB's) to DOE. GC resolution substantially better than proposed has been achieved.</p>
<p>Task 1.2 MVS Sensor Determine best MVS technique for detecting base materials and moderate contaminant levels. Develop a MVS probe design suitable for D&D characterization.</p>	<p>Fused NIR Raman-Mid IR reflectance determined to be MVS technique of choice. Commercially available probes will satisfy MVS sensor requirements.</p>
<p>Task 2.0 Demonstration Perform quantitative measurements of organic contamination levels, locate sensor position, provide 3D graphical representation of surface profile and contamination patterns.</p>	<p>An integrated GC sensor and CLR 3D mapper demonstrated 3D location of a manually positioned GC sensor as it quantitatively detected trace levels of contamination. A 3D graphical representation of surface geometry, contamination, location and level, and changes in geometry was provided. An efficient approach to CLR-based 6DOF (location and orientation) sensor tracking has been developed and will be implemented in Phase II.</p>
<p>Task 3.0 Topical Report Document work done in Phase I and requirements for Phase II.</p>	<p>Completed.</p>

Table 4-2. 3D-ICAS Development Phase I Success Achievement

SUCCESS CRITERIA	ACHIEVEMENT
(1) Accurate (average error less than 1mm) 3D map of concrete block both before and after milling of scarafacing is generated and displayed. Projected speed for a fieldable system shall be at least 1000 measurements/per second.	Accurate mapping to accuracy of better than 0.5mm demonstrated on concrete and other construction surfaces. Measurement data epoch of 1msec demonstrates innate capability to measure surfaces at 1000 measurements with planned digital processing power of CLR 3D mapping system under construction for NASA/DOE.
(2) The GC system shall be capable of desorbing and resolving a chromatograph containing up to 100 peaks in under a minute, for organic materials.	The developed GC system resolves PCB's with an elution pattern density of 210 GC peaks per minute. More importantly, capability to detect low ppb levels of PCB's with GC/MS clearly demonstrated.
(3) The MVS sensor shall have projected capability based on lab studies, of identifying base materials such as concrete, asbestos, and transite.	All these materials have been shown to be identifiable using fused NIR Raman-Mid IR reflectance spectroscopy and a neural net-based discrimination algorithm.
(4) Physical mapping data from the 3D mapper and contaminant data from the GC sensing systems are merged and displayed.	The integrated CLR 3D mapper/GC sensor demonstration produces graphical displays showing both quantitative surface geometry and quantitative contamination contours.

Table 4-3. 3D-ICAS Phase I Developments Affecting Phase II and Phase III Task Requirements

Phase I Development	Phase II Task Requirement Impact
Efficient CLR-based approach to 6DOF rather than 3DOF sensor end effector tracking.	Under Phase II Tasks 1.8, (Control Software) and 1.9 (Tracking Software), development will be simplified and sensor tracking improved from 3DOF to 6 DOF.
Fused NIR Raman-Mid IR reflectance chosen as best technical approach for MVS sensor rather than single spectroscopic technique.	Under Phase II, Task 3 (Develop Prototype MVS Sensor) increased sensor probe hardware will be used. This will result in the MVS sensor being able to recognize reliably, a broader range of materials of interest to DOE.
Determined that mobility platform may need to have greater vertical reach capability for DOE facilities such as K-25.	Under Phase III, Task 3.5, (Procure Sensing Platform Vehicle) a vehicle with an erectable mast or a gantry crane-based platform (no vehicle) will be considered. Phase III, Task 2.2 (Procure Mapping Platform Vehicle) will not be impacted.

APPENDIX B

Acronyms

3D-ICAS	3 Dimensional Integrated Characterization and Archiving System
3DOF	3 Degrees of Freedom
6DOF	6 Degrees of Freedom
ADC	Analog-to-Digital
C-C	Carbon-Carbon
C-H	Carbon-Hydrogen
C=O	Carbon-Oxygen
CCD	Charge-Coupled Device
CLP	Contract Laboratory Program
CLR	Coherent Laser Radar
CRC	Coleman Research Corporation
D&D	Decontamination and Dismantlement
DR	Diffuse Reflectance
DTGS	Deuterated Triglycerine Sulphate
ECD	Electron Capture Detector
FID	Flame Ionization Detector
FT	Fourier Transform
GaALAs	Gallium Aluminum Arsenide
GC	Gas Chromatograph
GC/MS	Gas Chromatography - Mass Spectroscopy
Ge	Germanium
He-Ne	Helium-Neon
InAs	Indium Arsenide
InGaAs	Indium Gallium Arsenide
InSb	Indium Antimonide
IR	Infrared
LaF ₃	Lanthanum Fluoride
MIR	Mid-Infrared
MS	Mass Spectroscopy
MVS	Molecular Vibrational Spectrometry

N-H	Nitrogen-Hydrogen
Nd ³⁺ :YAG	Neodymium-doped Yttrium Aluminum Garnet
NIR	Near-Infrared
NMR	Nuclear Magnetic Resonance
O-H	Oxygen-Hydrogen
PCA	Principal Component Analysis
PCB	Polychlorinated Biphenyls
PID	Photoionization Detector
SERS	Surface-Enhanced Raman Spectrometry
Si-O	Silicon-Oxygen
Si-OH	Silanol
SNR	Signal-to-Noise Ratio
SOM	Self-Organizing Map
SVOC	Semi-Volatile Organic Compounds
TCD	Thermal Conductivity Detector
TCE	Trichloro Ethylene
TD	Thermedics Detection, Inc.
UI	University of Idaho
VOC	Volatile Organic Compounds
ZrF ₃	Zirconium Fluoride