Rapid Surface Sampling and Archival Record (RSSAR) System

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Table of Contents

Executive Summary	1
Introduction	3
Background	3
Objectives	3
Competitive Analysis	4
Approach.....	4
Components of the RSSAR System	4
Sampler Heads	4
Transfer Line	5
Quick-Look Detector	6
Multisample Trapping Module (MSTM)	6
Thermal Desorption Autosampler and Interface.....	6
Project Description	7
Task 2.1 Multisample Trapping Module (MSTM)	8
Design Considerations	8
Sorbent Tube and Cap Design	10
Tube Selection.....	10
Sorbent Material and Sorbent Packing.....	11
Tube Caps.....	12
Magazine	13
Housing	13
Carousel.....	14
Magazine Loader.....	15
Chassis	15
Background	15
Housing	16
Mechanical Arrangement	16
MSTM Electronics	20
MSTM Firmware	23
MSTM Performance Testing	26
Objective	26
Testing Modifications	26
Experimental Methods	27
MSTM Testing Results	28
MSTM Specifications	32
Thermal Modeling	33
Task 2.2 Thermal Desorption Autosampler	36
Description.....	36
Interface to Thermal Desorption Autosampler	36
Interface Setup	36
Escapement.....	37
Chute	37
Electronic Interface	37
Performance Testing of Modified Thermal Desorption Autosampler.....	37
Objective	37
Description of the Test Equipment and Experimental Setup	37
Data Collection and Interpretation	38
Success of the Test	38

Task 2.3 Design and Thermal Testing of the Steel Sampler	40
Performance Requirements	40
Selection of the Heating Model	41
Prototype Sampler Head	41
Thermal Testing	42
Results	42
Task 2.4 Steel Sampler Performance Testing	45
Experimental	45
Results	45
Discussion	51
Task 2.5 Integrated Laboratory System	52
Testing with the Concrete Sampler Head	52
Preparation of Concrete Slabs	52
Experimental Setup	52
Results from Concrete Sampling	53
Discussion of Concrete Sampling	53
Testing with the Steel Sampler Head	54
Experimental Setup	54
Base-Neutral Compound Testing	55
Results from the Desorption of Base-Neutral Mixture with the Steel Sampler Head	55
Discussion of Testing the Base-Neutral Mixture with the Steel Sampler Head	56
Aroclor 1254 Testing	56
Desorption of Aroclor 1254 from 58-mil-thick Stainless Steel	56
Results from Desorption of Aroclor 1254 Using the Steel Sampler Head	57
Testing of the Three-Component Solution Using the Steel Sampler Head	57
Discussion of Integrated Laboratory System Testing Results	57
Task 2.6 (not funded)	
Task 2.7 Preliminary Design of Portable System	60
RSSAR Platform	61
MSTM Placement	61
Quick-Look Placement	61
Sample Head Placement	61
Laptop Computer	61
Power Supply/Distribution	61
Automated Position Acquisition	62
Quick-Look Detector Selection	62
Evaluation of Commercially Available Systems	62
Detector Evaluation Criteria	62
Commercially Available Detector Systems	64
Comparison of Detector Systems	64
Quick-Look Detector Recommendation	66
Conclusions and Recommendations	67
Steel Sampler Head	67
Multisample Trapping Module	67
Thermal Desorption Autosampler and Interface	68
Thermal Modeling	68
Integrated System Testing	68
Preliminary Design of Field Portable System	69
Summary	70

Commercialization Plans	71
Introduction to Commercialization Plans	71
The Markets for RRSAR Products	71
Competing Products and Technologies	73
Preliminary Strategy for Commercialization	74
Multisample Trapping Module	74
Laboratory Analysis	77
Rapid Surface Sampling and Archival Record System I	77
Rapid Surface Sampling and Archival Record System II	78
RSSAR Heated Sampling Heads	79
Research and Development	79
Bibliography	80
Acknowledgments	80

Figures

Figure 1. Configuration of the RSSAR system	5
Figure 2. Multisample trapping module.....	8
Figure 3 EAI packed tubes configuration.	11
Figure 4. Acceptable cap groove depth.....	12
Figure 5. MSTM sorbent tube cap design	13
Figure 6. MSTM magazine housing	14
Figure 7. Magazine carousel.....	14
Figure 8. Top view of MSTM	17
Figure 9. Front view of MSTM.....	17
Figure 10 Top	17
Figure 11. Front.....	17
Figure 12. Carousel drive assembly.	18
Figure 13. Needle drive assembly	18
Figure 14. Sample pump chassis assembly	19
Figure 15. Front panel.	21
Figure 16. Block diagram of MSTM firmware	26
Figure 17. Effect of moisture content on PCB removal	33
Figure 18. Effect of concrete permeability on PCB removal	34
Figure 19. Temperature distribution at 16.3 s intervals.....	35
Figure 20. Pressure distribution at 16.3 s intervals	35
Figure 21. PCB distribution at 16.3 s intervals.	35
Figure 22. Water distribution at 16.3 s intervals.	35
Figure 23. Depth of PCB front vs time.	35
Figure 24. Depth of water front vs time.....	35
Figure 25 1254 standards from a sorbent tube containing Carbotrap 370.....	38
Figure 26. Metal sampler head.	39
Figure 27. Temperature at the center of the rusted steel plate as a function of time after the heating element was turned on.....	42
Figure 28. Temperature of the rusted steel plate with a maximum temperature of 250 °C as a function of distance from the center of the plate.....	42
Figure 29. Temperature of the rusted steel plate with a maximum temperature of 280 °C as a function of distance from the center of the plate. The temperature of the plate is 250 ± 30 °C within a region 0.32 in in diameter at the center of the plate.	44
Figure 30. Sample chromatogram of base-neutral mixture	56
Figure 31. Sample chromatogram from analysis of three-component solution.....	58
Figure 32. Integrated RSSAR sampling system.....	60
Figure 33. Commercialization schedule.....	75
Figure 34. MOD-U-LAB	78

Tables

Table 1. Concentrations of analytes in test solution used for testing the multisample trapping module mated to the bulk sampling oven.	27
Table 2. Concentrations of model compounds used to calibrate GC using thermal desorption methods ...	28
Table 3. First experiment: Recovery of anthracene, 2,4,5-trichlorobiphenyl, and phenyldodecane from the multisample trapping module.	29
Table 4. Second experiment: Recovery of anthracene, 2,4,5-trichlorobiphenyl, and phenyldodecane from the multisample trapping module.	30
Table 5. Third experiment: Recovery of anthracene, 2,4,5-trichlorobiphenyl, and phenyldodecane from the multisample trapping module.	31
Table 6. MSTM specifications	32
Table 7. Heating time for temperature to reach 250 °C and temperature at the end of 1 min heating for rusted steel, steel, and 301 stainless steel plates	43
Table 8. Recovery of anthracene, 2,4,5-trichlorobiphenyl, and phenyldodecane from a 4-mil-thick carbon steel thermally desorbed by the steel sampling head (2 sec irradiation)	46
Table 9. Recovery of anthracene, 2,4,5-trichlorobiphenyl, and phenyldodecane from 4-mil-thick stainless steel thermally desorbed by the steel sampling head (2 sec irradiation).	47
Table 10. Recovery of anthracene, 2,4,5-trichlorobiphenyl, and phenyldodecane from a 4-mil stainless steel surface thermally desorbed by the steel sampling head (3 sec irradiation)	48
Table 11. Recovery of anthracene, 2,4,5-trichlorobiphenyl, and phenyldodecane from a 4 -mil rusted steel surfaces thermally desorbed by the steel sampling head (2 sec irradiation).....	49
Table 12. Recovery of anthracene, 2,4,5-trichlorobiphenyl, and phenyldodecane from a 4-mil rusted steel surface thermally desorbed by the steel sampling head for a period of 3, 4, or 5 sec	49
Table 13. Recovery of anthracene, 2,4,5-trichlorobiphenyl, and phenyldodecane from a 4-mil rusted steel surface thermally desorbed by the steel sampling head by pulsing irradiation for five 1-sec intervals	50
Table 14. Recovery of anthracene, 2,4,5-trichlorobiphenyl, and phenyldodecane from a 56-mil steel surface thermally desorbed by the steel sampling head by irradiating for 1 min at a power setting of 400 W and increasing power to 800 W for an additional 1 min	50
Table 15. Recovery of anthracene, 2,4,5-trichlorobiphenyl, and phenyldodecane from a 56-mil steel surface thermally desorbed by the steel sampling head by irradiating for 2 min at a power setting of 800 W	50
Table 16. Components of base-neutral test mixture.....	54
Table 17. Recovery of base-neutral test compounds (2 mg/ml or 2 µg/µl) from 56-mil-thick carbon steel with the steel sampler head	55
Table 18. Recovery of base-neutral test compounds (2 mg/ml or 2 µg/µl) from 58-mil-thick stainless steel with the steel sampler head	55
Table 19. Recovery of Aroclor 1254 from 58-mil-thick stainless steel by desorption with the steel sampler head	57
Table 20. Desorption of Aroclor 1254 from 56-mil-thick carbon steel	57
Table 21. Professional and trade magazines to be used in advertising campaign.....	76

Executive Summary

This report describes the results of Phase 2 efforts to develop a Rapid Surface Sampling and Archival Record (RSSAR) System for the detection of semivolatile organic contaminants on concrete, transite, and metal surfaces.

The characterization of equipment and building surfaces for the presence of contaminants as part of building decontamination and decommissioning activities is an immensely large task of concern to both government and industry. Because of the high cost of hazardous waste disposal, old, contaminated buildings cannot simply be demolished and scrapped. Contaminated and clean materials must be clearly identified and segregated so that the clean material can be recycled or reused, if possible, or disposed of more cheaply as nonhazardous waste.

DOE has a number of sites requiring surface characterization. These sites are large, contain very heterogeneous patterns of contamination (requiring high sampling density), and will thus necessitate an enormous number of samples to be taken and analyzed. Characterization of building and equipment surfaces will be needed during initial investigations, during cleanup operations, and during the final confirmation process, increasing the total number of samples well beyond that needed for initial characterization. This multiplicity of information places a premium on the ability to handle and track data as efficiently as possible.

GE also has a number of sites requiring building decontamination and decommissioning, and recognizes the limitations of currently existing technology to cost-effectively meet surface characterization needs. The most widely used current method involves wipe sampling. In wipe sampling, the surface is wiped with a solvent-soaked piece of cloth, paper or the like, and the wipe is sent to an off-site laboratory for analysis. This method of analysis has a number of problems:

- The method is extremely unreliable and highly dependent on the technique used by the operator.
- It cannot be used to lower the cost of a cleanup by providing real-time information to the remediators in a manner that allows them to operate in the most efficient manner.
- The use of solvents raises safety concerns about worker exposure.
- Whenever a large number of samples are required, characterization by wipe-sampling becomes a logistical nightmare. All samples must be manually tracked through the system, increasing the possibility of human errors.
- Off-site analysis with manual manipulation (extraction, etc.) of the wipe sample is very expensive.
- This method requires analysis of all the samples taken and provides no way of effectively screening out a large percentage of the clean samples to reduce analysis costs.
- Disposal of solvents and wipes results in increased wastes.

Aware of the shortcomings of traditional surface characterization technology, GE and EAI Corporation, with DOE support, have undertaken an effort to complete Phase 2 of a proposed four-phase program to develop the RSSAR system. The objective of this work is to provide instrumentation to cost-effectively sample concrete and steel surfaces, provide a "quick-look" indication for the presence or absence of contaminants, and collect samples for later, more detailed analysis in a readily accessible and addressable form. The Rapid Surface Sampling and Archival Record (RSSAR) System will be a modular instrument made up of several components:

- Sampling heads for
 - concrete surfaces
 - steel surfaces
 - bulk samples

- Quick-look detector
- Multisample trapping module to trap and store vaporized contaminants in a manner suitable for subsequent detailed lab-based analyses
- Thermal desorption autosampler and interface to facilitate the automated analysis of archived samples

GE has assembled a strong team to develop and build the RSSAR system. The EAI Corporation brings an expertise in surface sampling, air sampling, and solid-phase sorbents (as applied to chemical weapons treaty verification) coupled with proven manufacturing and marketing capabilities.

In Phase 2 GE and its principal subcontractor, EAI Corporation, Inc., have accomplished many of the objectives set out in the Phase 2 Proposal. The tasks that have been completed dealt with the design, construction, and testing of equipment that will make up the RSSAR system, such as the multisample trapping module, thermal desorption autosampler, and steel sampler head. Each task is critical to the development of a successful, practical, and commercially viable surface sampling system. In somewhat more detail, we have

- Designed, built and tested an archival multisample trapping module which traps contaminants from up to fifty samples and stores them for detailed analysis.
- Modified a thermal desorption autosampler to facilitate transfer of sorbent tubes from the MSTM and analysis of semivolatile contaminants.
- Developed an interface that allows the sample tubes in the magazine to be automatically loaded into the ATD unit where the eventual sample analysis occurs.
- Refined a concrete thermal model to aid in understanding the sampling process and interpreting the sampling results.
- Designed, built, and tested a steel sampler head for characterizing contaminants on metal surfaces.
- Conducted performance tests with representative contaminants on individual system components and the integrated system.
- Developed a preliminary design for a field portable system.

Based on the results of testing, several recommendations were formulated to improve performance during the planned Phase 3 design and testing of the field portable system. These recommendations include measures to improve the power transmission efficiency of the steel sample head, recommendations to simplify the design of the field portable unit, optimization of the quick-look detector, and heating of the multisample trapping module and transfer lines to improve the recovery of analytes.

In Phase 3 the team will design, fabricate and test a portable prototype system suitable for field use. The system will be used in field tests at a contaminated site. In Phase 4, the design of a production system will be completed and production units will be built.

The RSSAR system will provide DOE with a new tool to dramatically lower the costs associated with site decontamination and decommissioning activities. It will allow surfaces to be rapidly sampled for the presence of semivolatile organic contaminants, and will provide the means for quickly identifying clean surfaces. It will archive samples in a form that will allow cost-effective laboratory analysis and will provide automated tracking of sampling record and analytical results.

Introduction

Background

The purpose of this effort is to develop a rapid surface contamination measurement system that will provide a "quick-look" indication of contaminated areas, an archival record, and an automated analysis of that record. By providing rapid analyses and a large number of accurate measurements of surface and subsurface contamination, the cost of remediation of large industrial sites will be dramatically lowered by reducing both the characterization time and the material fraction that must be remediated.

The Department of Energy (DOE) sites contain very large areas contaminated with radionuclides and semivolatile organic compounds as the result of decades of nuclear weapon and fuel production activities. Concrete, transite, and metal surfaces have been exposed to these contaminants. Unknown but substantial portions of these surfaces have been contaminated to various depths. Because contamination concentrations can vary widely over adjacent exposed surfaces, these surfaces must be sampled at closely spaced intervals to provide accurate identification of contaminated areas. Consequently, a huge number of surface regions must be characterized, particularly because remediated areas must be sampled more than once for identification and verification.

Current surface characterization procedures are difficult, expensive, and slow. They require an unacceptably long time to perform and consume a large share—often around 30%—of remediation/disposition resources. Accordingly, they will not meet the challenge of providing low-cost, rapid, quantitative and certifiable surface characterization on the scale required by DOE as part of its decontamination and decommissioning activities.

Objectives

The objective of this effort is to help develop and demonstrate new and existing technologies that will enable the DOE to decontaminate and decommission their facilities in the most cost-effective manner possible. The costs and environmental risks associated with disposing of structures and equipment as hazardous waste are unacceptably high, owing to the nature of the contaminants and the sheer volume of material in question. The DOE recognizes that a large portion of its contaminated material and equipment must be processed in some manner to a state from which it can be recycled and reused. If recycle or reuse proves impossible, then the material must be cleaned in a manner to allow for its disposal as a nonhazardous substance to minimize the volume and cost of disposal for hazardous waste.

Characterization technology is key to accomplishing the DOE's decontamination and decommissioning goals. Building materials and equipment must be adequately characterized before, during, and after decontamination and decommissioning activities. The nature and level of contaminants must be initially established to determine whether cleanup is required. During the cleanup, analysis will be required as an element of cleanup process control. Ultimately, the material will have to be certified as clean before it can be recycled or disposed of.

A number of constraints must be met by any technology facing the challenge of characterizing the DOE's sites. It must be a cost-effective portable system capable of providing rapid results from the enormous amount of surface area to be screened. It must accurately assess the identity and level of contaminants in an analytical format acceptable to regulatory agencies. The technology must be robust, operable by persons with minimal amounts of training, and give screening results in a readily understandable format.

Competitive Analysis

Existing technology for analyzing surface contamination does not meet the above constraints. The most common and accepted current method for sampling surfaces for hazardous materials is the EPA wipe or swipe test, in which a measured surface area is wiped with a gauze cloth or other absorbent material soaked with an organic solvent. The wipe is then sent off to a laboratory, extracted with solvent, and the extracts are analyzed for the presence of the contaminants. The method, though widely used, suffers from serious limitations. It provides extremely variable results, because it relies on the technique and consistency of individual samplers and is inaccurate, with results depending upon the nature of the surface (rough, smooth, porous, rusted, etc.) The wipe method requires expensive offsite laboratory analysis that can result in delays of days to weeks and does not lend itself to efficient data handling. Furthermore, the method analyzes the surface only—not the region below, exposes workers to potentially dangerous and harmful solvents, and generates additional waste including wipes, solvents, and sample containers that must be disposed of as hazardous waste.

On porous surfaces, such as concrete, a freshly cleaned surface may pass a wipe test (contain $<10 \mu\text{g}/100 \text{ cm}^2$ contaminant) only to fail it at a later date as material from below the surface migrates upward. In spite of these limitations, wipe sampling is widely used to detect surface contamination.

Approach

This program, which concerns the development of a Rapid Surface Sampling and Archival Record (RSSAR) system, was undertaken to provide a solution to the cost and technical shortcomings of conventional methods for characterizing contaminated surfaces. It is directed to the development of a portable instrument system capable of sampling a variety of surfaces for semivolatile organic contaminants. The system under development provides rapid sampling (one sample per 100 sec on concrete), a quick-look indication of contamination level, and a stored record for detailed, automatable analysis.

This system is assembled from instruments incorporating several well-established techniques and instruments incorporating innovative techniques. It comprises thermal sampler heads, a quick-look module, and an archival multisample trapping module. The RSSAR system is composed of several modular units, as illustrated in Figure 1.

Components of the RSSAR System

Sampler Heads

Concrete, bulk, and steel sampler heads are being developed to handle the most frequent sampling requirements. The concrete surface sampler can be used to determine contamination levels at surfaces and down to a few millimeters below the surface for porous, low-thermal-conductivity materials, providing information also targeted by the standard wipe test. A bulk sampler head has been developed and demonstrated that can be used to measure contaminants in asbestos, paint scrapings, soil, particulate waste, and samples from drilling as well as calibration standards. To determine subsurface contamination, samples from drilling would be placed in the bulk sampler head connected to the RSSAR system for quick-look and archival analyses. The steel sampler head has been designed for the markedly different sampling conditions provided by nonporous surfaces with high thermal conductivity.

Concrete sampler head. The concrete sampler head is designed to heat the surface (and subsurface) of the area being sampled so as to volatilize any potential contaminants and draw them through the heated transfer line to the detector and, if required, onto the sampling carousel. The

Figure 1. Configuration of the RSSAR system. This modular system includes several sampler heads, a quick-look facility, an archival record, an organized set of stored samples, and an automated interface to couple this record into various types of analysis equipment.

sampler head consists of an aluminum cylinder, into which a concave reflector has been turned, and is covered by insulation. The head is heated by electrical resistance tapes located between the aluminum cylinder block and the insulation. The head can be rapidly heated to high temperatures (typically 250 °C), and provides a uniform sampling temperature for each location. The automated process involved in sampling will provide better reproducibility and reliability than the conventional wipe test method.

Bulk sampler head. The bulk sampler head is designed to volatilize potential contaminants out of bulk samples by thermal desorption. These samples would typically include drillings, pulverized concrete, soil, and particulate waste (rather than the surface sampling done by the concrete sampler head). The head consists of a small aluminum block into which a rectangular channel is milled. The entire head apparatus is heated, and is covered with glass matting and cloth for insulation. The head can be rapidly heated to high temperatures (typically 250 °C), which will thermally desorb semivolatile compounds of interest in the bulk sample.

Steel sampler head. The steel sampler head is designed for smooth, flat, and hard surfaces with high thermal conductivity like that provided from a steel surface. This head does not have to address the problems of water vapor evolution and depth penetration as much as the concrete sampler head because these problems are not as significant on this type of surface. Heating for this head is provided by an arc lamp and can obtain the required temperatures (~250 °C), to provide the necessary heat to thermally desorb the semivolatile compounds of interest.

Transfer Line

The transfer line must allow nearly complete transfer of the volatilized compounds from the sampler to the quick-look detector and, if necessary, to the sorbent tube. The line must be heated to

prevent the compounds from condensing in the line and/or minimize absorption by the line. Additionally, the line must be nonreactive so that compounds are not chemically altered as they pass between the sampling head and the detector or sorbent tube.

Quick-Look Detector

The purposes of the quick-look module are to provide a real-time guide of sampling strategy, a real-time practical indication of system performance, a personnel safety indicator, a redundant indicator channel, and a method to reduce the fraction of samples that are subjected to more time-consuming detailed analysis. The viability of quick-look has been demonstrated using both a photoionization detector and ultraviolet absorption. The quick-look detector will be used to screen the material desorbed from the surface being sampled. If compounds of interest are present at a predetermined level or concentration, the detector will trigger the sampling carousel to begin collecting a sample. If contaminants are not present above the trigger level, a sample will not be taken. As a result, the quick-look detector used in the RSSAR system should be sensitive as well as selective to the classes of compounds targeted. It should be portable, require minimal power sources, and little or no auxiliary support (gases, water, etc.). Since the contaminants of interest are principally PCBs, oils, and polyaromatic hydrocarbons, the detector should be selective for these classes of compounds, and should not respond to air, water, or benign contaminants. The ideal detector will also operate on line, polling the sample stream as it passes through the RSSAR system, and be nondestructive.

Multisample Trapping Module (MSTM)

The archival multisample trapping module traps contaminants and stores them for detailed analysis. This stored record, organized in a cassette format (as shown in Figure 1), is associated with corresponding sample information, to facilitate recordkeeping, to minimize handling and training requirements, to reduce errors caused by operator fatigue in the highly repetitive sample acquisition and analysis tasks, and to expedite automated readout. A single sample trapping module was tested initially and the results were used in the design and fabrication of an archival multisample trapping module. The archival MSTM allows trapping of up to 50 separate samples and transfer to a modified thermal desorption autosampler for subsequent analyses.

The MSTM consists of two components—a magazine and a MSTM chassis. The magazine accommodates up to 50 sorbent tubes so numerous samples can be taken automatically. The sorbent tubes will preserve the sample until it can be analyzed. Information about the sampling area as well as other physical sampling data will be saved within the magazine's nonvolatile memory, so that it can be correlated to that specific tube and sample in the subsequent analytical process.

The MSTM chassis contains all the necessary hardware to effect the sample collection mission. These components include the needle drive assembly, the sample pump plumbing and associated valving, a drive assembly to index the magazine, and the associated electrical components to control the operations of the system.

Thermal Desorption Autosampler and Interface

The thermal desorption autosampler accepts the organized record format and provides an automated interface to alternative readout instruments such as gas chromatography/mass spectrometry, tandem mass spectrometry, gas chromatography with electron capture detector, or a fast optical readout such as a photo-ionization detector. By manipulating sample and substrate size, quantities of PCBs of interest to the DOE (10 μg on 100 cm^2 surface) should easily be detectable with little additional optimization of techniques that have been developed. The automatic thermal

desorption (ATD) interface allows the sample tubes in the magazine to be automatically loaded into the ATD unit where the eventual sample analysis occurs. The downloading of tubes can be conducted without operator intervention, thus minimizing tube, sequence and information corruption or losses.

Project Description

Thermal sampling for semivolatile compounds has been chosen for development because this technology can provide substantially more reliable readings of surface contamination than wipe sampling. It also minimizes the production of contaminated sampling waste, lends itself to automated processing, separates chemical samples from radioactive materials, and is fast. In general, samples are acquired using thermal desorption of contaminants at approximately 250 °C by radiant heat.

The overall RSSAR system is modular and will use accurate sample acquisition, handling, and analysis techniques. The availability of an archival record that allows detailed analysis (and an occasional backup check on the quick-look detector) will expedite material disposition planning and regulatory approval. Consequently, the RSSAR system should provide a cost-effective approach for the measurement of semivolatile contamination required for large industrial site remediation.

Task 2.1 Multisample Trapping Module (MSTM)

Figure 2. Multisample trapping module.

Design Considerations

The MSTM (Figure 2) and ATD interface were designed and built by EAI Corporation of Abingdon, MD. Many factors were incorporated into these assemblies to support the mission and function of the RSSAR system. Examples of these design features include

- **Multitube capacity** – The MSTM was designed to accommodate as few as one but as many as fifty sampling tubes. Site surveys for contamination could require thousands of samples. As a result, the greater the number of samples that can be accommodated, the more time can be spent collecting the samples and not changing tubes within the system.
- **Sealed environment** – The MSTM and internal magazine were designed with no external knobs or buttons and limited external access. This approach was taken to minimize operator requirements, but also to facilitate QA/QC by eliminating operator sample handling in the sample collection and analysis process. A third added benefit is in maintenance of the system. The environment in which the RSSAR will operate could be extremely dirty and/or dusty. By sealing the system, failures as a result of contamination can be minimized.
- **Low weight** – While the ultimate design of the RSSAR is on a moving platform, man-portable applications, if possible, would be desirable. As a result, designs of the unit were established that minimized weight of the overall unit. However, in this first phase of actual fabrication, the system was assembled with a greater degree of robustness (steel instead of plastic, etc.) to ensure system viability.
- **Low power** – The MSTM was designed to operate on 12 and 5 Vdc so as to be a low power system. Again, referring to portability, a more flexible system would be one that can operate on battery power rather than relying on dedicated commercial power. As a result, the MSTM system is battery power capable. The ATD unit interface, which will reside with a stationary or field laboratory, does not have this requirement and therefore uses 110 Vac.
- **Low cost** – As with any product, cost is a considerable factor. Throughout the design and fabrication the objective has been to minimize cost wherever possible, but not when it risks or compromises system performance. To that end we have met all of the system performance criteria in a minimal cost unit. Overall price per unit will realize a cost decrease as volume of units increases and performance specifications and capabilities are better defined.

- **Smart** – Because of the minimum operator interfacing that will occur at the sampling site, the system must have the intelligence to control all aspects of the sampling process and record all data relevant to the sampling process.

In order to ensure success of the RSSAR instrument system within the aggressive constraints of the schedule, it was necessary to adopt a design philosophy based on EAI Corporation's experience, which utilized proven technology and techniques to the greatest possible extent. Unproven techniques were avoided whenever possible. When it was necessary to deviate from past experience, tests were conducted as early in the program as possible.

A systems engineering approach was implemented in which the total design, fabrication and development was broken into a series of discrete tasks or phases. The procedures controlling these design activities are documented in EAI Quality Assurance Procedures, which can be described as follows:

In order to successfully develop new instrument systems, it is necessary to have clearly established objectives. Minimum acceptable levels of performance must be decided. A differentiation between those features that are critical to the success of the project and those features that may be highly desirable, but are not critical, must be agreed upon. Without a yardstick against which to measure success, no framework exists for making decisions and tradeoffs.

The initial phase in the development of instrumentation is the concept phase. In this phase one or more concepts for solving the problem are advanced. This phase is followed by a feasibility phase, in which the concepts promoted during the concept phase are evaluated. A selection is made during this period as to which of the concepts described are most likely to yield success. This is generally accomplished by force ranking the alternatives available and establishing which will meet the minimum objectives established. It may be necessary to conduct limited tests to establish the validity of a particular approach. An estimate of the probability of success with each technique should be made, and the risks determined.

Once a feasible concept has been agreed upon, initial design begins. A design layout is prepared at this time, as well as breadboards of the electronic circuits involved. The software requirements are also drawn up and pseudo-code written. All facets of the program are carefully coordinated to ensure that everything works together. To facilitate this, a systems engineering course is implemented and interface control documentation is prepared. This is especially important if the project involves many different disciplines and many people. During the design phase, all of the engineering critical decisions relevant to the instrument are made.

A Preliminary Design Review (PDR) is held when the design is complete. At this time everyone connected with the project has the opportunity to review the plans and designs prior to detail design. This includes not only EAI Corporation personnel, but also customer personnel, vendors and other independent consultants as appropriate. It is usually beneficial to include individuals with broad, relevant experience, but with no direct connection to the project being reviewed, in a PDR. Such outside expertise brings a detached, objective and critical viewpoint to the discussion.

Questions raised at the PDR are resolved before proceeding with the detail design. This encompasses the detail drawings for fabricating and assembling the mechanical components, printed circuit board layouts, any ASIC design, and writing the source code for software. At the completion of the detail design phase, everything required to fabricate a prototype device is done.

At this point, the Critical Design Review (CDR) is conducted. Generally this involves the same people who participated in the PDR. This is the final opportunity for everyone involved in the project to comment on the design before it is committed to hardware.

Fabrication is accomplished with the assistance of a group of preferred vendors. The tasks to be performed on each project are evaluated by EAI Corporation engineering personnel. Packages of similar work are collected and sent to selected vendors for quoting. Quotations are generally solicited for complete subassemblies in order to clearly assign responsibility. New suppliers are surveyed prior to awarding any significant or critical tasks to ensure that they have the capability to perform the assigned tasks.

Acquisition can be divided into two distinct classes—the purchase of commercial items, and the subcontracting of specially fabricated parts. EAI Corporation has the resources to accomplish both functions; however, it is often expedient to have a subcontractor purchase the necessary commercial items as part of the task to avoid split responsibility and scheduling conflicts.

EAI Corporation informs vendors, as a matter of course, when they are involved in a development program and exactly what EAI's expectations are. For developmental items, the strategy is normally to assign a single vendor significant assemblies with the understanding they are to participate in the development and testing. This also includes the subsequent modifications that occur during prototype development.

EAI Corporation employs a rigorous control system to capture and document all changes that occur during the development of a prototype. A set of documentation will describe the "as-built" prototype. In addition, a corrected set of specifications and drawings to produce subsequent production items to the latest configuration can be provided.

Although the foregoing descriptions have focused on the technical and performance aspects of the development process, EAI Corporation is completely cognizant of the requirement to control both costs and schedule. During the early phases of the project a plan is established which defines the master schedule and the budget. Internal cost control methods are in place at EAI Corporation to detect deviations from the planned spending and schedule. This early detection allows time for reaction and correction of the problem.

Using the systems engineering approach, design, fabrication and testing of the RSSAR system were broken down into individual components. These components were

- Sorbent tube and cap design
- Magazine
- Quick-look detector
- Sampler (MSTM)
- ATD interface

The subcomponent requirements for each were identified and the requirements were defined. Design, investigation, and tests of each subcomponent were conducted in parallel. Design considerations and fabrication of each requirement are discussed in the following sections.

Sorbent Tube and Cap Design

Tube Selection

The selection of the sorbent tube and cap design was the most critical component of the MSTM, because it drove the selection of the ATD unit and facilitated the automation of the entire sample collection and analysis process. As discussed in the RSSAR Phase 1 report, we selected a Perkin Elmer model ATD-400 automatic thermal desorption unit as the platform on which the analysis of samples from the MSTM would be conducted. The Perkin Elmer ATD-400 was selected for a number of reasons. To summarize:

- It was the only commercially available unit that offered more than 16 tube automated analysis capability.
- It was the unit that required the fewest mechanical changes to facilitate automated analysis of the sorbent tubes.
- While there is no industry standard, Perkin Elmer possesses a large share of the commercial market for this type of product. As a result, selection of the ATD-400 allows us to capture the technical experience and market experience of the product and its users.
- The PE-ATD-400 can be interfaced to a number of different vendor gas chromatograph/detector systems (Hewlett-Packard, Varian, Shimadzu, etc.)

By selecting the Perkin Elmer ATD system, the mechanical configuration and physical dimensions of the sorbent tube were established. In order to maintain this standard, the MSTM was effectively built around these dimensions. The specifications of the Perkin Elmer sorbent tube are as follows:

Tube material:	stainless steel	Outside dimension:	0.250 (1/4) in.
	glass	Inside dimension:	0.190 (3/16) in.
	glass-lined stainless steel	Length:	3.50 in.

Sorbent Material and Sorbent Packing

Fifty stainless steel thermal desorption tubes (1/4 in. O.D. by 3.5 in., 9 cm Supelco, Inc.) were purchased empty and packed with approximately 220 mg of Carbotrap 370. Carbotrap 370 was determined during Phase 1 to have the best capability for trapping the contaminants of interest. It is a mixture of three graphitized carbons—Carbotrap B, Carbotrap C, and Carbotrap F—that differ only in their available surface areas: 100 m²/g, 10 m²/g, and 5 m²/g, respectively. The adsorbent tubes contained 40 to 80 mg of Carbotrap B, 100 to 200 mg of Carbotrap C, and 80 to 160 mg of Carbotrap F. The tubes varied in sorbent content because of the limited availability of Carbotrap F. However, all sorbent tubes had excess capacity to accommodate the quantity of contaminants used in the experiments. The weaker adsorbent, Carbopack F, was placed nearest to the inlet side of the tube. The stronger adsorbent, Carbopack B, was placed nearest the exit side of the sampling tube. Larger molecules are trapped by the weaker adsorbent. Smaller molecules are trapped by the stronger adsorbents. Once packed, the thermal desorption tubes were conditioned by purging the tubes with helium at 310 °C for 30 min. The graphitized carbons used in this study are highly inert, nonporous adsorbents with hydrophobic properties that minimize sample displacement by water. For the testing of the MSTM, twenty commercially packed (Supelco) tubes were obtained in addition to the fifty sorbent tubes which were packed and provided by EAI.

Figure 3 shows the bed configuration and amount of sorbent for those tubes packed by EAI.

Figure 3. EAI packed tubes configuration.

Tube Caps

The design and the configuration of the tube cap was the most critical component of the MSTM design. The ATD-400 uses Teflon endcaps with an o-ring to seal the tubes during storage and to position the tube in the ATD during subsequent analysis. By modifying the cap to include a septum that can be pierced, a sample stream could be passed through the sorbent tube using two stainless steel needles injected through each endcap positioned on the sorbent tube. In this manner, the cap could facilitate sampling during the collection phase yet still allow manipulation by the ATD unit. Using this design, the tube cap would provide a host of sample- and analysis-related functions:

- Provide an adequate seal to prevent the sorbent from becoming contaminated *before* sampling but not too tight to prevent removal/replacement of the cap by the ATD-400.
- Provide an adequate seal to prevent the sample from degrading or becoming contaminated *after* sampling but not too tight to not allow removal of the cap by the ATD-400.
- Provide an adequate seal to allow the sorbent tube to draw a vacuum while sampling but not allow leaks around the o-ring seal during sampling.
- Be highly inert and cost effective (inexpensive).
- Provide a barrier that can be pierced to allow access to the sorbent by the sample stream.

In summary, the cap and cap seal (o-ring fit) had to be strong enough for a sample to be drawn through the tube under vacuum but weak enough to allow the ATD unit to remove and replace the caps during its analysis cycle. Considerable effort was made to understand the parameters of the cap design that met these operational requirements. The optimum cap was found to be a function of the o-ring groove diameter inside the cap that holds the o-ring in place. A deep groove results in a cap that is loose and therefore leaks around the seal. A shallow groove results in a tight o-ring seal and the cap cannot be pulled from/inserted on the tube. There is, however, an optimum range where a good vacuum could be obtained without overcoming the insertion force of the ATD-400. Figure 4 shows the acceptable and unacceptable regions determined for the groove depth on the caps.

In this design, the cap has three major components: a Grade A, virgin PTFE (Teflon) body, a PTFE-lined septum inside an aluminum cap and a PTFE-coated Viton o-ring. Because all the materials are constructed from or coated with PTFE, the cap is highly inert. Currently, the cost for

Figure 4. Acceptable cap groove depth.

one cap is approximately \$5.03 (body, \$4.00; cap, \$0.13, o-ring, \$1.90). Considerably lower costs will be realized when buying in bulk; however, other inert (lower cost) materials will be investigated. In addition, the degree to which the caps can be reused (repeated piercing of the septa) has yet to be determined. Figure 5 shows the resulting design of the cap.

Lower costs can also be realized after initial purchase as the cap body and o-ring can be re-used. The aluminum cap with the PTFE-lined septum is a standard chromatography consumable used on crimp-top autosampler vials in both gas and liquid chromatography applications. They are currently sold in bulk and can be installed and removed from the cap body using standard crimping and decrimping tools. As a result, users will be able to rebuild and re-use their caps for an indefinite period of time.

Figure 5. MSTM sorbent tube cap design.

Magazine

The magazine is the subcomponent of the MSTM that holds the sorbent tubes and hardware (electrical and mechanical) to collect the samples and store data pertinent to the collection of those samples. This data can include control data (when to start the sample, when to stop the sample, desired flow rate, etc.) as well as real-time data collected during sampling (temperature, relative humidity, barometric pressure, etc.). The magazine consists of a metal housing containing a rotating carousel which holds up to 50 sorbent tubes. The magazine actually has 51 positions for the carousel—there is a “home” position where the needle access openings are closed, thus locking the device to prevent carousel rotation during shipment.

Housing

In the current design, the housing is a robust aluminum enclosure, designed to withstand the rigors of constant shipment and handling. A major function of its design is to position the carousel accurately in the MSTM. This is necessary for a number of obvious reasons. First, the proper performance of the carousel drive and the sample position reading encoder (see description of this feature in the next section) depends on the axis of rotation of the carousel being aligned with the carousel drive and the sample position encoder. Second, the sorbent tube must be positioned accurately for the proper insertion of the needle. This positioning has two degrees of freedom, and therefore the housing must control the angular alignment of the magazine as well as the position of the axis. Finally, the housing encloses the memory board and its connector board. A cam in the sampler opens a protective door automatically as the magazine is inserted into the sampler, allow-

ing access to the connector board. This cam arrangement also defines the positioning of the magazine and ensures that the connector board in the magazine aligns with the connector mounted in the sampler. The connector protective door closes automatically when the magazine is removed from the sampler.

The housing (Figure 6) contains a spring-loaded door to permit loading and unloading of the sorbent tubes. This door can be opened manually for loading by pressing on the plate behind the door through the hole provided in the housing.

Carousel

The carousel (Figure 7) is the rotating portion of the magazine located internal to the magazine. It has two large carrier wheels that index the sorbent tube when driven by the sampler. A drive plate on the top contains two slots which align with the drive pins of the MSTM's carousel drive as-

Figure 6. MSTM magazine housing.

Figure 7. Magazine carousel.

sembly. It is necessary for the magazine carousel to be in the home position when it is loaded into the MSTM; this allows the pins in the drive mechanism to align with the holes in the magazine. This position can be easily identified by the black closures in the needle access openings of the magazine. The locking devices must be removed if they are present before attempting to load the magazine into the sampler. A tool for manually rotating the carousel was developed to position the carousel if it has been moved from the home position. It is only possible to rotate the carousel in a clockwise direction as viewed from the top. The sampler carrier wheel can accommodate as many as fifty sorbent tubes at a time; however, it is not necessary to completely load the magazine. It is recommended that sorbent tubes be loaded contiguously starting with position no. 1 in the carousel. The magazine should be returned to the home position prior to removal from the sampler. Insertion of the locking device to prevent rotation when the magazine is not in the sampler is recommended.

On the bottom of the carousel, outside the housing, is an encoder wheel. This contains a gray code which identifies the tube currently in the sampling position. Care should be exercised in handling the magazine to avoid damage to this encoder. The position of the carousel may be read on the display on the front of the sampler and through the PC interface.

Magazine Loader

It is possible to load the tubes into the magazine by hand. Specific training for this operation is required, and beyond the scope of this report. A manual loader has been designed and fabricated to assist in manually loading sorbent tubes into the magazine. Currently this is the only technique for loading tubes into the magazine.

Carousel Memory

The magazine contains nonvolatile memory for 50 sorbent tube samples. The memory consists of a serial EEPROM available in 32K x 8 bit blocks. This memory is interfaced with the processor board through the I²C bus. The utilization of this memory depends on the mode of operation. In the RSSAR mode, it is capable of reading the temperature of the transfer line and the digitized signal from the quick-look detector. For the MSTM mode, the carousel memory maintains the sampling schedule and programmable parameters such as flow rates and sample times. The electrical interface for this memory is through a 9-track double-sided card edge connector, which also indicates proper insertion of the magazine in the unit by displaying this information on the front panel.

Chassis

Background

The design of the sampler was driven by conflicting goals. The requirements of the specific application for integration into the RSSAR system could not be compromised. There is, however, a strong desire to design an instrument with as wide a commercial appeal as possible. To maximize the benefits from the prototype, it is desirable to build the prototype as close to the final production units as possible. On the other hand, prudent design practice would allow for modifications to the prototype as the project progresses. These conflicting goals were achieved by designing in a modular fashion so that problems with one system or module did not jeopardize the whole program.

The housing was designed with flexibility in mind. This was accomplished by utilizing the systems engineering approach. The requirements for each function and operation were identified and the interface requirements for each module defined. A central structure was planned which supported all of the modules. The cabinet was purposely made larger than the expected requirements

dictated. This permitted the design of each module to be as close to the production version as possible while still allowing room for unanticipated changes. Furthermore, additional features were identified during the design process, but were not incorporated in the original design due to schedule considerations. Provisions were made to include these anticipated features to the extent practical during the design phase.

This strategy of design will permit subsequent improvements to be made to individual modules without undue impact on the remainder of the system. This will be particularly important if additional testing finds some modules are not performing as predicted, or are not sufficiently reliable. During the commercialization phase, redesign to incorporate cost reduction, size reduction or inclusion of additional features can be undertaken without committing to a total redesign of the instrument system.

Housing

The housing (Figures 8 through 11) is approximately 16 in wide by 9 in high and 12 in deep. It consists of the base, a front panel and a cover. The base also incorporates the back of the cabinet. Mounted to the base and front panel is the magazine support assembly. Mechanically, the magazine support assembly is the heart of the instrument, since it establishes the positioning of the magazine and supports all the major interfaces with the magazine.

The front panel provides all of the access required to the system as well as the operator interface. The magazine is inserted into the MSTM through a pair of spring-loaded doors. Sliding the magazine into the sampler opens the doors and as it is pressed home, completes the interface with the carousel drive and the sampler electronics. Inserting the magazine also initiates the MSTM.

Mechanical Arrangement

The mechanical arrangement of the MSTM consists of the carousel drive assembly, the needle drive assembly, and the sample pump chassis assembly. Each of these assemblies is discussed in detail in the following paragraphs.

Carousel drive assembly. The carousel drive (Figure 12) is powered by a dc motor with an integral gearbox mounted on the face. The output speed of the gear motor is 25 rpm. The motor drives a six-point Geneva mechanism and a subsequent gear train that reduces the angular motion of the Geneva by 8.5 to 1. This drive arrangement yields 51 index positions per revolution of the drive plate. A single revolution of the Geneva mechanism requires 2.4 sec to complete.

The carousel drive must be in the home position when the magazine is loaded so that the drive pins are aligned with the drive slots in the magazine. It takes 2 min, 2.4 sec for the carousel to make one complete revolution. This is the worst case for the carousel drive to return to the "home" position. An internal switch detects when the carousel drive is in the home position and automatically stops the rotation when the drive is seeking the home position under the control of the computer. This information is displayed on the front panel to inform the operator.

Needle drive assembly. The needle drive assembly (Figure 13) inserts two needles, one at each end, into the capped dry sorbent tube. This is accomplished by means of an upper and lower slide driven by opposite lead threads. The right-hand thread is located on the bottom of the needle drive assembly, and the left-hand thread on top. The screw is powered by a dc gear motor through a unity gear pair with an output speed of 300 rpm.

The total travel of each needle carrier is approximately 0.5 in. The travel is limited by two photo-sensors mounted on the slide guide bar. A flag mounted on the upper slide interrupts the photo-sensors and stops the motor. This is a factory preset travel and is not a field serviceable adjustment. The "in" or "out" transit time required by the needles is approximately 2.0 sec.

Figure 10. Top

Figure 11. Front

Figure 12. Carousel drive assembly.

Figure 13. Needle drive assembly.

The needles are available in several diameters. Ongoing studies will determine the optimum needle bore diameter for each application. The tradeoffs to be evaluated include flow rates vs. pressure drop vs. coring and septum life. The needles are held in place by means of a Luer Lock fitting and are easily changed using a tool fabricated for the MSTM. Access to change the needles is gained by manually opening the doors on the front of the sampler with the magazine removed. The needles can then be reached through the round holes provided in the top and bottom of the magazine support. The operator may find it more convenient to change the needles in the inserted position. They can be moved manually using the hand-held controller supplied with the sampler. Needles are replaced by sliding the tool over the needle and turning counterclockwise to remove the needle. Installation is the reverse of removal.

Sample pump chassis assembly. The sample is drawn through the sampling head, the transfer line, the quick-look detector and the sampler by a vacuum pump located in the MSTM. The quick-look detector initially evaluates the sample stream and determines if a sample is to be retained in a sorbent tube. A three-way valve is shifted when it is determined that a sample will be retained. This valve diverts the entire sample stream through the sorbent tube in the sampling position. The sample pump chassis assembly is presented in Figure 14. The absolute pressure is monitored on the inlet of the pump. This is to detect any anomalies in the system and record them as part of the data captured for the sample.

The effluent from the pump vents to atmosphere through a flow controller. The flow sensor uses a Pelton type turbine wheel and photodiodes to generate an electrical signal proportional to flow

Figure 14. Sample pump chassis assembly

rate. Rotation rate of the turbine wheel is linear over a wide dynamic range. The output signal is fed back to control the pump speed, monitored for irregularities, and/or total flow through the sorbent accumulated.

All of the above-described components are mounted on a separable chassis inside the MSTM. This facilitates ease of maintenance as well as changing pump size when sampling requirements change.

The wetted exposed parts of the sample flow path within the MSTM are all either stainless steel or Teflon. All air-flow-controlling hardware (pump, solenoid and flow controller) is located behind the sorbent tube in the sample flow path. After the sample stream has passed through the sorbent tube, less stringent requirements are placed upon the inertness of the materials contacted. However, careful consideration of the chemical compatibility of the material selected with the expected sample materials is still required.

MSTM Electronics

The MSTM is a device which automatically collects air samples in sorbent tubes for later analysis. The sampler is designed for minimal operator interface and/or unattended automated operation. The sampler has three modes of operation: MSTM, RSSAR and standby:

- In the MSTM mode, the sampling schedule is programmed in the carousel memory. After the sorbent tube is exposed, the processor returns to standby. The schedule for sampling, flow rates, and sampling time are maintained by the carousel memory. The carousel memory also maintains other data specific to each tube—for instance, humidity and temperature.
- In the RSSAR mode, sampling is on demand, triggered by the quick-look detector. Following each sample, the carousel is rotated and needles inserted in preparation for the next sample. Different parameters are maintained for each sorbent tube in this configuration (output from the quick-look detector, etc.). The trigger level is determined by analysis of the quick-look detector baseline signal to optimize the amount of sample captured. Memory space is provided in the carousel for the digitized output of the quick-look detector.
- In the standby mode, the 12-V power supply to the motor drive board is turned off. Electro-optic sensors are also turned off. The processor will continue to monitor the schedule and poll the sensors. Program execution is determined by the carousel memory unless interrupted through the external serial port. If the RSSAR evolves to a battery-operated configuration, this will greatly enhance power conservation.

Power supply. Main power to the unit is 117 Vac, with a 1-A fast-acting fuse. This source is used solely for two dc power supplies: one 5 V at 2 A and one 12 V at 1.2 A. For 12-V battery operation, a 12- to 5-V converter is required.

Processor. The MSTM uses a 80C552 microcontroller that is mounted on a board with its peripheral processing chips. It maintains a real-time clock and display and an interface to the carousel memory and sensors. It also controls the motors, and regulates the sample flow. The processor has a startup routine which initializes the sampling schedule. It is also programmed to recover from power failure conditions. When power is returned after a failure during motor movement, the needles will retract and/or the carousel drive will return to the parked position automatically. 28-pin JEDEC sockets on the processor board are used for EPROM to store program code with 100 ns access time.

Internal interfaces. The single board computer (SBC) has an I²C bus; 8-channel, 10-bit A/D converter; two pulsewidth modulation (PWM) outputs; three serial interfaces; and forty digital I/O lines. The SBC interfaces with the front panel display and indicators, the motor control board, and the sensor interface board.

Pinouts for connectors and interfaces are as follows:

Summary of 552 utilization:

- Port 0: Low order address and data
- Port 1: Position switches and I²C bus
- Port 2: High order address for program memory and parallel interface adapter
- Port 3: Serial port, external interrupts, timer, R/W strobes
- Port 4: Motor control interface
- Port 5: A/D conversion

Parallel interface adapter:

- Port A: Position sensors for carousel
- Port B: Front panel display
- Port C: Front panel LCD display

Serial interface. SBC functions can be executed with commands sent through the serial interface. The serial interface is accessed through a 9-pin RS-232 connector on the back of the sampler. Communication through this port is accomplished by connecting this port to a computer configured as a terminal emulator at 9600 baud. The sampler provides a prompt and indicates status. To send a command, single-letter, case-sensitive, abbreviations are typed. This interface also provides means for setting the pump flow rate, the time of day/year, and transferring data to and from the carousel memory.

System and real-time clocks. The processor (system) clock is 11.0592 MHz. This clock speed determines the frequency range for the PWM, which is 85 Hz to 21.7 kHz. The system clock also determines the speed of execution for each instruction, which is between 181 and 362 ns.

The processor maintains a real time clock with a Dallas Semiconductor 1286 Watchdog timekeeper. This is a 28-pin chip with battery and alarm function. Using this chip, time and date are displayed on the LCD front panel. If not reset every second, the watchdog timer interrupts the processor. Clock functions are set through the external serial interface.

Front panel display. The front panel of the sampler (Figure 15) has a 2-line by 16-character LCD display. One line is used for date and time. The second is used to indicate status or fault messages. The tube number is also displayed on the second line. Three indicator LEDs indicate power, status, and fault status.

Figure 15. Front panel.

Front panel messages include

insert magazine	magazine inserted
injectors down	injectors up
change magazine	

Sensors. Carousel position (tube 1–51) is determined by reflective mask on the bottom of the carousel in gray code. This code is read by six opto-electric sensors: 6 I/O bits through port A of the parallel interface adapter and J6. Pressure, temperature, and humidity can be monitored by the sampler through the A/D converter and recorded in the carousel memory. This data can be used to correct sample volumes for standard temperature and pressure. Data is processed through the analog-to-digital converter (ADC) interface of the processor (Port 5, J8:10–18).

Flow control. The vacuum pump and pump control circuitry have been designed to maintain a constant flow through the sampler. The flow rate is continuously adjustable from 40 to 200 ml/min. This range can be extended with the use of different pumps and/or flow meters. However, the same control circuit can be used with different pumps or flow meters and maintain this linear response. The current pump is a diaphragm design with a fixed displacement. The flow is controlled with a pulsewidth modulator which determines the speed of the pump motor. The flow control circuit uses a flow transducer and a servo loop and can control the flow to within +5%.

A differential pressure transducer is used to monitor the flow path. If the pressure drop across the tube is within predefined limits, a leak-free system (injector needles, septa, and the sorbent tube) can be assumed. A large pressure drop would indicate an occluded or restricted sample stream and would cause the system to shut down. The pressure monitoring circuitry limits the maximum vacuum in the sample stream to 60 in of water. This limit is adjustable and is dependent upon the specifications of the vacuum pump. When the vacuum in the sample line exceeds 60 in of water, the pump speed is automatically reduced and a flow fault is declared through P4.5. The processor also monitors line pressure through A/D interface P5.6, while sampling. A fault is declared if line pressure exceeds upper and lower limits. This data is contained in a lookup table and depends on flow rate and sorbent. If the pressure is too low, there may be a leak. If the pressure is too high, there may be a blockage.

The flow rate is set locally with a trimpot (0–5 V) or by the SBC. Other trimpots are available for calibration.

Motor control board. The motor control board interfaces between the processor board and the electromechanical components of the sampler. These components include the carousel and the injector drive motors, the solenoid valve, and the pump. It also contains processor I/O for the position sensor. The needle drive motor and the carousel motor are interlocked at this level so that only one motor can be energized at any given time. Resettable fuses are used in-line with the power supplies for the motors. Additionally, 5-sec timeout circuits are reset when the next position is reached. These timeout circuits will shut the system down when a command (needles in, needles out, rotate etc.) cannot be executed within the 5-sec period. This will prevent the system from severely damaging itself and/or burning out motors or other system circuitry. Carousel position, injector position, and the solenoid valve can be controlled with commands through the serial interface or with switches on the motor control board. Optionally, a handheld controller is also available.

Printed circuit board specifications. The motor control board is a 3.85-in by 8-in rectangular, single-layer circuit board manufactured and assembled according to commercial standards. Component features for this board include

- Trimpots are 20 turn and mounted on the top edge of board.
- Processor interface is through breakaway headers on left side of board.
- Switches are mounted on the top edge of the board.
- Output connections for motors and inputs for power supplies with board mounted terminal blocks, located on the right-hand side of the board.
- Resistors are 1/8 W unless otherwise specified.
- Components are mounted "through hole" with no surface mounting.
- 30% board space is allowed for expansion.

RSSAR interfaces. The RSSAR system uses a quick-look detector that monitors the sample stream exiting the sample head. This detector provides an operator or computer a trigger which starts the sample cycle within the MSTM. The quick-look detector also provides an analog signal as the sample is desorbed from the surface being tested. This "desorption profile" can be digitized and recorded with the tube data, providing a historical record of the actual trigger event and stored in the carousel memory. The RSSAR mode differs from the MSTM mode in protocol and interfaces in that

- The RSSAR mode is activated through the serial interface.
- The carousel is advanced and injectors inserted in preparation for a sample.
- Site-specific operator data is entered through the serial interface.
- Solenoid valve is activated to bypass the sample tube.
- The pump is activated and preset to pump continuously at 100 ml/min.
- When analyte is detected by the quick-look, the 'start sample' message is sent.
- The solenoid is deactivated, routing sample through sorbent tube for approximately 45 sec.
- Quick-look data and vapor-train temperature data is piped through the serial port and reformat-
ted by the SBC for storage in the carousel memory. Only a finite amount of the quick-look and
transfer line data is captured.
- After a preset period of time (and therefore volume), the sampling is concluded.
- The process then returns to step 2 or the RSSAR mode is terminated by returning to standby.

MSTM Firmware

The firmware for the 80552 microcontroller can be broken down into three main tasks: device interfacing, user serial interfacing, and system control.

Device driver subroutines simplify access to the magazine memory, LCD display, position sensor, serial port, and real-time clock. The user serial interface provides a command line menu for external control of the sampler, by either an operator or a master control computer. The system control loop monitors the status of the sampler mechanical mechanisms and sends proper control signals to the motor control board.

All firmware is written in C and compiled and assembled using tools by Avocet Systems, Inc. The firmware was built using the large memory model, in which all data except the stack and scratch pad registers were kept in slower, external RAM. Limitations in using the smaller, internal RAM did not justify the minimal improvement in program execution speed.

Device interfaces. The device interfaces are a set of subroutines that encapsulate specific code needed to communicate with the peripheral electronic devices connected to the SBC. Details such as poor selection, handshaking, timing, data conversion, and error detection are handled by the driver subroutine. This practice simplifies and streamlines the main code and facilitates debugging. Any change in the way a device functions entails modification to only the driver, not the entire program, and makes it easy to upgrade the system in later generations.

Carousel interface. Communication with the internal memory of the magazine is via a two-wire I²C bus. Each chip in the memory module is individually addressable on the bus. The driver subroutines handle all the addressing, bus timing, and error detection and recovery to read and write data to the nonvolatile memory. Data can be transferred in single bytes or in blocks up to 64 bytes in length, to increase system performance. Due to the internal structure of the memory chips, block sizes cannot exceed 64 bytes, with 64 blocks per chip.

Since the optimum block size is 64 bytes, a second level of driver subroutines implements a simple file structure based on a 64-byte block. One chip stores identification information and header data specifically for the individual magazine. Two chips are used to store data on an individual tube at two samples per blocks (128 bytes) per tube. The remaining five chips are reserved for up to 500 quick-look samples, with two samples per block. The file storage and retrieval subroutines make the block transfers transparent to the rest of the system, save for the size limit, of each data type. Upgrading the overall memory size as larger nonvolatile memory chips become available on the market can easily be accomplished.

LCD interface. The LCD is controlled via an 11-wire parallel interface connected to the 8255A programmable peripheral interface (PPI) chip, which is memory mapped into the microcontroller's data bus. This interface is bidirectional, with eight data pins and three control pins. The driver subroutine handles all the cursor commands and handshaking, so that characters and strings can be placed anywhere on the screen with as much ease as a standard print function. The electronic interface is an industry standard, so the driver will work with any LCD screen that adheres to this standard.

Position sensor. The position sensor is connected to the PPI chip. When called, the driver subroutine obtains the current position reading from the PPI and converts it from gray code to binary. It then returns an integer corresponding to the current tube number, or an error code if the position sensor is reading out of range (a tube number greater than fifty).

Real-time clock. The drivers for the real-time clock perform a number of functions. They read the current time and date from the clock and format it for storage or display. Another routine obtains a user-supplied string, checks it for errors and sets the time or date of the clock. The clock also stores setup parameters for the sampler in its nonvolatile memory. Because the real-time clock is memory mapped into the microcontroller's data bus, no drivers are needed to access this data.

Serial port. The serial port interface routines are interrupt driven. An internal interrupt is triggered whenever a character arrives into or is transmitted from the microcontroller's internal universal asynchronous receiver/transmitter (UART). The UART interrupt starts an interrupt routine that places incoming characters into a circular queue and moves outgoing characters from the transmit queue. Pointers keep track of current locations in the circular queues. All program communication with the serial port is via the transmit and receive queues. The standard input and output routines have been modified to work with this buffered output scheme. Using this method, the microcontroller need not wait for strings to be transmitted before continuing with the next program sequence. Also, the chance of dropped characters due to a high processing load on the microcontroller is minimized.

Serial interface. The user interface to the sampler is via a standard RS-232 serial port. Using standard terminal software available for any computer, the user can control all features of the sampler. Also, the serial port allows the sampler to be controlled by another computer. Commands are entered via a two-character sequence, with additional data entered as requested. Informative prompts give the user immediate feedback for every entry.

The serial commands are broken down into five sets. To enter a command, the user types the first letter of the command set, followed by the character for the desired command. For example, to command the sampler to rotate the carousel to the next tube, the user would enter 'C' for the Control command set, followed by 'R' for Rotate. The sampler supplies feedback by completing each word after the user enters the first letter to verify that the user entered the correct command. The following is a summary of sampler commands:

1. Control
 - Home: Rotate carousel to home position
 - Bypass valve: Open the valve to bypass the sorbent tube
 - Close valve: Close the valve to direct flow through the sorbent tube
 - Needles in: Insert needles into sorbent tube
 - Needles out: Remove needles from sorbent tube
 - Rotate: Rotate carousel to next tube
 - Start sample: Close valve, record start time, and begin flow integration
 - Finish sample: Open valve, record end time, and record total flow
2. Set
 - Time: Set the time on the real-time clock
 - Date: Set the date on the real-time clock
3. Write
 - Quick look: Record up to 128 bytes to the desired tube entry
4. Display
 - Quick look: Display the desired quick look entry
 - Tube: Display the desired tube entry
5. Edit
 - Tube: Enter information for individual data fields of a tube
 - Status: Obtain a short summary of the sampler's operating status, including needle and tube position, pump speed and total flow volume.

System control loop. The system control loop is the central routine of the sampler firmware, in which all the functions are coordinated for smooth operation. This loop has two main tasks:

- monitor sampler operations for errors or successful completion and
- monitor the serial queue for commands and send them to be processed.

Because the processor cannot ignore one function for the other, it must constantly switch between the two. Status information is stored in nonvolatile registers in the real-time clock. The processor uses this status information to recall what commands are in process after switching back into a loop.

The system control loop also monitors the sampler for faults. It calculates timeout values and checks whether or not commands are completed in the allotted time in order to detect mechanical failures. The loop also monitors the state of the position switches built into the MSTM and prohibits the execution of any command that may cause harm to the system. This provides another level of safety in addition to the mechanical and electrical interlocks. Descriptive error messages are sent to the serial interface and displayed on the LCD screen for diagnosis.

The MSTM electronics and firmware were designed to allow flexibility and expansion. Capabilities and functions of the system can be augmented or added in the future if system requirements change. Figure 16 summarizes the firmware components of the MSTM system.

Figure 16. Block diagram of MSTM firmware.

MSTM Performance Testing

Objective

The objective of this testing was to verify proper operation of the multisample trapping module as measured by the ability to consistently achieve >70% recovery of the three model compounds.

Testing Modifications

Initial efforts to test the multisample trapping module identified several modifications which were required to obtain satisfactory performance. A heated transfer line was installed between the needle assembly and the bulk sampling oven head. This modification was necessary to prevent the condensation of the high boiling model compounds and to reduce the amount of water that condensed in the line. The heated transfer line was fabricated from 18 inches of Silicosteel® and was attached to the top inlet of the needle assembly via a Swagelok fitting. A cable heater was wrapped around the transfer line and controlled with an Omega® temperature controller via a thermocouple. A second read-only thermocouple was installed at the opposite end of the transfer line. The transfer line was wrapped with insulation.

The second modification of the MSTM was the reversal of the inlet and outlet ports of the needle assembly. In the prototype MSTM, sample collection would occur by drawing air through a sorbent tube in an upward direction. The MSTM was modified so that air would be drawn from the top of the sorbent tube toward the bottom of the sorbent tube to facilitate the flow of condensed water out of the MSTM by using gravity and the vacuum pump downstream of the sorbent tube.

The third modification was the addition of a cooling coil downstream from the sorbent tube and before the vacuum pump. The cooling coil was made from 12 in of 1/4-in copper tubing. The cooling coil was added to prevent hot gases from reaching the vacuum pump and solenoid valves. Performance testing of the MSTM later demonstrated that it was also necessary to heat the block

of metal that supports the needle assembly for efficient transfer of analytes from the sampling head to the sorbent tube.

Experimental Methods

Testing of the MSTM. A test solution of anthracene, 2,4,5-trichlorobiphenyl, and phenyldodecane was prepared in pesticide grade methylene chloride. The concentration of each of the analytes is shown in Table 1. The bulk sampler oven was mated to the MSTM. Sorbent tubes packed with Carbotrap 370 were loaded into the magazine so that the grooved end of the tube faced up. In Phase 1 of this study it was determined that Carbotrap 370, a mixed bed adsorbent tube, was

deemed the material most suitable for the model contaminants used in this study. With the MSTM in standby mode the needle assembly was actuated and the needles were inserted through the septum cap of the adsorbent tube. Air flow was established through the sorbent tube and allowed to reach equilibrium (1–2 min). Air flow in the standby mode was 100 ml/min.

Desorption of analytes from the bulk sampler oven. The bulk sampling oven was heated to 250 °C. The transfer line between the bulk sampling oven and the MSTM was heated to 250 °C. A known amount of test solution was placed into an aluminum pan and the pan was inserted into the bulk sampling oven. For each trial, 10, 15, 20, or 25 µl of test solution was pipetted with a positive displacement pipettor into an aluminum pan. The solvent was allowed to evaporate. Once air through the sorbent tube had reached equilibrium, the aluminum pan was inserted in the bulk sampling oven tray and the tray was inserted into the heated oven. Sampling time was 5 min. Air flow during sample collection was 40 to 60 ml/min. Approximately 200 ml of air was passed over the sorbent tube. After 5 min of sample collection, the solenoid valve was switched to standby mode, the needles were withdrawn and the bulk sampling oven tray was cooled to 40 °C or lower before a sample was reintroduced.

Thermal desorption. The Perkin Elmer ATD 400 was modified so that it could operate in back-flush mode. This mode of operation was necessary for the desorption of the high boiling compounds used in this study. The ATD employs two desorption steps to transfer analytes to the GC column. In the primary desorption step the analytes are refocused on a quartz trap. For our study the quartz trap was packed with graphitized Tenax. The thermal desorption tubes were loaded into the thermal desorption autosampler so that the grooved end of the tube faced the back of the ATD 400. A known amount of internal standard was syringed into the grooved end of the tube. The internal standard used (2.08 µg/µl in methylene chloride) was p-terphenyl. The conditions for the primary desorption were 300 °C for 30 min. The desorb flow was set to 15 ml/min. The inlet split was set to 135 ml/min. The conditions for desorption from the trap were 300 °C for 30 min. The outlet split was set at 100 ml/min. The total split was 100:1. During the primary desorption step, the quartz trap was maintained at 4 °C. The transfer line between the ATD 400 and the GC was maintained at 225 °C. The valves in the ATD 400 were heated to 225 °C.

The analysis was performed using a gas chromatograph (Model GC-14A Shimadzu, Inc.) which was equipped with a flame ionization detector. The GC column used was DB-5 (J&W Scientific), 0.53 mm I.D. x 30 m, with a film thickness of 1.5 µm. A standard solution with the three model compounds and the oxidation product (anthraquinone) of one of the analytes was prepared. This solution was used to calibrate the gas chromatograph. The GC was calibrated by placing known

Table 1. Concentrations of analytes in test solution used for testing the multisample trapping module mated to the bulk sampling oven

Analyte	Concentration in test solution (µg/µl)
anthracene	1.1
2,4,5-trichlorobiphenyl	1.0
phenyldodecane	1.4

amounts (10, 15, 20, 25, or 30 μl) of the standard solution on a thermal desorption tube and thermally desorbing the prepared tube. Para-terphenyl (10.4 μg) was used as an internal standard to gauge the efficiency of the thermal desorption instrument and the gas chromatograph. In order to not saturate the flame ionization detector the split flows on the thermal desorption instrument were set so that only 0.9% of the sample on the tube reached the GC column. The same split flows were used for the analysis of the thermal desorption tubes generated from the component testing. A five- point calibration line was used to generate a standard curve. Correlation coefficients of 0.99 were obtained for the four compounds (anthracene, 2,4,5-trichlorobiphenyl, phenyl-dodecane, and anthraquinone). Table 2 lists the concentrations of the analytes used for calibration of the GC.

Table 2. Amounts (μg) of model compounds used to calibrate GC using thermal desorption methods.

	10 μl	15 μl	20 μl	25 μl	30 μl
anthracene 1.2 $\mu\text{g}/\mu\text{l}$	12	18	24	30	36
2,4,5-trichlorobiphenyl 1.0 $\mu\text{g}/\mu\text{l}$	10	15	20	25	30
phenyldodecane 1.1 $\mu\text{g}/\mu\text{l}$	11	16.5	22	27.5	33
anthraquinone 1.0 $\mu\text{g}/\mu\text{l}$	10	15	20	25	30
p-terphenyl (internal standard)	10.4	10.4	10.4	10.4	10.4

Known amounts of the three model contaminants were placed into the bulk sampler oven and volatilized. The bulk sampler oven was heated to 250 $^{\circ}\text{C}$. Volatilized materials were trapped on a sorbent tube packed with Carbotrap 370 contained within the MSTM.

MSTM Testing Results

Results from the performance testing of the multisample trapping module are shown in Tables 3 through 5. As seen in the tables, results were somewhat inconsistent, which led to the performance of several repeat experiments. To demonstrate that good recovery of the test analytes could be obtained with the MSTM, heat was applied, with a heat gun, to the metal block of the needle assembly during sample collection. This corrective action resulted in recoveries of >70%, exceeding the test plan objective and validating the concept of the MSTM. In all but one sample during the last series of experiments, recoveries were >100% for all contaminants, which indicates potential carryover of materials from previous samples. This was confirmed by analysis of the blank samples,

Table 3. First experiment: Recovery of anthracene, 2,4,5-trichlorobiphenyl, and phenyldodecane from the multisample trapping module.

<i>Test volume</i>	<i>Model compounds</i>	<i>Theoretical recovery (μg)</i>	<i>Measured recovery (μg)</i>	<i>Percent recovered</i>
10 μl test solution	anthracene	11	9.6	87
	2,4,5-TCB	10	10	95
	phenyldodecane	14	11.9	85
10 μl test solution	anthracene	11	9.1	82
	2,4,5-TCB	10	9	90
	phenyldodecane	14	11.5	82
15 μl test solution	anthracene	16.5	14.3	86
	2,4,5-TCB	15	13.2	88
	phenyldodecane	21	16.6	79
15 μl test solution	anthracene	16.5	13.2	80
	2,4,5-TCB	15	13	86
	phenyldodecane	21	16.5	78
15 μl test solution	anthracene	16.5	10.2	62
	2,4,5-TCB	15	11.7	78
	phenyldodecane	21	14	67
15 μl test solution	anthracene	16.5	2.1	13
	2,4,5-TCB	15	3.7	25
	phenyldodecane	21	4.8	23
20 μl test solution	anthracene	22	1.5	7
	2,4,5-TCB	20	1.2	6
	phenyldodecane	28	1.5	5
20 μl test solution	anthracene	22	2	9
	2,4,5-TCB	20	2.8	14
	phenyldodecane	28	3.1	11
blank	anthracene	0	1.6	—
	2,4,5-TCB	0	2.9	—
	phenyldodecane	0	3.1	—

Table 4. Second experiment: Recovery of anthracene, 2,4,5-trichlorobiphenyl, and phenyldodecane from the multisample trapping module.

<i>Test volume</i>	<i>Model compounds</i>	<i>Theoretical recovery (μg)</i>	<i>Measured recovery (μg)</i>	<i>Percent recovered</i>
10 μl test solution	anthracene	11	5.9	54
	2,4,5-TCB	10	8.5	85
	phenyldodecane	14	10.3	74
10 μl test solution	anthracene	11	22.6	>100
	2,4,5-TCB	10	35.6	>100
	phenyldodecane	14	43.3	>100
15 μl test solution	anthracene	16.5	5.6	34
	2,4,5-TCB	15	11.8	79
	phenyldodecane	21	13.3	63
15 μl test solution	anthracene	16.5	11.2	68
	2,4,5-TCB	15	17.2	>100
	phenyldodecane	21	24.3	>100
20 μl test solution	anthracene	22	30.2	>100
	2,4,5-TCB	20	16.4	82
	phenyldodecane	28	21.4	76
20 μl test solution	anthracene	22	4.3	20
	2,4,5-TCB	20	4.8	24
	phenyldodecane	28	6.1	22
25 μl test solution	anthracene	27.5	59.5	>100
	2,4,5-TCB	25	30.3	>100
	phenyldodecane	35	37.9	>100
25 μl test solution	anthracene	27.5	4.8	19
	2,4,5-TCB	25	7.1	28
	phenyldodecane	35	8.6	25
blank	anthracene	0	2.1	—
	2,4,5-TCB	0	1.6	—
	phenyldodecane	0	1.5	—

Table 5. Third experiment: Recovery of anthracene, 2,4,5-trichlorobiphenyl, and phenyldodecane from the multisample trapping module.

<i>Test volume</i>	<i>Model compounds</i>	<i>Theoretical recovery (μg)</i>	<i>Measured recovery (μg)</i>	<i>Percent recovered</i>
10 μl test solution	anthracene	11	16.4	>100
	2,4,5-TCB	10	15.3	>100
	phenyldodecane	14	19.4	>100
10 μl test solution	anthracene	11	18.3	>100
	2,4,5-TCB	10	16.1	>100
	phenyldodecane	14	20.8	>100
15 μl test solution	anthracene	16.5	24.9	>100
	2,4,5-TCB	15	21.6	>100
	phenyldodecane	21	28.3	>100
15 μl test solution	anthracene	16.5	40.9	>100
	2,4,5-TCB	15	34.6	>100
	phenyldodecane	21	41.7	>100
20 μl test solution	anthracene	22	14.6	66
	2,4,5-TCB	20	12.6	63
	phenyldodecane	28	15.9	57
20 μl test solution	anthracene	22	29.9	>100
	2,4,5-TCB	20	26.0	>100
	phenyldodecane	28	33.1	>100
25 μl test solution	anthracene	27.5	0	0
	2,4,5-TCB	25	0	0
	phenyldodecane	35	0	0
blank	anthracene	0	13.8	—
	2,4,5-TCB	0	10.9	—
	phenyldodecane	0	13.9	—

MSTM Specifications

Specifications for the multisample trapping module are listed in Table 6.

Table 6. MSTM specifications

Magazine

Capacity	50 samples
Size of sorbent tube	0.5 in. dia. x 3.5 in long (Perkin Elmer ATD-400 compatible)
Sorbent tube caps	EAI Corp. part no. 00-3001

Sampler

Needle drive

Travel	0.5 in
Speed	15 inches/minute
Travel time	2.0 sec
Motor speed	300 rpm
Motor voltage	12 Vdc
Motor current	100 mA
Motor power	1.2 W

Carousel drive

Geneva mechanism	60° per revolution of driver
Index time	2.4 sec
Motor voltage	12 Vdc
Motor current	185 A
Motor power	2.22 W

Pump

Valve

Type	3-way, normally open
Pressure rating	95 psig
Vacuum rating	18 in. Hg (244 in. H ₂ O)
Voltage	12 Vdc
Current	55 mA
Resistance	218 ohms

Pressure switch

Flow controller

Flow range	40–2000 ml/min.
Accuracy	±3% full scale
Linearity	±3% full scale
Repeatability	±1% full scale
Temperature range	0 to 50 °C
Temperature sensitivity	±0.2% per °C
Maximum pressure	40 psi @ 20 °C
Voltage	12 Vdc
Current	30 mA
Output	0–5 Vdc

which indicated significant contaminant concentrations. Therefore, the use of additional blanks was implemented in subsequent experiments along with periodic baking out of the system to minimize the potential for carryover between samples.

Thermal Modeling

In Phase 2 of this contract, the concrete modeling effort built upon the preliminary model described in the Phase 1 report. In the preliminary work, the governing equations describing the diffusion of thermal energy, water, and PCBs in porous concrete were solved using a finite difference algorithm to determine the liquid water concentration, vapor pressure, and temperature fields in concrete for a few simple initial cases. The details of the model and these results are described in the Phase 1 report.

In Phase 2, the dependence of PCB recovery on the recoverable water content of the concrete and its permeability were examined, since in many practical measurement cases these quantities are likely to be among the most important variables which are not known and are difficult to measure. In particular, water contents from 0 to 1000 kg/m³ and permeabilities from 10⁻¹⁷ to 10⁻¹⁵ m² have been simulated. The extent of these ranges, particularly in the case of water content, covers most practical environmentally aged concrete structures.

According to the model, the water content has two major, and offsetting, effects upon PCB recovery. On one hand, the buildup of large pressure gradients, as the concrete is heated beyond 100 °C and the water boils, helps to transport PCB vapor to the concrete surface. However, the necessity to supply latent heat of vaporization when the water actually vaporizes and diffuses through the concrete slows heating to very high temperatures. The model calculates both of these effects, permitting the temperature, pressure, water, and PCB concentration fields to be visualized. When applied to the case of concrete contaminated with 1% PCBs (Aroclor 1254) to a depth of 2.5 mm and exposed to a heat flux of 100 kW/m², the model reveals the following notable results:

1. The PCB extraction from the contaminated layer is nearly independent of the water vapor content at all exposure times.
2. The heat front propagates into the concrete at a rate which is nearly linear with time, rather than proportional to the square root of time as predicted by a one-dimensional conduction theory. The enhanced rate of propagation appears to arise from recondensation of water vapor driven more deeply into the concrete.

The sensitivity of PCB removal to moisture content is shown in Figure 17. The removal efficiency is fairly insensitive to moisture content as long as the moisture content is between 50 and about 400 kg/m³, a range encompassing values expected in environmentally aged concrete. At lower moisture contents, the reduced amount of water vapor available to force diffusion of the PCB vapors out of the

Figure 17. Effect of moisture content on PCB removal.

concrete decreases the removal rate. At higher moisture contents, the increased latent heat requirements reduce the heating rate and hence the PCB removal rate. It should be noted that unrealistically high moisture contents (1000 kg/m^3) were required to observe this significant decrease in PCB removal rate.

The model also indicates that highly permeable concrete is expected to have higher PCB removal rates, all other conditions being the same. For example, in a 30-sec simulation, concrete with an intrinsic permeability of 10^{-15} m^2 had twice the removal of PCBs in comparison to concrete with a permeability 100 times smaller.

These results are plotted in Figure 18. Although this effect is weak, it is still significant because the permeability can be increased by several orders of magnitude by cracking. Extension of these results to heterogeneous concrete would suggest PCBs would be removed preferentially from regions containing microcracks as compared to uncracked regions.

To illustrate the practical insight that the model provides, a specific example is examined in some detail in Figures 19 through 22. In this case concrete with an intrinsic permeability of 10^{-17} m^2 and water content of 200 kg m^{-3} is exposed to 100 kW m^{-2} . The initial Aroclor 1254 concentration was 1% by weight, and the contamination and water content were initially uniform throughout the concrete. In Figure 19, the temperature profile indicates that a temperature in excess of 450°C will be reached after 1 min of heating. Figure 20 shows the pore pressures that result from boiling water and expanding gases. After 1 minute, pressures over 45 atm are predicted. This result is consistent with concrete scabbling techniques which use high heat fluxes (direct flames) to pop off the surface layers of concrete. The PCB distributions in Figure 21 show the propagation of the PCB/no-PCB front moving down from the concrete surface. PCBs are shown to be removed from the surface first, and a resulting front is formed, which on one side has PCBs at the initial concentration and on the other side has no PCBs remaining. The fact that the concentration does not significantly increase at any given position in the sample indicates that very little of the PCBs migrate downward, away from the surface. By contrast, the water profiles shown in Figure 22 show significant "banking" of the water below the wet/dry interface of the water front. At some locations in the concrete, the liquid water content nearly doubles its initial value.

The propagation of the PCB and water fronts is examined as a function of initial water content in Figures 23 and 24. The depth of the PCB front in Figure 23 is shown to be insensitive to the initial moisture content. A constant rate of migration is also observed in the water fronts shown in Figure 24. These results suggest that the sensitivity of thermal sampling and the depth to which it can sample are directly related to the sampling time.

These modeling results are encouraging for the prospect of useful, accurate PCB measurements in concrete by thermal sampling. When this sampling equipment has been developed to the point where sufficient data on controlled samples is available, the model can be validated and used to help determine the relationship between measurements and contamination distributions in unknown porous materials.

Figure 18. Effect of concrete permeability on PCB removal.

Figure 19. Temperature distribution at 16.3 s intervals.

Figure 20. Pressure distribution at 16.3 s intervals.

Figure 21. PCB distribution at 16.3 s intervals.

Figure 22. Water distribution at 16.3 s intervals.

Figure 23. Depth of PCB front vs time.

Figure 24. Depth of water front vs time.

Task 2.2 Thermal Desorption Autosampler

Description

The ATD-400 interface is a separate component relative to the MSTM system. The thermal desorption autosampler (ATD) is located in a field or stationary analytical laboratory with a gas chromatograph away from the sampling location. When the sorbent tubes are ready for analysis, the magazine, loaded with samples on sorbent tubes, is sent to this laboratory. The interface automatically loads the tubes into the desorber with identity being referenced by position. The electronics consists of a pulsed sequential circuit which causes the ATD-400 carousel to rotate and dispense the sorbent tubes. Software and a serial interface are used to download the sampling data from the carousel memory to a local computer.

The electronics are contained in a control box powered by a separate 12-V supply. The control box has one momentary contact switch which starts the loading process. The control box interfaces with the ATD-400 to sense carousel position and to advance the carousel. This control box interfaces with EAI mechanical components to activate a solenoid valve for a pneumatic actuator to dispense one tube at a time. The control box also senses the last tube with an electro-optical interrupter to stop the cycle. The pneumatic actuator uses compressed air at 40–100 psi.

Interface to Thermal Desorption Autosampler

An analysis of the requirements for a successful ATD interface was performed. Several prerequisites were established to ensure commercial acceptance and success beyond the simple technical provisions to interface with the ATD. It was recognized that minimum modifications to the Perkin Elmer ATD-400 are highly desirable since this enhances the compatibility with currently fielded ATD units.

Because laboratory bench space is always a constrained resource, minimizing the amount of additional bench space required by the interface was also considered. An analysis of laboratory operations suggested the interface device have the capability to load all 50 tubes into the ATD unit carousel which takes maximum advantage of the ATD-400 capacity to analyze 50 sorbent tubes.

Interface Setup

To facilitate the installation of the ATD interface, the mechanism is designed to mount over the superstructure of the Perkin Elmer ATD-400. The electronic controls are housed in an enclosure which is fastened to the interface with disconnects for electronic communication. The interface was designed to allow it to easily move between ATD units. Its primary purpose is to unload the tubes from the MSTM magazine and load them into the ATD-400. Maximum estimated time for this operation on a 50-tube magazine is approximately 5 minutes. With analytical run times upwards of 60 minutes per tube, it is not economical to dedicate an interface to an individual ATD-400 unit.

Because a pneumatic power is used as one of the drive mechanisms for the ATD, the interface utilizes pneumatics to operate the escapement component of the interface. The pneumatic connection of the interface uses a quick connect to facilitate mounting and dismounting. A tee is placed in the air supply of the ATD unit with the male end valve body of the quick connector attached. The female end hose connector is linked to the ATD interface.

The Perkin Elmer ATD-400 is altered by the addition of "Y" cables to several of the internal electronic connections. These are terminated in a connector which couples the device to the ATD-400.

Escapement

The escapement allows a single sorbent tube to drop into the appropriate slot in the ATD unit carousel. The control is effected by the electronics. Power is provided by the pneumatics which interface with the electronics by means of a solenoid valve. When the electronics signal calls for a tube to drop, the solenoid valve is actuated. This in turn actuates the escapement cylinder which extends and releases a sorbent tube into the ATD unit carousel. The extended cylinder also holds back the remaining sorbent tubes, so that only a single tube is deposited in the carousel. When the signal is removed, the spring return cylinder retracts and permits another sorbent tube to drop into the loading position.

Chute

The chute is the rectangular shaped component located directly below the magazine and above the ATD carousel and escapement. The chute is open in the front to observe tubes exiting the magazine. The chute acts as a buffer to catch the tubes as they exit the magazine. The escapement device has a switch to sense when tubes are in the escapement. As long as tubes are detected in the escapement the MSTM magazine and ATD carousel will continue to index. Only when all the tubes are unloaded from the magazine and into the ATD carousel, will actual analytical analysis begin.

Electronic Interface

The electronic interface connects the ATD interface to the ATD-400 to orchestrate the transfer of tubes between the two. Through this device, the coordination between the interface and the ATD carousel is a one-for-one indexing of tubes—as one tube drops from the magazine and is accepted by the ATD-400 carousel both positions index forward one space.

This is accomplished through circuitry built into the ATD interface which drives (controls) the magazine and the escapement mechanism but is also wired to the controls of the ATD-400 carousel. In this manner, the circuitry takes over control of the ATD-400 carousel to load all the tubes from the magazine. Upon completion of this operation, control of the carousel is returned to the ATD unit.

Performance Testing of Modified Thermal Desorption Autosampler

Objective

The thermal desorption autosampler was tested to determine the performance when analyzing standard amounts of Aroclor 1254 that were loaded onto sorbent tubes.

Description of the Test Equipment and Experimental Setup

The Perkin Elmer thermal desorption autosampler was coupled to a Shimadzu GC14A gas chromatograph equipped with a FID detector. The thermal desorption instrument was re-plumbed so that it would operate in backflush mode. The backflush mode allows analytes to be focused on the adsorbent that is packed in the trap. With the backflush configuration, analytes enter and leave the same end of the cold trap, therefore higher boiling species are not forced through the entire bed of the trap during thermal desorption.

The desorption unit was run in a splitless mode. The GC used a 30-meter megabore column (0.53 mm ID by 1.5 μ m film thickness, DB5, J&W). Data was collected and analyzed with Class-VP, a Shimadzu data handling software package. Operational testing of the ATD interface was not included in this evaluation.

Test Procedures. Four concentrations of Aroclor 1254 —4.05, 10.86, 20.39 and 53.98 ppm— were prepared in hexane. A 100- μ l aliquot of each Aroclor solution was loaded onto a separate sorbent tube containing Carbotrap 370, the sorbent that was identified in Task 1.6. After loading, the sorbent tube was placed on the thermal desorption autosampler and processed through the desorption cycle. When the desorption cycle was completed, the trapped PCBs were purged onto a GC and analyzed with a FID detector. PCB concentrations were quantified by integrating the total area of the Aroclor 1254 in the resulting chromatograph. A minimum of two samples was run for each PCB concentration. To confirm that PCBs could be removed from the sorbent in a consistent and uniform manner, this procedure was repeated 4 days later.

Data Collection and Interpretation

The original plan was to compare the data collected with the amount of Aroclor 1254 originally loaded onto the sorbent tube. Since the thermal desorption unit is connected directly to the column, the instrument utilized in this task is not equipped with an injection port. Without the ability to bypass the desorption unit, the determination of the absolute efficiency of Aroclor 1254 removal from the sorbent has proven difficult.

Determination of the recovery efficiency was attempted by loading the corresponding amount of Aroclor 1254 into an empty sorbent tube and/or a sorbent tube containing glass wool. Comparison of the total Aroclor 1254 areas from these tubes with corresponding tubes containing Carbotrap 370 reveals that tubes containing no Carbotrap 370 trap show a significant loss of PCBs. At this time, it is unclear why the tubes without the sorbent are losing PCBs but the losses may be attributed to the instrument purge cycle.

When calibrating by this type of method, the amount of PCBs removed from the sorbent is not related to the analysis of trapped PCBs onto a sorbent. The most accurate and time-efficient manner to prepare a standard curve for this type of analysis would be to use the sorbent tubes as vessels for the addition of standards to calibrate the instrument. As long as the removal of PCBs from the sorbent is a constant defined percentage, the usage of the sorbent in the calibration procedure will provide a real-time control, compensating for any irreversible loss of PCBs to the Carbotrap 370.

Success of the Test

The data in Figure 25 show that the repeatability of the sampling technique is very good. Both runs show good linearity (correlation coefficient >0.98) and the reproducibility of the data in two separate runs is excellent. Figure 25 illustrates that the Aroclor 1254 is removed from the sorbent in a linear manner that is consistent, reproducible and independent of concentration (0 to 54 ppm). Figure 26 is a chromatogram from the 54-ppm Aroclor standard after thermal desorption. These results demonstrate the success of the thermal desorption autosampler in providing consistent, reproducible results when analyzing the Aroclor 1254 mixture of PCBs.

Figure 25. 1254 standards from a sorbent tube containing Carbotrap 370.

Figure 26. Chromatogram from 54-ppm Aroclor standard.

Task 2.3 Design and Thermal Testing of the Steel Sampler

Performance Requirements

A steel sampler head was constructed to sample PCBs, oils, and polyaromatic hydrocarbons on metal surfaces. The ultimate practical objective for this head is to sample an area of 1 cm² or somewhat larger areas on flat or moderately curved steel surfaces by heating those surfaces to a temperature near 250 °C for a few seconds, causing any semivolatile contaminants to be vaporized from the surface. The size constraint for the sampling area is imposed in part by the likelihood that some metal surfaces of interest will be slightly curved. Efficient collection of vaporized analytes by a flowing gas cannot be maintained by a general purpose sampler (i.e., one not designed to match the curvature of the surface) unless the curvature of the surface over the sampled area is relatively small. Another constraint to the sampling area is the large amount of energy required per unit area to heat the surface of a highly conducting sample.

As explained more fully in the Phase 1 Final Report, simple one-dimensional heat transfer can be used to estimate the rate at which thermal energy must be coupled into a surface to heat it from room temperature to a temperature near 250 °C. The surface temperature change as a function of time t is given to a good approximation by

$$T(t) = \frac{2P}{k} \left(\frac{\alpha t}{\pi} \right)^{1/2} \quad (1)$$

where P is the heat flux (in typical units of watts/cm²) absorbed at the surface, k is the thermal conductivity, and α is the thermal diffusivity, given by $k/C\rho$. Here C is the thermal capacity, and ρ is the density. Using this equation, one can calculate that only about 5 W/cm² must be coupled into a typical concrete surface to heat it to 250 °C in 60 sec. The depth of propagation of elevated temperatures into the material is given approximately by

$$D = \sqrt{\alpha t} \quad (2)$$

Because α is very small for concrete, the elevated temperature region will extend into the concrete only several millimeters after 60 sec of heating.

Although the more detailed concrete model described in this report provides a somewhat different picture, the simple calculation described above is sufficient for engineering design. This utility extends to metal surfaces, where the results are considerably different. A typical value for the room temperature thermal diffusivity of carbon steel is $\alpha = 0.1$ cm²/sec, while for stainless steel it is near 0.04 cm²/sec. These values reflect the much larger thermal conductivity values for metals, near 0.5 W/(cm °C) and 0.15 for stainless steel 304. As a result, much higher power densities must be coupled into a metal surface to heat it from room temperature to 250 °C in a reasonable time. For example, a coupled power density of 200 W/cm² is needed to heat the surface of a carbon steel sample 3 mm (or more) thick in 1 sec. The thicker sample will be heated to just about 3 mm deep in this 1-sec period.

A constraint on the time envelope of heating is imposed by the fact that in many cases it may be highly desirable to heat just the surface of the sample, since if the sample is heated substantially all the way through then underlying components (such as motor windings) may be damaged. Further, much more energy is required to heat a thick sample all the way through rather than to just heat the surface. Therefore heating times longer than a few seconds may not be tolerable.

These considerations indicate that an optimum metal sampler would heat the surface with short pulses, each less than a few seconds in duration. It is well known that any one of a number of laser types can provide this level of heating (and substantially more). However, we believe that the combination of cost, complexity of use, and safety considerations associated with each laser type are sufficient to make this choice impractical.

Selection of the Heating Method

First, for exposure times on the order of a second, one must consider a continuous wave (CW) laser with output power on the order of 1 kW even for 1 cm² sampling area (taking into account losses associated with transmission of the laser output to the surface and coupling losses at the surface). Such high-power lasers are large and heavy, cost well over \$50K, require 20 kW or more of input power and extensive safety precautions.

For an exposure time on the order of 1 msec, from equation 1, a laser pulse energy on the order of 40 J is required (again taking into account coupling and transmission). If this laser is implemented as a flashlamp-pumped Nd:YAG laser, it will cost near \$50K, and will present even more serious safety problems than the CW laser. Further, multiple pulses probably will be necessary to sample each area, because the surface will stay warm for only about twice as long as it takes to heat it.

Shortening the pulse further (as, for example, by Q-switching the laser to produce a pulse length on the order of 10⁻⁶ to 10⁻⁸ sec) is expensive. Although the pulse energy requirement is reduced in proportion to the square root of the pulse length, overall system costs remain at least the same, around \$50K or more. These costs are dropping over time, and eventually diode pumping may allow a cost effective and practical short-pulse system; however, we estimate that time to be 5 to 10 years in the future.

Accordingly, we investigated energy sources utilizing a short-pulse flashlamp. Use of a flashlamp rather than a flashlamp-pumped laser avoids the inefficiency of the laser in converting the incoherent flashlamp light into more-or-less coherent laser light. On the other hand, the flashlamp light is inefficiently coupled into an area as small as 1 cm² unless the lamp is also small. Examination of product availability revealed one product line that appeared to be marginally capable to heat a 1-cm² area of steel to 250 °C in 100 µsec. Unfortunately, the circuit element necessary to switch this lamp, a particular high-current thyatron, is no longer manufactured because of insufficient demand.

Finally, we investigated a continuous wave alternative which can produce 500 W of average light power in a small enough source to be efficiently transmitted and coupled into a 1-cm² area. This non-laser source avoids the high cost of coherent sources, and can be incorporated into a relatively convenient package. Two of these sources and a matched power supply were obtained and incorporated into a relatively convenient package that has delivered over 300 W of optical power.

Prototype Sampler Head

The prototype metal sampler head is designed in the form of a 5-cm-diameter by 5-cm-high heated cylinder connected to the optical power source and sampling system by flexible conduits. A detailed description of the construction details for the sampler has not been included in this report because patentability issues are being examined. A photograph of this sampler is shown in Figure 27.

Figure 27. Metal sampler head

Thermal Testing

This section describes the thermal tests conducted to evaluate the performance of the steel sampler head. The general protocol followed the procedure outlined in the contract test plan. Thin metal foils were mounted in a metal hollow square holder and heated by the metal sampler head. Transverse dimensions of the foil were 3 in by 3 in, with the peripheral 0.25 in held within the clamp. One side of each foil was coated with a high-temperature black paint to provide near unity emissivity for IR radiation temperature measurements, which reduced errors from nonunity emissivity to a calculated range less than $\pm 4^\circ\text{C}$. The infrared measurements were made using an Inframetrics IR imaging radiometer equivalent (for this purpose) to the AGEMA Model 870 instrument described in the test plan.

The foil thickness was increased from 4 mils (as stated in the test plan) to 10 mils to slow down the time response and reduce buckling. As required, three foil types were tested, including a standard structural steel, rusted steel, and stainless steel. Total irradiation time for each test was 1 min, since the source was continuous rather than the 1 msec pulsed source contemplated for the test plan. The thermal image of the plate was recorded on videotape continuously during heatup. Subsequent data analysis allowed determination of spatial and temporal temperature profiles of the plates.

Results

The temperature rise as a function of time for the rusted steel plate is shown in Figure 28.

Figure 28. Temperature at the center of the rusted steel plate as a function of time after the heating element was turned on.

The initial rate of rise of this data can be used to calculate the power density P coupled into the metal. First, the time constant over which the front and back surfaces of the metal foil should come to nearly the same temperature is given by

$$t_0 = Z^2 / \alpha \quad (3)$$

where Z is the foil thickness. For the steel foils, this works out to 5.9 msec, such that over a time scale on the order of 1 sec the front and back surfaces are at essentially the same temperature. The initial rate of temperature rise is given by

$$\frac{dT}{dt} = \frac{P}{ZC\rho} \quad (4)$$

From Figure 28 this rate is 80 °C/sec. From the known values of C , ρ and Z we calculate that the coupled power density is 8 W/cm². This value is well below the design level. Four factors are likely contributors to this low level:

1. The source is not shuttered at present. It must be turned on electrically to initiate the test, and some time is required (at least several seconds) before full power is reached.
2. There appears to be a fabrication flaw in the power coupler between the light source and the metal sampler head. The input to the coupler is overheating, and direct measurements of the coupling efficiency are lower than reasonable expectations by a factor of 2.5.
3. Because of the abovementioned overheating, it was necessary to run the source at 400 W input power, rather than its rated 1000 W input for these measurements. The output efficiency goes up with increased power, so this necessity may account for a factor of 3.5.
4. The surface coupling at the metal sampling head can be increased by a nominal factor 2.5 by improved design.

It is possible that these changes will increase the coupled power density up to the minimum practical level, which is at least 100 W/cm² or perhaps even to the desired level of 250 W/cm². It is clear that a task must be addressed in Phase 3 to accomplish this increase if the metal sampler head in its present form is to become part of the final system. Nevertheless, the power density delivered by the present design is sufficient to heat foils up to greater than 60 mils thick to 250 °C for analyte collection efficiency tests. Table 7 shows the average heating time for the temperature to reach 250 °C and the (near equilibrium) temperature after 1 min. The variation between multiple runs on the same-type foil is insignificant. The variation between the runs on different-type foils is consistent with the greater absorption of the rusted steel foil, compared with the unrusted steel foil, and the smaller thermal conductivity of stainless steel.

Table 7. Heating time for temperature to reach 250 °C and temperature at the end of 1 min heating for rusted steel, steel, and 301 stainless steel plates

	<i>Rusted steel</i>	<i>Steel</i>	<i>301 stainless steel</i>
Time to reach 250 °C (sec)	6.5	8.0	6.7 ± 0.4
Temperature after 1 min heating (°C)	355	295	375

In Figure 29 the spatial distribution of temperature on the rusted foil is shown at the time when the peak temperature reached 280 °C. The spatial extent within a range of 60 °C (± 30) is 0.66 cm², compared with a nominal irradiated area of 1 cm². (The actual primary irradiated area is slightly smaller, corresponding to the primary beam from the coupler with active diameter of 0.25 in, slightly expanded in the short distance from the coupler to the surface.) This distribution is reproducible on each foil and is close to meeting the success criterion of 250 °C ± 30 °C over 75% of the irradiated area specified for the test plan.

Figure 29. Temperature of the rusted steel plate with a maximum temperature of 280 °C as a function of distance from the center of the plate. The temperature of the plate is 250 $\pm$ 30 °C within a region 0.36 inch in diameter at the center of the plate.

Task 2.4 Steel Sampler Performance Testing

The purpose of this task is to test the utility of the steel sampler head using three types of steel specimens. These samples, containing known amounts of three model compounds, allowed sampling efficiency data to be obtained to ascertain the performance capabilities of the sampling head.

Experimental

Three different types of steel were evaluated with the steel sampling head—stainless steel, carbon steel, and rusted steel. Coupons of each material, 4 mil thick and 4 in long by 4 in wide, were cut from stock material. The rusted steel test coupons were prepared by wetting one side of a carbon steel coupon in water for approximately one day.

A standard test solution was prepared to contain 1.1 µg/µl of anthracene, 1.0 µg/µl 2,4,5-trichlorobiphenyl (2,4,5-TCB), and 1.4 µg/µl of phenyldodecane, the three model compounds which are being evaluated. Each test coupon was spiked with a known amount (15, 20, or 25 µl) of test solution and the solvent was allowed to evaporate prior to desorption with the steel sampling head. The test coupon was held in place under the steel sampling head by a holder fashioned out of 1/4-in. steel. The steel sampling head itself was heated to approximately 120 °C without the arc lamp being energized. The sampling head was positioned over the spiked area, turned on, and the surface of the test coupon was heated to temperatures sufficient to desorb the contaminants. A lamp power setting of 400 W was used. The arc lamp within the steel sampling head was energized for ~2–3 sec, as indicated in the results for each set of experiments. Previous temperature measurements were made on carbon steel and stainless steel coupons using a thermocouple spot welded on the back center of the coupons. These measurements produced peak centerline temperatures of ~239 °C ±3 °C and 280 °C ±10 °C for carbon steel irradiated for 2 and 3 sec, respectively. The back side of the stainless steel heated more quickly to temperatures of 330 °C ±6 °C and 508 °C ±9 °C in 2 and 3 sec, respectively. Based on these results, irradiation periods of 2 and 3 sec were selected since adequate desorption temperatures should be obtainable within that time period over the desired sampling area on these thin foils. Two packed thermal desorption tubes connected in series were mated to the exit port of the steel sampling head for each of the experiments. A vacuum pump downstream of the thermal desorption tubes drew air at the rate of 100 sccm. The vacuum pump facilitated the transfer of desorbed analytes from the steel surface to the adsorbent tube. Blanks were also run as part of the test series. A known amount of internal standard (10.4 µg of p-terphenyl) was added to each tube prior to thermal desorption in the Perkin Elmer ATD 400.

Results

Table 8 shows the recoveries of the model compounds from the carbon steel specimens after analysis of the thermal desorption tubes. As seen in the table, recoveries ranged from 71% to 93%. For each model compound and at each concentration, these recoveries exceeded the test plan objective of 60%. The average contaminant recovery for all carbon steel tests exceeded 82%. The average recoveries for anthracene, 2,4,5-trichlorobiphenyl, and phenyldodecane were 81%, 86%, and 80%, respectively.

Table 9 shows the initial recoveries of the model compounds from the stainless steel specimens after irradiation for 2 sec. Results are based on analysis of the thermal desorption tubes. As seen in the table, recoveries were less consistent than those obtained from the carbon steel specimens and ranged from 26% to 82%. The average recovery for all contaminants during these tests with

Table 8. Recovery of anthracene, 2,4,5-trichlorobiphenyl, and phenyldodecane from a 4-mil-thick carbon steel thermally desorbed by the steel sampling head (2 sec irradiation).

<i>Carbon steel test volume</i>	<i>Model compounds</i>	<i>Theoretical recovery (μg)</i>	<i>Measured recovery (μg)</i>	<i>Percent recovered</i>
15 μl test solution	anthracene	16.5	13	79
	2,4,5-TCB	15	13.9	93
	phenyldodecane	21	18.2	87
15 μl test solution	anthracene	16.5	15.3	93
	2,4,5-TCB	15	13.0	87
	phenyldodecane	21	17.4	83
20 μl test solution	anthracene	22	17.6	80
	2,4,5-TCB	20	17.9	90
	phenyldodecane	28	23.5	84
20 μl test solution	anthracene	22	16.3	74
	2,4,5-TCB	20	16.4	82
	phenyldodecane	28	20.6	74
25 μl test solution	anthracene	27.5	19.4	71
	2,4,5-TCB	25	20.6	82
	phenyldodecane	35	26.9	77
25 μl test solution	anthracene	27.5	24.0	87
	2,4,5-TCB	25	20.0	80
	phenyldodecane	35	27.0	77
blank	anthracene	0	0	0
	2,4,5-TCB	0	0	0
	phenyldodecane	0	0	0
blank	anthracene	0	1.4	—
	2,4,5-TCB	0	0	0
	phenyldodecane	0	0	0

2 sec of irradiation was 57%. The average recovery was slightly less than the test plan objective of 60%. The average recoveries for anthracene, 2,4,5- trichlorobiphenyl, and phenyldodecane were 57%, 61%, and 53%, respectively.

Table 10 shows the final recoveries of the model compounds from the stainless steel specimens after repeating the previous irradiation but extending the time to 3 sec. Results are based on analysis of the thermal desorption tubes. As seen in the table, recoveries were much better than those obtained from the initial experiments where stainless steel specimens were irradiated for 2 sec. For all but one set of experiments, which may be an anomaly, the recoveries ranged from 60% to 100%. The average recovery for all contaminants during these tests was 81% and exceeded the test plan objective of 60%. The average recoveries for anthracene, 2,4,5- trichlorobiphenyl, and phenyldodecane were 74%, 92%, and 77%, respectively.

Table 11 shows the initial recoveries of the model compounds from the rusted steel specimens after irradiation for 2 sec and subsequent analysis of the thermal desorption tubes. As the table

Table 9. Recovery of anthracene, 2,4,5-trichlorobiphenyl, and phenyldodecane from 4-mil-thick stainless steel thermally desorbed by the steel sampling head (2 sec irradiation).

<i>Stainless steel test volume</i>	<i>Model compounds</i>	<i>Theoretical recovery (μg)</i>	<i>Measured recovery (μg)</i>	<i>Percent recovered</i>
15 μl test solution	anthracene	16.5	8.6	52
	2,4,5-TCB	15	9.7	65
	phenyldodecane	21	12.3	59
15 μl test solution	anthracene	16.5		—
	2,4,5-TCB	15		—
	phenyldodecane	21		—
20 μl test solution	anthracene	22	9.3	42
	2,4,5-TCB	20	5.3	27
	phenyldodecane	28	7.4	26
20 μl test solution	anthracene	22	13.4	61
	2,4,5-TCB	20	16.4	82
	phenyldodecane	28	20.1	72
25 μl test solution	anthracene	27.5	17.9	65
	2,4,5-TCB	25	19.8	79
	phenyldodecane	35	20.8	59
25 μl test solution	anthracene	27.5	18.7	68
	2,4,5-TCB	25	12.5	50
	phenyldodecane	35	16.8	48
blank	anthracene	0	0	0
	2,4,5-TCB	0	0	0
	phenyldodecane	0	0	0
blank	anthracene	0	1.4	—
	2,4,5-TCB	0	0	0
	phenyldodecane	0	0	0

shows, recoveries were lower than those obtained from the carbon steel and stainless steel specimens and ranged from 5% to 68%. The average recoveries for anthracene, 2,4,5-trichlorobiphenyl, and phenyldodecane were 29%, 41%, and 24%, respectively. The average recovery for all contaminants during the 2-sec rusted steel tests was 31.2%. This average recovery was far below the test plan objective of 60%. Therefore, the experiments were repeated using longer irradiation times, pulsed irradiation, different power levels, and thicker specimens.

In the series of experiments designed to improve the recovery of analyte from a 4-mil-thick rusty steel coupon by increased irradiation time, the surface was irradiated with the steel sampling head for a period of 3, 4, and 5 sec (Table 12). The recovery of anthracene, 2,4,5-trichlorobiphenyl, and phenyldodecane ranged from 16% to >100% (probably the result of carryover from previous analyses). The average recovery was 38%, 73%, and 29% for anthracene, 2,4,5-trichlorobiphenyl, and phenyldodecane, respectively. The average recovery for all three analytes based on irradiation time was 28%, 46%, and 66% for the 3-, 4-, and 5-sec irradiation periods, respectively, indicating better recoveries of analytes at longer exposures and higher temperatures.

Table 10. Recovery of anthracene, 2,4,5-trichlorobiphenyl, and phenyldodecane from a 4-mil stainless steel surface thermally desorbed by the steel sampling head (3 sec irradiation).

<i>Stainless steel test volume</i>	<i>Model compounds</i>	<i>Theoretical recovery (μg)</i>	<i>Measured recovery (μg)</i>	<i>Percent recovered</i>
15 μl test solution	anthracene	16.5	13.6	82
	2,4,5-TCB	15	15.2	100
	phenyldodecane	21	19.7	94
15 μl test solution	anthracene	16.5	15.3	69
	2,4,5-TCB	15	17.4	87
	phenyldodecane	21	16.8	60
20 μl test solution	anthracene	22	15.9	72
	2,4,5-TCB	20	17.8	89
	phenyldodecane	28	21.9	78
20 μl test solution	anthracene	22	17.9	81
	2,4,5-TCB	20	20.6	100
	phenyldodecane	28	23.8	85
25 μl test solution	anthracene	27.5	18.7	68
	2,4,5-TCB	25	21.3	85
	phenyldodecane	35	23.7	68
25 μl test solution	anthracene	27.5	3.7	14
	2,4,5-TCB	25	0	0
	phenyldodecane	35	0	0
blank	anthracene	0	4	—
	2,4,5-TCB	0	7.8	—
	phenyldodecane	0	8.1	—
blank	anthracene	0	0	0
	2,4,5-TCB	0	0	0
	phenyldodecane	0	0	0

To evaluate the effect of pulsed irradiation on the recovery of analytes from rusty steel (4 mil thick), a known amount of test solution (15 μl) was placed on the surface of the rusty steel and the beam was pulsed on for five 1-sec intervals. The beam was off for 10 sec between intervals. The steel head was heated to 220 °C. The transfer line between the steel test coupon and the adsorbent tube was heated to 220 °C. The lamp power setting was 400 W. The amount of analyte that was recovered ranged from 55% to 81% (Table 13).

To evaluate the performance on sampling thicker specimens, 15 μl of test solution was placed on a 56-mil-thick carbon steel plate (no rust). The steel sampling head was heated to 220 °C. The transfer line was heated to 220 °C. A two-tube train was used for trapping. Air flow through the sorbent tubes was maintained at 100 ml/min. The beam, at a power setting of 400 W, was turned on for 1 min. During this time the temperature of the steel plate rose to 134 °C. The lamp power setting was increased to 800 W and maintained for 1 min. During this time the steel plate temperature rose to 220 °C. The steel plate was kept at 220 °C for 2 min. As shown in Table 14, the amount of analyte that was transferred from the steel surface to the sorbent tube, aided by the vacuum system, ranged from 46% to 79%.

Table 11. Recovery of anthracene, 2,4,5-trichlorobiphenyl, and phenyldodecane from a 4-mil rusted steel surfaces thermally desorbed by the steel sampling head (2 sec irradiation).

<i>Rusted steel test volumes</i>	<i>Model compounds</i>	<i>Theoretical recovery (μg)</i>	<i>Measured recovery (μg)</i>	<i>Percent recovered</i>
15 μl test solution	anthracene	16.5	6.0	36
	2,4,5-TCB	15	6.8	45
	phenyldodecane	21	6.4	30
15 μl test solution	anthracene	16.5	7.3	44
	2,4,5-TCB	15	10.2	68
	phenyldodecane	21	9.7	46
20 μl test solution	anthracene	22	5.5	25
	2,4,5-TCB	20	6.4	32
	phenyldodecane	28	4.6	16
20 μl test solution	anthracene	22	7.7	35
	2,4,5-TCB	20	9.9	50
	phenyldodecane	28	6.6	24
25 μl test solution	anthracene	27.5	6.8	25
	2,4,5-TCB	25	9.3	37
	phenyldodecane	35	7.9	23
25 μl test solution	anthracene	27.5	2.1	7.6
	2,4,5-TCB	25	3.3	13
	phenyldodecane	35	1.8	5
blank	anthracene	0	0	0
	2,4,5-TCB	0	0	0
	phenyldodecane	0	0	0
blank	anthracene	0		
	2,4,5-TCB	0	0	0
	phenyldodecane	0	0	0

Table 12. Recovery of anthracene, 2,4,5-trichlorobiphenyl, and phenyldodecane from a 4-mil rusted steel surface thermally desorbed by the steel sampling head for a period of 3, 4, or 5 sec.

<i>Analyte</i>	<i>Irradiation time (sec)</i>	<i>Theoretical recovery (μg)</i>	<i>Measured recovery (μg)</i>	<i>Percent recovered</i>
anthracene	3	16.5	3.2	19
2,4,5-TCB	3	15	7.2	48
phenyldodecane	3	21	3.4	16
anthracene	4	16.5	6.0	36
2,4,5-TCB	4	15	10.7	71
phenyldodecane	4	21	6.7	32
anthracene	5	16.5	9.5	58
2,4,5-TCB	5	15	17.8	>100
phenyldodecane	5	21	8.2	39

Another experiment was conducted in which a 56-mil-thick carbon steel plate (no rust) was irradiated with the steel sampling head for 1 and 2 min with the lamp power setting at 800 W. As shown in Table 15, the recoveries of analyte ranged from 48% to 83% for the 1-min exposure and the recoveries ranged from 51% to 84% for the 2-min exposure.

Table 13. Recovery of anthracene, 2,4,5-trichlorobiphenyl, and phenyldodecane from a 4-mil rusted steel surface thermally desorbed by the steel sampling head by pulsing irradiation for five 1-sec intervals.

<i>Analyte</i>	<i>Theoretical recovery (μg)</i>	<i>Measured recovery (μg)</i>	<i>Percent recovered</i>
anthracene	16.5	10.4	63
2,4,5-TCB	15	12.2	81
phenyldodecane	21	11.5	55

Table 14. Recovery of anthracene, 2,4,5-trichlorobiphenyl, and phenyldodecane from a 56-mil steel surface thermally desorbed by the steel sampling head by irradiating for 1 min at a power setting of 400 W and increasing power to 800 W for an additional 1 min.

<i>Analyte</i>	<i>Theoretical recovery (μg)</i>	<i>Measured recovery (μg)</i>	<i>Percent recovered</i>
anthracene	16.5	7.6	46
2,4,5-TCB	15	11.9	79
phenyldodecane	21	12.9	61

Table 15. Recovery of anthracene, 2,4,5-trichlorobiphenyl, and phenyldodecane from a 56-mil steel surface thermally desorbed by the steel sampling head by irradiating for 2 min at a power setting of 800 W.

<i>Analyte</i>	<i>Irradiation time (min)</i>	<i>Theoretical recovery (μg)</i>	<i>Measured recovery (μg)</i>	<i>Percent recovered</i>
anthracene	1	16.5	7.9	48
2,4,5-TCB	1	15	12.4	83
phenyldodecane	1	21	15.3	73
anthracene	2	16.5	9.9	60
2,4,5-TCB	2	15	12.6	84
phenyldodecane	2	21	10.7	51

Discussion

Heating of the thin (4 mil) steel coupons specified in the test plan was almost instantaneous with the amount of radiant energy imparted by the steel sampling head raising temperatures to the desired region within two to three seconds. Because of the rapid heating rate for these thin specimens and challenges associated with the measurement of surface temperatures, it was difficult to estimate the precise sampling temperature upon completion of irradiation. However, based on thermocouple measurements from the back side of the steel coupons and previous infrared spectrometry, it is likely that temperatures were on the order of 250 °C to 300 °C for the carbon steel and higher for the stainless steel specimens upon sample completion. Thicker (up to 1/8 in) steel coupons required more time to heat the compounds to sufficient desorption temperatures and provided more uniform temperatures which would make it easier to control sampling temperatures to 250 °C $\pm$ 30 °C. In experiments with 1/4-inch steel coupons we have found that the thicker steel foils only heat to approximately 150 °C with the current lamp configuration and power setting. Since only approximately 20% of the lamp power was actually transmitted to the surface of the test coupon, a more efficient system for delivering the power density of the lamp to the steel coupon will be included in recommendations for Phase 3. This will allow heating of these thicker specimens to a temperature of approximately 250 °C.

The first tube of the two-tube train was efficient at trapping the analytes that were desorbed from the steel test coupons. Analysis of the second tube from selected experiments revealed that the test compounds had been trapped sufficiently by the first tube in the train.

Results from the performance testing of the steel sampler head for sampling of carbon steel and stainless steel surfaces indicates acceptable recoveries of contaminants. The recovery of 2,4,5-trichlorobiphenyl appears to be uniform at around 80% in these latter experiments with 4-mil-thick rusty steel and 56-mil-thick carbon steel. There is more scatter in the recovery of anthracene. Of the three surrogate compounds, the 2,4,5-trichlorobiphenyl congener appears to be the easiest to recover.

Some of the difficulties seen with the recovery of analytes from rusted steel may be attributed to the diffusion of the test solution over a larger surface area on the rusted specimen. Test solutions dropped onto stainless steel or carbon steel diffuse into a smaller area. This may be because the effect of surface tension is less on a rusty surface than on stainless steel or carbon steel. Another plausible explanation for poorer recoveries on rusted steel is that rust has more oxygen and water adsorbed to it than stainless steel or carbon steel. Upon heating the water evaporates and these gases expand. If the rate of expansion is much greater than the rate at which the pump is operating, then there is the possibility of overpressure and the release of analytes out of the steel sampling area.

Task 2.5 Integrated Laboratory System

The purpose of this task is to test the integrated laboratory system, consisting of the concrete and/or steel sampler head coupled through the quick-look detector to the multisample trapping module. Sorbent tubes are then transferred to the thermal desorption autosampler and are analyzed by gas chromatography (electron capture). Because the water vapor evolved from concrete interfered with some of the analyses, several of the integrated laboratory tests were performed using the steel sampler head instead of the concrete sampler as originally planned.

Testing with the Concrete Sampler Head

Preparation of Concrete Slabs

Concrete slabs, 8 inches in diameter, were prepared from a commercial concrete mix which was mixed with water according to the manufacturer's specifications and poured into aluminum molds. The prepared slabs ranged from 0.5 to 1 inch in thickness. The slabs were allowed to cure for at least 30 days prior to use. The surfaces of the slabs were kept moist by misting with deionized water for the first week.

Experimental Setup

The inlet side of the photoionization detector (HNU model PI 52-02A) was mated to the concrete sampler head via 8 in of 1/8-in OD stainless steel tubing. The outlet side of the photoionization detector (PID) was connected using 18 in of 1/8-in stainless steel tubing to a male pipe fitting that had been drilled to accommodate a 10/32 luer needle holder. An 18-gauge by 0.75-in needle was used to introduce the sample onto sorbent tubes. All the transfer lines were wrapped with a cable heater and Fiberfrax insulation. The cable heater was controlled with a temperature controller (Omega) via a J-type thermocouple. A second thermocouple was installed for readout purposes. The transfer lines between the concrete sampler head and the PID were heated to 250 °C. The concrete sampler head was heated to 200 °C. The output signal of the PID was recorded on a Hewlett Packard integrator (HP 3396A).

Two sorbent tubes were connected with a 1/4-in Swagelok union using graphite/polyimide ferrules (Vespel). The inlet and outlet of the tubes were fitted with the septum caps designed by EAI. Due to difficulties encountered with earlier testing of the MSTM, the magazine and the needle assembly were bypassed. The vacuum pump and solenoid valves of the MSTM were connected to the exit side of the second sorbent tube. A glass trap was installed after the second sorbent tube to prevent water from reaching the vacuum pump and solenoid valves. In addition, a calcium sulfate (CaSO_4 with indicator) drying column was installed to prevent water vapor from reaching the solenoid valve.

For each desorption experiment a known amount of three-component test solution was prepared. The three-component test solution contained 1.1 $\mu\text{g}/\mu\text{l}$ of anthracene, 1.0 $\mu\text{g}/\mu\text{l}$ of 2,4,5-trichlorobiphenyl, and 1.4 $\mu\text{g}/\mu\text{l}$ of phenyldodecane. The concentration of the Aroclor test solution was 54 ppm. Runs were conducted with 100 μl of a 54-ppm Aroclor 1254 solution or with 15, 20 or 30 μl of the three-component test solution. The surfaces of uncontaminated concrete specimens were spiked with test compounds and the solvent was allowed to evaporate, leaving the model contaminants on the concrete surface. During Phase 1 of this study, contaminated concrete specimens were prepared and tested with the concrete sampler head and the near-vacuum UV detector. Recovery of the test compounds was within a factor of two of the expected results. It was surmised that the recoveries were lower than the theoretical amounts because of chemical conversion of the analytes in the concrete matrix or because of volatilization. Therefore, during Phase 2

testing on concrete, clean specimens were spiked rather than premixing concrete with contaminants prior to drying to eliminate the uncertainties about recovery.

The spiked region was chosen so that it would fall within the window of the concrete sampler head. Air flow (100 ml/min) was established through the sorbent tubes and allowed to reach equilibrium. The concrete specimen was lifted into contact with the sampler head with the aid of a lab jack. The lamp was turned on (6 A) for 2 to 5 min. At the end of the sampling period, the cake was lowered and the sorbent tubes were removed. The lamp of the concrete sampler head was turned on (6 A) for 2 to 5 min. Total air flow through the sorbent tubes ranged from 200 to 500 ml. The sorbent tubes were analyzed in the ATD 400 using the method described previously.

Results from Concrete Sampling

During preparation of equipment prior to performance testing, difficulties were encountered with the concrete sampler head that necessitated the replacement of the lamp contacts. The lamp contacts contain a spring that loses its elasticity with the high heat that it experiences during sampling sequences. We recommend that a ceramic insulator be used in this region to shield the lamp contacts from high heat.

Problems were also encountered with the concrete sampler head mated to the PID. The PID was not capable of handling the large volume of water vapor that is evolved when sampling concrete. During the desorption of the three-component test solution and the Aroclor solution from concrete there was little or no output signal from the PID, yet the PID responded properly to volatile organic compounds released in the absence of concrete.

The performance of the PID in the presence of concrete was checked by desorbing 20 μ l each of more volatile organic chemicals, including toluene (bp 110 °C), anisole (bp 154 °C) and dodecane (bp 215 °C) from a concrete cake. The concrete cake was predried with the lamp of the concrete sampler head. No output signal was seen from the PID; however, three peaks corresponding to toluene, anisole and dodecane were seen in the chromatograms. Recovery of each of the analytes was good (>75%), indicating that there were no leaks in the system. Sorbent tube #1 of the two-tube train indicated that it had trapped a trace amount of toluene, a large amount of anisole and dodecane. Tube #2 showed a larger amount of toluene and anisole. No dodecane was observed. We surmise that the water vapor carried the lower boiling, more polar toluene and anisole into the second sorbent tube.

The response of the PID was examined in several additional experiments to confirm that the presence of water vapor generated from the water present within the concrete matrix was the source of the problem with the PID. In one experiment a known amount of the three-component test solution was placed on an aluminum pan and desorbed with the concrete sampler head. An output signal of three unresolved peaks was observed on the integrator. In another experiment the same amount of test solution was placed on an aluminum pan. The aluminum pan was placed on a concrete cake and desorbed. No output signal was observed on the integrator. This indicates that the HNU photoionization detector is not able to operate in the moist environments that may exist when sampling concrete.

Discussion of Concrete Sampling

There are several ideas to explain the lack of signal in the presence of water vapor. The ionized molecule generated by the PID may be absorbed by the water vapor before reaching the detector, or the water vapor may prevent the ionization of the test compounds. Our recommendations for sampling concrete surfaces would be to use the near-vacuum ultraviolet light (NVUV) detector as the quick-look method for examining material given off by contaminated concrete. In Phase 1 of this study the concrete sampler head was mated to the NVUV detector. This detector produced

very reliable and reproducible data over a period of 1 to 3 min in desorption trials. We recommend that further work with this detector be pursued in Phase 3 of this study. A miniaturized and field-rugged NVUV detector could be designed and built by an experienced vendor.

A two-tube train was employed to handle the large volume of water that is evolved when concrete surfaces are heated. The latent heat of vaporization of water was sufficient to warm the first sorbent tube so that it was too hot to touch. Experience in Phase 1 of this study taught us that a two-tube train may be necessary to handle the large volumes of water that is present in concrete and to ensure that analytes are trapped by the second sorbent tube, since sorbents become inefficient at trapping when they become hot. Steam is also a good medium for distilling analytes and may actually enhance the removal of analytes from a concrete surface but its latent heat will decrease the efficiency of the sorbent.

Due to difficulties encountered with earlier testing, the magazine and the needle assembly of the MSTM were bypassed for this evaluation. However, the needle and cap design that EAI has designed and manufactured were included in the testing and meet the intent of the evaluation.

During field use, consideration should be given to using a carbon column to trap any organics that may escape the sorbent tubes and a drying column to trap water vapor that may evolve from concrete before reaching the solenoid valve and vacuum pump.

Testing with the Steel Sampler Head

Experimental Setup

Three different test solutions were desorbed with the steel sampler head: a mixture of anthracene, 2,4,5-trichlorobiphenyl, and phenyldodecane, Aroclor 1254, and a 46-component base-neutral test mixture (Table 16).

The base-neutral test solution was purchased from Accustandard and used as received. The Aroclor 1254 solution was prepared in hexane from concentrated Aroclor 1254. The three-component test solution was prepared from anthracene, 2,4,5-trichlorobiphenyl, and phenyldodecane.

During laboratory trials where the steel sampler head was mated to the photoionization detector, two integrated circuits found on two separate controllers of the PID failed. Failure was attributed to induced electrical noise in these circuits. The initial startup voltage of the steel sampler head is 30 kV. During the startup there appeared to be leakage of the voltage to the controllers of the PIDs. Due to

Table 16. Components of base-neutral test mixture

Base-neutral mixture: 2.0 mg/ml in benzene:CH₂Cl₂:AcCN (2:2:1)

acenaphthene	3,3-dichlorobenzidine
acenaphthylene	diethyl phthalate
anthracene	dimethyl phthalate
azobenzene	2,4-dinitrotoluene
benz(a)anthracene	2,6-dinitrotoluene
benzidine	di-n-octyl-phthalate
benzo(b)fluoranthene	bis (2-ethylhexyl)phthalate
benzo(k)fluoranthene	fluoroanthene
benzo(ghi)perylene	fluorene
benzo(a)pyrene	hexachlorobenzene
4-bromophenyl phenyl ether	hexachlorobutadiene
butyl benzyl phthalate	hexachlorocyclopentadiene
bis (2-chloroethoxy) methane	hexachloroethane
bis (2-chloroethyl) ether	indeno(1,2,3-od)pyrene
bis (2-chloroisopropyl) ether	isophorone
2-chloronaphthalene	naphthalene
4-chlorophenyl phenyl ether	nitrobenzene
chrysene	n-nitrosodimethylamine
dibenz (a,h)anthracene	n-nitrosodiphenylamine
di-n-butyl phthalate	n-nitrosodi-n-propylamine
1,2- dichlorobenzene	phenanthrene
1,3- dichlorobenzene	pyrene
1,4- dichlorobenzene	1,2,4-trichlorobenzene

time constraints, design and implementation of the proper shields for electrical interference was not undertaken. Therefore, the PID was not used in the desorption studies of the integrated system with the steel sampler head.

Base-Neutral Compound Testing

Desorption of Base-Neutral Test Solution

For these trials the steel sampler head was preheated to 220 °C. The stainless steel (1/8-in OD) transfer line between the outlet side of the steel sampler head and the sorbent tubes was heated to 230 °C. Two sorbent tubes were joined by a Swagelok union downstream of the heated transfer line. Carbon steel (56 mils thick) or stainless steel (58 mils thick) were used for the desorption of the test solution. Air flow through the sorbent tubes was set at 100 ml/min.

A known amount (6, 8, or 10 µl) of base-neutral test solution was spiked onto the steel surface just prior to desorption and the solvent was allowed to evaporate. The steel sampler head was brought into contact with the steel surface. The lamp was ignited for 2 min. The steel sampler head was allowed to remain on the surface of the test coupon for 2 min beyond the time that the lamp was lit, for a total of 4 min. The tests were conducted in duplicate with three different concentrations of test solution. At the end of the sampling period, the sorbent tubes were changed. The steel specimen was cleaned with methylene chloride, toluene and acetone. A stain remained on the steel after the solvent cleanup. The stain was removed with a stainless steel brush attached to a Dremel tool. For the analysis of the tubes, standards were prepared by syringing known amounts (2, 4, 6, or 10 µl) of base-neutral test mix into thermal desorption tubes. The area counts of the tubes from the sampling trials were compared with the area counts of the standards and interpreted. The conditions for the primary thermal desorption step were 310 °C for 30 min. The cold trap was maintained at 4 °C during the primary desorption step. The conditions for the secondary desorption were 310 °C for 30 min. The ATD 400 was operated in split mode with a 100:1 split.

Results from the Desorption of Base-Neutral Mixture with the Steel Sampler Head

The recoveries for the carbon steel trials are shown in Table 17 and in Table 18 for the stainless steel trials.

Mixed results were obtained from the desorption of base-neutral compounds from carbon steel and stainless steel. Recoveries ranged from less than 33% to greater than 100% for both the carbon steel and the stainless steel. The chromatograms for these compounds indicated high resolution as shown by the sample chromatogram in Figure 30.

Table 17. Recovery of base-neutral test compounds (2 mg/ml or 2 µg/µl) from 56-mil-thick carbon steel with the steel sampler head

<i>Base-neutral solution spiked onto steel (µl)</i>	<i>Base-neutral mix (µg)</i>	<i>Flow rate after 4 min</i>	<i>Amount recovered (µg)</i>	<i>Percent recovered</i>
6	12	88	<4	<33
6	12	82	<4	<33
8	16	92	<4	<33
8	16	91	17.7	>100
10	20	83	17	85
10	20	62	19.8	99

Table 18. Recovery of base-neutral test compounds (2 mg/ml or 2 µg/µl) from 58-mil-thick stainless steel with the steel sampler head.

<i>Base-neutral solution (µl)</i>	<i>Base-neutral mix (µg)</i>	<i>Flow rate after 4 min</i>	<i>Amount recovered (µg)</i>	<i>Percent recovered</i>
6	12	72	6.7	56
6	12	69	11.1	93
8	16	77	<4	<33
8	16	49	>20	>100
10	2	68	12.8	64
10	20	70	>20	>100

Figure 30. Sample chromatogram of base-neutral mixture after thermal desorption .

Discussion of Testing the Base-Neutral Mixture with the Steel Sampler Head

The desorption of the base-neutral test mix was complicated by the variable volatility and reactivity of the 46 compounds. The high boiling nature of these materials suggests that an optimized steel sampler head may be necessary for complete desorption of these materials from a steel surface. The fact that the solution stains the steel surface and requires buffing suggest that some type of bonding may be occurring between the polynuclear aromatic compounds and the metal surface. The N-nitrosodimethylamine, N-nitrosodiphenylamine and N-nitrosodi-n-propylamine may have reacted with the hot steel to form a stable iron-nitrogen compound. Azobenzenes are susceptible to reduction by iron. The significant drop in the observed flow rate from 100 sccm to as low as 40 sccm suggests that some physical process may have occurred.

Aroclor 1254 Testing

Desorption of Aroclor 1254 from 58 mil thick stainless steel

For these trials 35, 50 or 100 μ l of a 54-ppm Aroclor 1254 solution was pipetted with a positive displacement pipettor onto the surface of 58-mil-thick stainless steel and the solvent was allowed to evaporate. The spotted area was kept to 1 cm². The steel sampler head was heated to 220 °C, the transfer line was heated to 235 °C. Two adsorbent tubes were connected in series at the end of the transfer line. Air flow through the tubes was 100 ml/min. The steel sampler head beam was kept on for 2 min at a power setting of 400 W. A thermocouple welded to the bottom side of the steel test coupon was used to monitor temperature.

A 100- μ l aliquot of each Aroclor 1254 standards was syringed into packed thermal desorption tubes. The concentration of the standard solutions used was 4.05, 10.9, 20.4, and 54 ppm. A calibration line with $r = 0.99938$ was generated from the area counts recorded from the flame ionization detector. This calibration line was used to quantify the amount of Aroclor 1254 that was trapped in the desorption experiments.

Results from Desorption of Aroclor 1254 Using the Steel Sampler Head

The results from analysis of sorbent tubes obtained in the Aroclor 1254 experiments on stainless steel are reported in Table 19. By using 58-mil-thick stainless steel it was possible to heat the coupon to 247 °C with the steel sampler head. These temperatures are sufficient to desorb Aroclor 1254. The recoveries ranged from 64% to greater than 100%. Although some of the recoveries fall short of the 70% outlined in the test plan, use of the steel sampler head is generally a viable method for desorption of Aroclor 1254 from steel surfaces. However, the variability in the recoveries casts doubt on the capability to accurately quantify the surface contamination levels. Some of the inconsistencies illustrate the statistical variability and inherent difficulties encountered when working at low concentrations. Due to time constraints the experiments were not repeated.

Table 19. Recovery of Aroclor 1254 from 58-mil-thick stainless steel by desorption with the steel sampler head

<i>Test solution (54 ppm) spiked onto steel (μl)</i>	<i>Aroclor concentration spiked onto steel</i>	<i>Aroclor recovered by thermal desorption (ppm)</i>	<i>Percent recovered</i>
35	18.89	35	>100
35	18.89	12	64
50	26.99	27	100
50	26.99	31	>100
100	53.98	36	66
100	53.98		

The results from analysis of sorbent tubes obtained in the Aroclor 1254 experiments on carbon steel were similar to the results obtained on stainless steel and are reported in Table 20. The recoveries ranged from 48% to greater than 100% and were quite variable. Due to time constraints the experiments were not repeated. The reason for the four recoveries in excess of 100% has not been determined.

Table 20. Desorption of Aroclor 1254 from 56-mil-thick carbon steel

<i>Test solution (54 ppm) spiked onto steel (μl)</i>	<i>Aroclor concentration spiked onto steel</i>	<i>Aroclor recovered by thermal desorption (ppm)</i>	<i>Percent recovered</i>
35	18.89	21.9	>100
35	18.89	35	>100
50	26.99	55	>100
50	26.99	31	>100
100	53.98	26	48
100	53.98	43	80

Testing of the Three-Component Solution Using the Steel Sampler Head

Test results from testing of the three-component (anthracene, 2,4,5-trichlorobiphenyl, and phenyl-dodecane) solution were lost when the flame on the gas chromatograph-flame ionization detector (GC-FID) detector was extinguished.

A sample chromatogram from the analysis of the three component solution after thermal desorption is shown in Figure 31. Results show the high resolution and discrete peaks which can be used to identify and quantify the model compounds.

Discussion of Integrated Laboratory System Testing Results

Results from performance testing of the integrated laboratory system illustrate the complexities of system integration when utilizing a variety of sampling devices and coupling them with quick-look detectors, sorbent samplers, and analytical instrumentation. At each step of the process, a component failure can result in loss of analytical data. Although each problem by itself may be readily resolvable, a number of these issues still must be overcome in developing a reliable field portable system.

Figure 31. Sample chromatogram from analysis of the three-component (anthracene, 2,4,5-trichlorobiphenyl, and phenyldodecane) solution.

When using thermal sampling for a wide variety of semivolatile hydrocarbons, the inherent variability in sampling efficiency for each of the compounds is amplified through the use of a multi-component system. Although the thermal sampling method is effective at desorbing semivolatile components from a surface, it is difficult to obtain consistent, reliable, quantifiable results for a wide range of contaminants. Therefore, based on the results to date from these experiments, we recommend the following for consideration in Phase 3:

- Focus efforts to optimize system performance on a class of contaminants (such as PCBs or semivolatile hydrocarbons).
- Streamline the sampling system and ensure that all parts in contact with contaminants are sufficiently heated to prevent condensation of the contaminants of interest.
- Consider integrating the steel and concrete sampler into a single unit capable of sampling either type of surface.
- If a photoionization detector is desired for quick-look applications, explore the use of field portable units and ensure that the units can function in the presence of large amounts of water vapor.
- Utilize two fully loaded sorbent tubes when collecting samples with large amounts of water vapor present.
- Increase the purging of the sorbent tube in the thermal desorption autosampler to minimize the potential for carryover of water which could extinguish the flame in a GC-FID.
- Ensure that the quick-look detectors are properly shielded to minimize the potential for induced electrical noise.
- Explore the development of a field portable near-vacuum ultraviolet detector for quick-look applications when sampling surfaces with the likelihood of generating large amounts of water vapor (such as concrete).

Note: Task 2.6 was deleted from Phase 2

Task 2.7 Preliminary Design of Portable System

Figure 32. Integrated RSSAR sampling system.

Figure 32 is a preliminary design of an integrated RSSAR system. Many factors were considered in this preliminary design with others yet to be incorporated. Transitioning the MSTM and other components from a “breadboard” design must consider a number of factors, which are discussed in the following sections.

RSSAR Platform

Because the RSSAR system is to operate primarily as a field sampling device, a number of factors must be considered relative to the RSSAR platform. First and foremost is system mobility. Currently, the subcomponents of the RSSAR (MSTM, quick-look detector etc.) are too heavy to consider one-person portability as a viable option. In addition, “shore” power (110 Vac) is also a requirement. The prospect of carrying a device in the proposed sampling environments immediately raised issues of operator safety.

As a result, the most attractive alternative was to integrate the components into of a cart or wagon-like platform. This design has the advantage of providing a platform that can accommodate fairly heavy weight requirements as well as provide a large degree of mobility. The design above includes large diameter pneumatic tires to facilitate movement over rough terrain—operations on a smooth surface such as concrete or pavement cannot be assumed.

An additional advantage of the cart platform is that it allows compartmentalizing the subcomponents of the RSSAR. This can provide advantages to service and maintenance on the system as the subcomponents can be modularized for fast and simple component removal and replacement.

A final advantage of this design is the system provides its own working surface. Space is available for operators to store floor plans, maps, additional sampler heads and magazines, and provide space on which the operators can write.

MSTM Placement

The MSTM will be integrated into the RSSAR platform for optimal ergonomic use. The major factor affecting the placement of the MSTM in the RSSAR is the ability to install and remove magazines. Logic dictates that access to the MSTM be either on the front or top of the unit to facilitate the operation. Additionally, the MSTM should be located such that the entire MSTM component can be removed or that service to the unit can be accomplished with minimal disassembly of the RSSAR.

Quick-Look Placement

The quick-look detector is positioned on top of the RSSAR chassis for a number of reasons:

- The operator can easily observe if the detector is on and operating correctly.
- Operator maintenance can be accomplished more easily in this position than if it was located internal to the system.
- The position facilitates changing lamps in the detector, which allows the operator to choose selectivity toward certain target compounds

The power supply and associated controller for the detector will be located internal to the platform.

Sample Head Placement

The sample head(s) will be connected to the MSTM via a length of heated transfer line. Because the RSSAR has three different head configurations, the system will have the ability to store two heads while one is attached to the transfer line. Quick disconnects to facilitate changing heads will be investigated. Otherwise, mechanical assist devices will be considered to minimize any potential fatigue factor that might result from the weight of the sample head and transfer line or from long-term sampling operations.

Laptop Computer

We are still developing the level of interface required between the operator and the RSSAR, which we would like to minimize as much as possible. Given the amount of interfacing required, a tactile keypad up to a laptop computer may be necessary. The design above shows a laptop computer, which represents the highest potential interfacing requirement. Carrying a laptop, while slightly heavier and requiring some degree of training, has the added benefits of flexibility provided by the numerous personal computer applications available today. On the negative side, the personal protective gear the operator of the RSSAR will have to wear during operation is unclear. For example, if a full face respirator and heavy butyl rubber gloves are required, the use of a computer is not as viable, and the interface will have to be simplified—large buttons, oversize displays, etc.

Power Supply/Distribution

As mentioned earlier, the MSTM requires 5 and 12 Vdc, which is provided by two step-down transformers located inside the unit. The primary voltage for the MSTM is 110 Vac. The quick-look detector also uses 110 Vac, which may or may not be stepped down through its own power supply/control unit located within the RSSAR chassis.

The sampling heads themselves also require power. The power requirements for these devices are currently under investigation but as a minimum will require 110 Vac. Finally, the laptop computer will have the option of operating using either internal RSSAR power or internal computer battery power. Internal RSSAR power will provide 110 Vac, which can be used by the computer's power supply. Internal computer battery power will be an organic capability of the computer but the operational performance period will be dictated by the life time (charge) of the battery.

Because of the cart design of the system, battery backup or battery-only operations are future possibilities. The cart can accommodate the space required to store the batteries as well as the capacity to absorb the increased weight requirement for such a configuration.

Automated Position Acquisition

A significant aspect of sample data relative to the operation and mission of the RSSAR is the location from which the sample was taken. Because the design philosophy of the RSSAR has been to minimize operator interfacing to the system as much as possible, automated methods to determine sample location need to be evaluated.

The difficulty in determining sample location for the RSSAR is that samples are taken in three-dimensional space. For example, a sample taken from an outside wall has three components of information that fix the point in space—the X and Y coordinates relative to the surface of the earth can be described in longitude and latitude, but there is also the position in the Z direction, which describes the height off the "ground" at which the sample was taken.

Devices such as global positioning systems (GPS) and ultrasonic (electronic) tape measures can be automated to provide the X and Y component. The Z component can be provided by automatically measuring the angle of inclination and distance the sample head is from the RSSAR unit. From these two pieces of information, height on a wall can be calculated. Automated collection of sample position will be addressed in Phase 3 of the development project.

Quick-Look Detector Selection

Evaluation of Commercially Available Systems

One task in the in Phase 2 development of the RSSAR system was the evaluation of commercially available detector systems and the selection of a detector technology and/or system that is most suitable for the system. Overall factors for consideration include the RSSAR mission and requirements already defined for the RSSAR system. Specific considerations for the quick-look detector are discussed below.

Detector Evaluation Criteria

All detectors are certainly not equivalent. Each has advantages and disadvantages, strengths and weaknesses for any given application. No one detector is universally superior to another because the specific detector use determines which technology is most applicable. The following paragraphs describe the characteristics that must be evaluated when determining the most appropriate detector for the RSSAR system.

Sensitivity. Sensitivity is a measure of the minimal amount of material entering the detector for which the detector can register a positive response. The minimal level at which the detector must register a positive response in the RSSAR system is 10 µg contaminants per minute in a gas stream flowing at 2 standard cubic feet per hour (scfh). Any detector system that cannot meet this requirement may be eliminated from consideration. By gas chromatography standards, the quantity to be detected is achievable. The ideal quick-look detector will have adequate sensitivity for the target compounds.

Selectivity. Selectivity refers to the types or classes of compounds to which a detector will register a response in the presence of other compounds of noninterest. Some detectors are universally selective, meaning they are not selective at all but will respond to any compound that passes through them. Other detectors respond to specific elements or functionalities in a compound (nitrogen-phosphorous, flame photometric, and electron capture) while others measure the mass (mass selective detector) of the compounds that pass through the detector. The best detector for the RSSAR system will be highly selective for PCBs, PAHs, and other aromatic hydrocarbons but insensitive to air, water, or other benign aliphatic contaminants that may be present in the sampling stream.

Logistical support requirements. Because the RSSAR system is designed to be portable, detector systems that require large external power sources, multiple compressed gases, or large volumes of specialty gases, and in some cases radioactive sources, should be rated lower in overall application. Another consideration is the amount of gas flow that the detector can accommodate yet still function. Some detectors may require low sample flows (<5 mL/min.), which would require a separate off-line flow system to allow characterization of the potentially fast flowing (>60 mL/min.) sample stream. Other detectors may require a higher flow than that provided by the system, necessitating the use of a makeup or auxiliary gases. The RSSAR system detector should be able to accommodate system available power (110 Vac), and require little or no auxiliary gas supply.

Destructive vs. nondestructive detectors. A destructive detector is one that chemically alters the species of interest as it passes through the detector to produce a product compound unlike that which entered the detector. A nondestructive detector is capable of measuring a response for the analyte without altering its chemical nature. Nondestructive detectors would be preferable for the RSSAR system, because the entire sample stream (containing target analytes) may need to be captured on the sorbent tube. If a destructive detector were used, the detector would either need to be placed off-line, thereby destroying a portion of the sample (as well as requiring an additional pump to draw the sample) or, if placed in the sampling stream, be able to turn itself off or divert the stream to the sorbent tube during the sampling process. This would require additional valving and communication mechanisms. The system would be much simpler to design if an on-line nondestructive detector were used which would be operated constantly, regardless of whether sample was or was not being collected.

Size and weight. Not all detectors used for analyzing gas streams are equivalent in size and weight. System sizes range from the size of a home microwave oven to systems the size of a cassette tape. Since the RSSAR system is being designed for portability, systems of smaller size and weight are preferable.

Durability. Some detector systems are sensitive and selective, but would be poor choices for the RSSAR system because they lack the ruggedness and durability required for a mobile sampling system. Some detector systems function reliably as long as they are not moved and the environmental conditions in which they operate are not changed. Other factors to consider include the power cleanliness and vibration that the system is subjected to in day-to-day operations. These environmental conditions may require keeping the system under vacuum 24 hours a day, keeping purge gases flowing, or keeping the temperature constant. Particularly sensitive detectors may suffer in that whenever the detector is turned off and then on again, significant time is required to stabilize detector performance, achieve a vacuum or eliminate contamination.

Cost. Finally, cost of the detector system must also be considered. The cost is not only the initial purchase price, but includes the cost of operating the system—i.e., support gases, consumable parts, and system lifetime. High cost, high maintenance detectors will quickly defeat the cost benefits for developing the RSSAR system for on-site sampling and sample screening.

Commercially Available Detector Systems

Comparison of Detector Systems

A number of detector systems are commercially available. Most of these detectors have been developed for gas chromatography (GC) applications. These detectors were used as a starting point for evaluation for the integration into the RSSAR system. Requirements for GC detectors are not unlike those required for the RSSAR application. In some cases these requirements are more stringent (upper operating temperature, sensitivity etc.) and in other areas the requirements are not as extreme (volume throughput, size etc.). As a result, each of these detector technologies was evaluated against the characteristics desired in the quick-look detector described above.

Thermal conductivity detector (TCD). The TCD produces a signal based on the differential thermal conductivity of analytes relative to that of a carrier gas. This essentially makes the TCD a universally selective detector as it will respond to any compound having a different thermal conductivity than that of the carrier gas. The response will be highly variable, depending on the amount of moisture in the sampling area, the amount of moisture in the air as well as the thermal conductivity of the compound or compounds passing through the detector. In this case, the TCD would respond to both compounds of interest and interferents. Although the TCD is small, inexpensive, nondestructive, easily transportable, and rugged, it lacks the selectivity required by the RSSAR system.

Flame ionization detector (FID). The FID produces positive ions by pyrolyzing the sample in a hydrogen flame. These ions cause a change in the potential between the flame tip and a collector electrode located inside the detector. The FID is fairly selective for hydrocarbons (compounds containing C-H bonds), and has high sensitivity. However, its selectivity cannot distinguish between the contaminants of interest (PCBs, PAHs, other aromatics), and hydrocarbons and other interferents which are not of interest, as all these classes of compounds generally contain C-H bonds. Since most contaminated areas containing the contaminants of concern also contain other oil-like components, a large detector response would be inconclusive. Additionally, the use of an FID requires a supply of hydrogen and air to operate the flame, which would require compressed gases or gas generators to be brought with the unit. The FID is also a destructive detector and would have to be set up off line, because it cannot accommodate the flows developed in the RSSAR. Although the FID is small, inexpensive, and rugged, these shortcomings make it unacceptable for use in the RSSAR system.

Nitrogen-phosphorous detector (NPD). The NPD operates on a principal similar to the FID, but is selective for only nitrogen- and phosphorous-containing organic compounds. Therefore, it is not applicable for use in the RSSAR system.

Flame photometric detector (FPD). The FPD measures molecular emission of species excited in a flame, and is specific for nitrogen- and sulfur-containing compounds. Again, because its selectivity excludes the contaminants of interest, it is also not applicable for use in the RSSAR system.

Electrolytic conductivity detector (ELCD). The ELCD converts any halogen, nitrogen, or sulfur compound into an ionizable gas, which is bubbled through and dissolved into a suitable solvent. The dissolved gases cause an increase in the conductivity of the solvent resulting in an increase in signal and therefore specific detection of the analytes. This detector is both very selective and very sensitive. PCBs are the only target contaminant that could be detected by this technology and, as a result, is not suitable for the RSSAR system. In addition, this detector requires the pumping and storage of the electrolyte solvent presenting logistical support problems in the system.

Electron capture detector (ECD). The ECD responds to highly electronegative compounds (i.e., halogen-containing compounds). In the detector, a radioactive ^{63}Ni source generates a steady beam of electrons which generate a current. When an electronegative species passes through this beam, the current decreases, resulting in detection of the analyte. This detector is both selective and sensitive for PCBs; however, the level of response for aromatic compounds (the other target analytes) is orders of magnitude lower. The poor response of the ECD for the aromatic compounds compared to the PCBs makes it a poor choice for the RSSAR system. The radioactive source would also complicate portability as a result of licensing and testing requirements required to operate a radioactive source. Because of the ECD's sensitivity it is very susceptible to contamination. This detector is best used under highly controlled environmental and operational conditions found in the laboratory, not the variable conditions and extremes presented during portable and field analysis.

Atomic emission detector (AED). The AED operates by passing the gas stream through a microwave-induced helium plasma. The helium plasma causes atomization and excitation of compounds entering the plasma. The resulting emission spectra produces elemental lines characteristic of the atoms that make up the compound. This detector is highly selective for many elemental species in a compound; i.e., organometallics, phosphorous, sulfur, and halogens and would be a useful selective detector for PCBs and other chlorine-containing compounds. Unfortunately, aromatics would only be detected on the carbon channel, which presents the same limitations as the FID. In addition, the AED is prohibitively expensive (\$50K), large (about the size of a microwave oven), requires multiple auxiliary gases (hydrogen, nitrogen, helium, and oxygen) and is destructive.

Mass selective detector (MSD). The MSD bombards the sample stream entering its source with a steady stream of electrons, which effectively breaks the molecules apart to form multiple fragmentation ions. The MSD then separates and measures the masses of these fragments. The fragmentation pattern is unique and indicative of the compound that generated them. This detector is sensitive but somewhat universal. During RSSAR operations, a large collection of fragments from the multiple molecules would be observed passing through the system. These fragments would be difficult if not impossible to interpret, especially in any sort of automated sampling system such as the RSSAR. In addition, the MSD requires a vacuum pump, is large (about the size of a laser printer), heavy (50 lb), and is susceptible to vibration and environmental effects (humidity, temperature, etc.). The MSD is also destructive and is not an ideal choice for this application.

Photoionization detector (PID). The PID works on the principal of photoionization. In this detector, the gas stream passes by a high intensity ultraviolet lamp. Compounds in the gas stream with ionization potentials lower than the energy output of the lamp are ionized and detected. Other compounds in the stream with potentials higher than that of the lamp are not ionized and pass undetected. In the case of the RSSAR system, a lamp with an energy of 10.2 eV will ionize PCBs, PAHs, and aromatic hydrocarbons. However, aliphatic hydrocarbons, water, and air which have much higher ionization potentials will not be detected. The PID meets the sensitivity requirements of the system, is small, requires only a small power control unit for operation, is low maintenance, and can handle the type of gas flows developed by the system (60–200 mL/min.). Commercial systems utilizing PID technologies have been designed for portable and field applications and should be easily converted to a portable system such as the RSSAR. However, when sampling materials containing large amounts of water, detection of contaminants may be masked by water vapor.

Ultraviolet detector (UV). UV detectors provide a signal based on a molecule's ability to absorb energy in the ultraviolet region. Compounds with discrete functionalities (hydroxyl, ethoxy, pi bonds

etc.) will absorb energy at specific wavelengths as a result of those functionalities. Thus, the UV detector can be highly selective. For each compound, or similar class of compounds, there can be a wavelength in the gas phase at which this absorption is maximized. In the case of the compounds of interest to the RSSAR project, these wavelengths are 195 nm for trichlorobiphenyl (a PCB), 235 nm for anthracene (a PAH), and 180 nm for phenyl dodecane (an aromatic hydrocarbon). This technique suffers from significant problems in that olefinic hydrocarbons can cause interferences at the 180-nm wavelength. At these low wavelengths, many other compounds are potential interferences. Most existing UV detectors are designed to operate at either a signal wavelength, or to scan over a broad wavelength. Scanning at a single wavelength would limit the selectivity, and scanning over a range would be time consuming and would be rather large in size due to spectrometer requirements. A custom-made detector system may be able to operate at multiple selected wavelengths simultaneously, but its cost would be prohibitive. GE has demonstrated this as a feasible method for detection, but its viability in the presence of other hydrocarbons has yet to be evaluated. Some development effort will be required to design a cost-effective field portable detector.

Quick-Look Detector Selection

After evaluating available detector systems for the desired characteristics, the photoionization detector (PID) and near-vacuum ultraviolet (NVUV) detectors were determined to be the most viable and applicable detectors available. The PID can selectively detect the contaminants of interest for the RSSAR system, but introduction of water into the system (either from the surface being sampled, or from the ambient air) will cause some dampening of the ionization process. The PID is small, low maintenance and has been used in numerous applications of this type (on-site, portable, etc.). The cost of the unit was also reasonable, with commercially available system prices ranging from \$1500 to \$10,000. While the effectiveness of the NVUV was demonstrated in Phase 1, additional effort will be required to develop a field portable unit.

Commercially available PID systems vary greatly. Some systems are designed as environmental monitoring systems. Others operate only at ambient temperatures, and would not be as useful in the RSSAR system due to concerns of condensation and system contamination. Other detectors require an auxiliary gas to sweep the lamp and associated optics to reduce the likelihood of contamination. This would require addition of either compressed gas cylinders or a gas generator to the RSSAR to provide the gas. Some PIDs for gas chromatography systems are expensive, offering specialized capabilities that are essentially not required for the RSSAR application.

Of all the commercially available PID systems evaluated (over ten were investigated), the detector systems sold by HNU was found to provide the most flexibility, sensitivity and economy. This particular brand of PID has already undergone testing by the GE team for suitability to this application during the Phase 1 effort. An alternative sample cell of a greater volume (as high as 2.5 scfh) is now available and can accommodate the large on-line gas flows potentially required by the system. Additionally, the detector can be heated to temperatures typical for the heated sampling head and transfer line (250 °C), making integration even simpler; other vendors have much lower upper temperature limits for their systems. Higher operating temperature operations are important as it minimizes potential condensation of analytes in the system and detector. Finally, the HNU was also available at the lower end of the price range, costing approximately \$4,500.

However, based on results from the integrated laboratory testing with the PID, it was determined that the large amount of water vapor produced when sampling concrete and other wet materials may mask any contaminants present in the sample. Therefore, it is recommended that a field portable version of the NVUV detector be considered for Phase 3.

Conclusions and Recommendations

In Phase 2 GE and its principal subcontractor, EAI Corporation, Inc., have completed most of the objectives outlined in the Phase 2 proposal. The tasks that have been completed dealt with the design, construction, and testing of equipment that will make up the RSSAR system, such as the multisample trapping module, thermal desorption autosampler, steel sampler head, and integrated system. Based on the results of testing which was conducted, several recommendations were formulated to improve performance during the planned Phase 3 design and testing of the field portable system. These recommendations are included in the following discussion of results for each major component of the RSSAR system.

Steel Sampler Head

A steel sampler head for characterization of contaminants on metal surfaces was designed, built, and tested. The testing was conducted on specimens of three types of steel—carbon steel, stainless steel, and rusted steel. For 4-mil-thick carbon steel sampled using radiant heat for 2 sec, recoveries of model contaminants ranged from 71% to 93% with an average of 82%. Optimum recoveries from 4-mil-thick stainless steel required a 3-sec sampling with radiant heat and yielded recoveries ranging from 60% to 100% with an average of 81%. Rusted steel was more difficult to sample but generally yielded recoveries ranging from 50% to 100% when heated for at least 4 sec for 4-mil-thick specimens or up to 2 min for 56-mil-thick specimens. Due to the variations in thermal conductivity between the different types and thicknesses of steel, it may be necessary to optimize sampling protocols based on the surface to be measured. Recommendations for Phase 3 improvements include

- Modify the light transmission system to increase power transfer efficiency from the current level of approximately 20% to 50%. This will enable the sampling system to heat thicker metal samples to the temperatures needed for thermal desorption of contaminants.
- Simplify the sampling head, power supply, and cooling system to render the unit field transportable.
- Shield the power supply and distribution system to minimize interference (electrical noise) induced in the electronics of the photo-ionization detector.
- Obtain laboratory data on the heating rates of various types and thicknesses of metals that may be encountered in the field to optimize the duration, and power settings for sampling a variety of surfaces.

Multisample Trapping Module

An archival multisample trapping module was designed, fabricated, and tested. The MSTM traps contaminants from up to fifty samples and stores them for detailed analysis. Performance testing of the MSTM yielded inconsistent results, which have been attributed primarily to the existence of cold spots within the system. The recoveries of model contaminants ranged from a low of 5% to a high in excess of 100% (most likely attributed to carryover from previous analyses). Difficulties were encountered in consistently maintaining system temperatures high enough to avoid condensation of contaminants. Based on these results, it was determined that additional blanks would be run and periodic bakeout of the system would be conducted during future testing of the MSTM to minimize carryover of contaminants between samples. In addition, several recommendations were formulated for consideration in the Phase 3 design of the field portable system. These recommendations include:

- Minimize the length of vapor transport lines used to convey samples.
- Maintain all system components that are in contact with sample vapors at approximately 200 °C $\pm$ 25 °C.
- Improve heating and alignment of the needle drive assembly.
- Segregate or insulate temperature-sensitive electronic components from lines which need to be heated.

Thermal Desorption Autosampler and Interface

A thermal desorption autosampler was modified from its original configuration to facilitate the transfer of sorbent tubes from the MSTM and subsequent analysis of semivolatile components. An interface was developed which allows the sample tubes in the magazine to be automatically loaded into the ATD unit where the eventual sample analysis occurs. A mixture of PCB congeners (Aroclor 1254) was used to evaluate the performance of the thermal desorption autosampler for the measurement of PCBs. The results demonstrated the consistency of the thermal desorption autosampler in providing reproducible measurements of a mixture of PCBs independent of the concentration.

During Phase 3, the performance of the system could be improved by using a gas chromatograph with an electron capture detector in conjunction with the thermal desorption autosampler to provide better sensitivity when measuring PCBs. This modification would also minimize interference from other contaminants that may be present at a field site.

Thermal Modeling

The dependence of PCB sampling on the recoverable water content of the concrete and its permeability were examined. These efforts built upon Phase 1 modeling efforts where the governing equations describing the diffusion of thermal energy, water, and PCBs in porous concrete were solved using a finite difference algorithm to determine the liquid water concentration, vapor pressure, and temperature fields in concrete. The results of these modeling efforts indicate that PCB removal efficiency is fairly insensitive to moisture content as long as the moisture content is between 50 and 400 kg/m³. The model also indicates that higher permeability concrete should have higher PCB removal rates with other conditions remaining the same. While the relation to removal rate and permeability is much weaker than linear, the fact that the local permeabilities within a real concrete specimen can vary by several orders of magnitude makes this effect significant. Extension of these results to heterogeneous concrete would suggest that PCBs would be removed preferentially from regions containing microcracks rather than uncracked regions. Nevertheless, the variation appears to be within useful measurement accuracy.

Integrated System Testing

Performance tests with representative contaminants were conducted on an integrated system consisting of the concrete or steel sampler head, the MSTM sorbent tube sampling train not including the magazine and peripherals, and a photoionization detector for quick look measurements. The sorbent tubes were desorbed through the thermal desorption autosampler coupled to a gas chromatograph. Results indicated that the photoionization detector was subject to interferences from water vapor when sampling concrete. It was also observed that tubes packed with more sorbent had greater capacity to handle the water evolved when sampling concrete. Dual tubes were required for recovery of contaminants in the presence of significant water vapor.

Sampling of four types of contaminants—a mixture of 46 base-neutrals, Aroclor 1254, the three model contaminants, and an oil mixture—yielded variable results. This illustrates the complexity

of sampling a broad range of contaminants using a variety of sampling devices coupled with quick-look detectors, sorbent samples, and analytical instrumentation. Based on these results, several additional recommendations include

- Focus efforts to optimize system performance on a class of contaminants (such as PCBs or semivolatile hydrocarbons).
- Streamline the sampling system and ensure that all parts in contact with contaminants are sufficiently heated to prevent condensation of the contaminants of interest.
- Consider integrating the steel and concrete sampler into a single unit capable of sampling either type of surface.
- If a photoionization detector is desired for quick-look applications, explore the use of field portable units and ensure that the units can function in the presence of large amounts of water vapor.
- Utilize two fully loaded sorbent tubes when collecting samples with large amounts of water vapor present.
- Increase the purging of the sorbent tube in the thermal desorption autosampler to minimize the potential for carryover of water which could extinguish the flame in a GC-FID.
- Ensure that the quick-look detectors are properly shielded to minimize the potential for induced electrical noise.
- Explore the development of a field portable near-vacuum ultraviolet detector for quick-look applications when sampling surfaces with the likelihood of generating large amounts of water vapor (such as concrete).

Preliminary Design of Field Portable System

A preliminary design for a field portable integrated sampling system was developed. A cart platform is utilized to house the multisample trapping module, quick-look detector, power supplies, and computer data logging system. The platform is coupled through heated transfer lines to an appropriate sampling head such as the concrete sampler, steel sampler, or bulk sampler. Detailed analysis of the archived sorbent tubes contained within the magazine will be completed in a separate field laboratory containing the thermal desorption autosampler and gas chromatograph. Electric power to the cart system is provided through an umbilical cord and reel from household or industrial electric utility suppliers or through an electrical generator at remote locations. Recommendations to be considered in the detailed design of the field portable system are as follows:

- Simplify the concrete and steel sampling heads to make them more lightweight and energy efficient with greater reliability and maintainability.
- Ensure all sample transfer lines are minimized in length and are adequately heated to prevent condensation of contaminant vapors.
- Utilize isolated power supplies to minimize induced electrical interference.
- Design system for high-quality performance and reliability (6 sigma).
- Utilize a gas chromatograph with an electron capture detector for field laboratory measurements of PCBs in the presence of other contaminants.
- Evaluate the possibility of a direct coupling of the sampling heads to the field gas chromatograph to streamline the system and eliminate potential areas for failure. This would eliminate the need for the multisample trapping module, sorbent tubes, thermal desorption autosampler, and associated analysis of additional blanks. A potential disadvantage of this approach is that the presence of air (and inherent oxygen) in a direct coupled system may introduce analytical artifacts and inaccuracies.

- Consider developing a field portable near-vacuum ultraviolet detector to mitigate interferences from water vapor experienced with the photoionization detector.

Summary

Results from Phase 2 testing of the RSSAR system indicate that the basic concept of using thermal desorption for sampling of various semivolatile organic contaminants from building surfaces and materials is viable. Sampling of model contaminants representing polychlorinated biphenyls, oils, and polyaromatic hydrocarbons resulted in sufficient recoveries of contaminants to assess building contamination levels in a much more representative manner than current technology using wipe samples. Additional effort will be required during Phase 3 to optimize the design of the sampling heads, multisample trapping module, quick-look detector, and thermal desorption autosampler for field application of the RSSAR system.

EAI Corporation's Commercialization Plans

Introduction

The Rapid Surface Sampling and Archival Record (RSSAR) system offers a number of opportunities for commercialization. One key to commercialization of RSSAR as a system is the ability to make the analysis module portable. EAI Corporation, a codeveloper of the RSSAR system, offers an air transportable modular analytical laboratory as a product now, but this unit must be reconfigured for the ATD-400 and the ATD interface for automatic tube loading from the magazine. Adding the analytical laboratory module to the RSSAR in a portable configuration will increase the cost by over \$150,000. The full field portable configuration will have a limited market because of its overall price.

However, several components of the RSSAR system provide products that appear to fill voids in the commercial sector. These components include the sampling heads, the magazine sampler, and the ATD interface. EAI plans to fully develop this series of components and the RSSAR system itself into commercial products.

The following paragraphs outline EAI's preliminary plans to commercialize the products mentioned above. The next section describes the underlying basis of the products for the commercial market. A summary of the market is presented that identifies potential competing products, followed by a preliminary set of strategies for marketing the products.

The Markets for RSSAR Products

The RSSAR concept of heating a matrix to be sampled in order to collect a sample from within that matrix is a more efficient and reliable means of determining the presence or absence of contaminants. Compared with wipe samples (the present EPA-accepted method of sampling surfaces), the heated sampling heads offer a more reproducible and reliable sampling method that will significantly reduce false negatives and enhance the confidence that areas indicated as contaminant free are in fact clean.

Thus, the underlying premise of providing a more effective sampling system is clearly evident. Tied to the generation of an enhanced sample are the other components of the RSSAR system, including the quick-look detector, improved sample collection, automated sample handling (from the magazine to the ATD-400), and an automated data flow. Each of these components offers something unique in the broad environmental and workplace health markets.

The present state of the art in the commercial sector is represented by wipe samples and one- and two-tube samplers. Samples are individually taken with a swab, individually packaged, and individually marked. Analysis involves labor-intensive procedures in an analytical laboratory. When large areas are involved, extensive sampling is required. The sampling effort is labor intensive, with accompanying quality control considerations. At the same time, no immediate results are available at the sampling site that might allow for an altered sampling regime based on specific sample findings.

The quick-look detector provides a means for determining when a sample should be collected. This capability permits the sampling of large areas while collecting only from areas identified as yielding contaminated samples. More samples can be taken without the necessity of analyzing each one, since the analysis of only positive samples is necessary.

While the quick-look detector in the RSSAR system is either a PID or NVUV, a number of detectors better suited for other compounds of interest are available. The multisample trapping module

(MSTM) is capable of interfacing with virtually any detector for the quick-look capability. Thus, the RSSAR system can be adapted to a number of sampling environments and missions.

The heart of the RSSAR system is the MSTM. The capabilities in the MSTM make it a significant advance over currently available sample collection devices. For the RSSAR system it offers a means to efficiently collect, mark, and secure a number of samples as part of the sampling process. The ability to record the characteristics of each sample (the conditions under which it was taken, such as time, flow rate, and duration) in a nonvolatile microprocessor memory enhances quality control across the sampling and analysis process.

Beyond the RSSAR system, the MSTM can be adapted to other sampling heads. This broadens its commercialization opportunities because it offers an inexpensive way to perform limited sampling (tens to hundreds of samples) using the best suited sampling head technology. While the RSSAR sampling heads can be "tuned" for compounds (the heads have been optimized for PCBs), there may be better sampling heads for specific applications.

Further, the MSTM has extensive applications as a standalone sampler for ambient air sampling. The 50-tube configuration with the programmable sampling regime feature provides a wide range of flexibility in sampling applications.

The use of the sampler has two dimensions: The first dimension is to sample and collect samples of ambient air in the workplace to establish and then confirm the environment on a continuing or routine basis. Samples would be collected in a predetermined sampling program and analyzed. With the capability to capture the characteristics of the sampling (temperature, humidity, barometric pressure, flow rate, duration, time and date, fluctuations in air flow), the ability to identify both changes in workplace conditions and possible causes is available.

A second dimension is the ability to archive samples themselves for extended periods (up to 30 years). While sample collection and contemporary analysis provides written documentation, the targeted nature of routine analyses does not permit subsequent analysis for other compounds. Archived in controlled (cold) storage, selected samples would provide the opportunity to later analyze previously collected samples for specific compounds in response to health and safety questions or even litigation.

The MSTM does not sample ambient air any better than other sorbent tube collection systems—i.e., single-, dual-, and four-tube devices. However, the MSTM does offer a number of advantages:

- The 50 tubes allow for less labor-intensive sample collection.
- The data captured by the nonvolatile memory follows the tubes from sampling through the analytical report without human involvement.
- The magazine configuration eliminates the handling, marking, and chain of custody for individual tubes.
- The ATD interface for the magazine reduces the time and labor required for analysis by automating sample handling and analysis.

The result of these advantages is a collection and analysis in which quality control requirements are significantly reduced while quality control procedures for individual tubes are virtually eliminated. The only manual handling and chain of custody are for the magazines. In addition, labor associated with sample collection, handling, quality control, and analysis can be reduced by more than 50%.

The ATD interface would be marketed as part of the RSSAR system. However, it is not considered a viable product as a standalone item. Since a part of the market is to provide laboratory analysis for the MSTM magazines, selling the ATD interface would give other laboratories the ability to obtain the same sample analysis advantages that are recognized by and will be captured by EAI. An integral part of the market strategy for the MSTM as a standalone sampler is to create and capture the business of analysis of the MSTM magazines. The ATD interface and the software architecture to transfer data from the magazine's nonvolatile memory to the analytical instrumentation for incorporation into a report on each individual tube is a capability unique to this system. Coupled with the capability to automate the entire analysis process, laboratory analysis of samples can be accomplished at approximately 60% of normal laboratory analytical costs.

Over the past 10 years the use of solid sorbents for ambient air sample collection has grown from less than 5% of the sampling market to approximately 50%. This tenfold increase has been accompanied by a corresponding expansion in the development and acceptance of analytical methods. Thus, methods for analyzing a wide range of compounds have been established. With the acceptance of solid sorbents as a collection medium for a wide range of samples the MSTM magazine's roles are compatible with RSSAR applications, other sampling applications using heated heads, and applications surrounding ambient air sampling.

Competing Products and Technologies

The RSSAR system is without direct competition as a system. There are no systems on the market to collect and archive surface samples using thermal desorption coupled to solid sorbent technology. In addition, the quick-look detector provides an additional capability that is not available as part of any other sample collection system.

However, a number of technologies for direct analysis of vapor or ambient air samples are available or are in development. A large number of air monitors designed to detect specific compounds in ambient air are available. These types of monitors detect, record, and, in many cases, provide an alarm when certain levels of the target or family of target compounds are present. Examples include CO₂, NO_x, SO_x, and many highly toxic or flammable compounds.

The specificity of these ambient air monitors clearly differentiates them from the capabilities of the RSSAR system and the standalone MSTM. These monitors do not provide any archival sample and do not permit laboratory analysis that offers the flexibility to examine samples in greater detail across a range of compounds. While a paper record, such as strip charts, may be produced as documentation, the ability to do confirmation analysis after the fact is lacking. Simply stated, air monitors and detectors only monitor ambient air within a highly specific band of compounds or for a single compound at a specific point in time. Once this time period has passed, any information not obtained from the analyzer is lost. Air samplers collect over a period that can range from minutes to hours per sample, which permits characterization of the ambient air across virtually all constituents in the air for the period sampled.

The incorporation of various types of analytical technology, such as gas chromatography, into air monitors will provide capabilities that expand the applications of these monitors. But the analytical flexibility and archiving capability will still be lacking.

A second set of technologies that will compete directly with the RSSAR system in sampling of materials for contamination is the development of "mini" gas chromatography (GC), mass spectrometer (MS) and GC/MS. These technologies are now emerging and will be able to provide laboratory analysis quality results at the sampling site. The primary advantage of this type of system is that in a matter of minutes the field sampling technician will have analytical results. The rapid

availability of highly detailed profiles of each sample will permit modification of the sampling procedure to enhance sampling efficiency and the collection of information.

However, the disadvantages of these systems are that the front end for sampling (the GC or GC/MS) is expensive and no archival sample is retained. In addition, the ability of RSSAR to provide a quick-look for specific compounds counters, to a degree, the ability of GC and GC/MS technologies to provide rapid results. Sample analysis where there is no contamination takes just as long as those where contamination is found. Other disadvantages of the GC-GC/MS technologies are the need for a rugged instrument for field use, the requirement for a highly trained technician or a chemist to operate the device, and longer sampling time as the GC-GC/MS analysis must be completed.

There are a number of heated sampler heads in development using a range of technologies for heating and focusing that heat on the sampled area uniformly. The sampler heads are being developed to target specific types of matrices, such as concrete, soil, metal, and other materials. At this point there are no commercially available heated sampler heads with the ability to support the extraction of semivolatile from a range of matrices. In the future, the competition in heated sampling heads will be determined to a great extent by the ability of the technology to be readily "tuned" or calibrated in the field for a wide range of specific compounds, by the provision of a power source that is adequate for operation but not too cumbersome for field use, and by the reduction in size and weight to make the heated sampling heads both practical to use and portable.

In summary, for the RSSAR system and the MSTM, with and without the quick-look detector, there are no directly competing products. However, there are a number of ongoing technology and product development efforts for systems that perform a similar surface sampling function as the RSSAR using GC and GC/MS types of approaches. But these systems lack any mechanism for creating an archival sample.

Preliminary Strategy for Commercialization

The set of instrumentation described earlier in this section is viewed as interrelated for strategic business planning. By establishing an approach that allows one product to build on the viability and success of the previous product, the business strategy for commercialization relies on the relationships between products.

The MSTM is seen as the cornerstone product of the strategy for commercialization. As a stand-alone sampler it has a broad range of sampling applications in industry and the U.S. Government. With the acceptance of the MSTM by industry and the field testing of the RSSAR as part of the EPA's SITE Sampling Technology Demonstration program—with the accompanying acceptance and verification of the sampling and archiving techniques—the technical basis for the product line will have been established.

The following sections describe the marketing of each of the products that will evolve from the current work and the previous work of EAI on MSTM development. The schedule for implementation of the various aspects of the commercialization strategy is shown in Figure 33.

Multisample Trapping Module

Within the RSSAR system the sample collection instrument has been identified as the multisample trapping module (MSTM) to reflect the function of that component. However, for the stand-alone version, the instrument has been designated the Multitube Air Sampling System (MASS). The strategy for commercialization has a number of parts which are designed to build sales of MASS and the related laboratory analysis of the tubes from the magazines, at the same time the RSSAR is in Phase 3 of the development.

The initial marketing of MASS will involve trade shows, publications, industry associations, and the Internet. MASS was introduced at the Pittsburgh Conference in Atlanta in March 1997. The largest analytical chemistry conference of the year, PITTCON provides wide visibility for the product. As a precursor to PITTCON, a mailing and facsimile campaign provided targeted groups with information and an invitation to visit the company's booth in the exhibition hall.

The "traffic" at PITTCON provided both an understanding of the interest in the product and insights into potential customer reactions to the product through questions, concerns, and observations. PITTCON assisted in verifying that the initial target industries are in fact the best starting point. At this juncture those industries have been identified as chemical production, petroleum refining, steel and other metal production and fabrication, printing, and environmental.

In addition to PITTCON, exhibits will be provided at trade shows in each of five targeted industries and in the specialized field of industrial hygiene. The exhibition of MASS at these trade shows will be supported before and after the fact by marketing of the key trade and industry associations. The information derived from this marketing will focus on key players in each industry, the position of industry on workplace health and safety, current approaches to workplace sampling, and industry concerns with future litigation resulting from workplace health issues.

From the association visits, industries/companies to be targeted before each trade show will be identified and a mailing and facsimile campaign conducted. The same two key factors as sought at PITTCON—interest in and reactions to the product—will be sought at the other trade shows.

Continuing liaison with the major trade associations will build on and add to the market knowledge base. Information relevant to each industry can be developed and updated from these contacts. Examples of this type of information include key positions and individuals responsible for workplace health and safety, mailing lists, trends in each industry, other approaches to workplace sampling used by industry, activities or incidents which might impact on marketing, and significant industry events and meetings.

	Year 1				Year 2				Year 3			
	1Q	2Q	3Q	4Q	1Q	2Q	3Q	4Q	1Q	2Q	3Q	4Q
MASS: (MSTM) System	Pitt- Con	Mktg	Production		Pitt- Con				Pitt- Con			
RSSAR I System		Lab Demo	EPA Field Demo	REFINE	Pitt- Con		REGULATORY ACCEPTANCE		Pitt- Con		PRODUCTION & SALE	
Heated Sampling Heads		Lab Demo	EPA Field Demo	REFINE	Pitt- Con		PRODUCTION &		Pitt- Con		SALES	
RSSAR II System		Lab Demo	INTEGRATE MOD-U-LAB		Pitt- Con	REGULATORY ACCEPTANCE			Pitt- Con	PRODUCTION & SALES		
Laboratory Analysis		System Testing	ANALYSIS OF MASS/MSTM TUBES									
Sample Archiving		System Setup	ARCHIVING WITH ONGOING TEST PROGRAM									
Research & Development												

Figure 33. Commercialization schedule.

From the trade association marketing, trade shows, and networking by the EAI staff, contacts in targeted industries will be identified and pursued. This direct marketing has two objectives. First, the marketing should develop sales leads and sales. Second, the marketing will appreciably add to the knowledge base of the particular industries.

Two other efforts will support MASS marketing: advertising in selected publications and the establishment of an Internet home page. MASS will be announced in laboratory, industrial hygiene, and environmental magazines that introduce new products. Examples include *American Laboratory*, *American Environmental Laboratory*, *Industrial Safety and Hygiene News*, *Laboratory Equipment*, and *Pollution Engineering News*.

Concurrent with the product announcements, a number of advertisements will be placed in professional and trade magazines. Table 21 provides a preliminary listing of candidate magazines. Trade association magazines for the targeted markets will also be considered. The content, tone, and thrust of advertisements will be built on the market knowledge from trade shows, industry trade associations, and initial networking.

An Internet home page will be initiated by EAI to advertise and give details of not only MASS but the entire family of instrumentation and services. The RSSAR system, the heated sampling heads, the air transportable modular analytical laboratory (MOD-U-LAB), analytical laboratory services, and sample archiving as well as MASS will be described. The specifics of the Internet strategy must be developed, to include the type of information, the format, the approach to product availability, and similar points.

These initial marketing activities are projected to continue, with increasing emphasis on direct marketing to large industrial firms in the targeted industries. The ability to obtain one or two large companies as customers is one key to early success. EAI's contacts at DuPont, Monsanto, Dow, and U.S. Steel will be used as a starting point. Consideration will be given to trial periods on a no-cost or reduced-cost basis in exchange for a company providing a test bed for MASS.

Table 21. Professional and Trade Magazines to be Used in Advertising Campaign

<i>American Environmental Laboratory</i>
<i>American Laboratory</i>
<i>Engineering Digest</i>
<i>Washington Technology</i> (business newspaper for government systems integrators)
<i>Information Technology</i> (newspaper for users and procedures of electronic information services)
<i>Environmental Lab</i> (serving the in-lab and on-site analytical community)
<i>Industrial Safety and Hygiene News</i>
<i>Laboratory Equipment</i>
<i>Industrial Hygiene News</i>
<i>Pollution Equipment News</i>
<i>Chemical Equipment</i>
<i>Lab Reporter</i>
<i>Chilton Distribution</i> (transportation and business logistics)
<i>Chemical and Engineering News</i>
<i>Technology Transfer Business</i>
<i>Environmental Testing and Analysis</i>
<i>American Scientist</i>
<i>Aerospace and Defense Science</i>

Two additional activities will be undertaken: First, initial marketing activities will be assessed and the strategic market plan will be prepared. This plan will build on the knowledge gained as well as consideration of the marketing results to date. Second, with industry-specific information that has been developed as background, presentations for target markets will be prepared and given.

The objective in addressing these groups is to market the benefits of ambient air sampling and archiving of samples for the long term. Major points in these presentations will be the scientific basis for the air sampling, analysis, and archiving as well as the cost benefit. The primary thrust will be documentation of the ambient air quality.

Material developed from the meetings with potential customers will be a significant input to the marketing plan. Support from these groups will be a factor in the commercialization.

Laboratory Analysis

An integral part of the marketing of MASS and the sampling version of RSSAR is marketing of sample analysis. The concept is for MASS/MSTM magazines to be shipped in specially designed packing cases to the EAI laboratory. The service at the laboratory is the cost-effective (estimated at 30% to 40% below market) automated analysis of tubes. Each analysis and its documentation will include the sampling parameters collected by MASS's nonvolatile memory at the time of sample collection. If requested, the laboratory will store a representative set of samples in a secure refrigerated storage area with backup power for a defined period—days, weeks, months, years.

Analysis and sample storage marketing will be conducted at the same time the sampler and the RSSAR system are marketed. The marketing approach will focus on independent analysis and documentation of the results, the quality control advantages of the magazine and a fully automated system versus individual tubes, and the capability to retain samples for future analysis. Since the laboratory will be designed and structured to perform fully automated analyses using a variety of instruments, marketing will emphasize the dedicated nature of the laboratory to support the company's sampling instruments.

Rapid Surface Sampling and Archival Record System I

The RSSAR system will be marketed in two configurations. The first configuration is the sampling components, including the sampling heads, transfer lines, quick-look detector, and the MSTM with its 50-tube magazine. This configuration has been designated RSSAR I. The purpose of a sampling configuration is to offer a low-price alternative to potential competing GC-GC/MS field sampling and analysis technology.

The second configuration is the full RSSAR system (RSSAR II), with the MOD-U-LAB designed to interface with the MSTM. Thus, in the RSSAR system, both sample collection and analysis can occur on-site. It should be pointed out that the MOD-U-LAB is not integrated into the MSTM, but is set up in the same area for on-site analysis. The tubes will not be analyzed one at a time as collected, but as a magazine is completed. The advantage of the field analysis over real-time field sampling using GC and GC/MS is that sampling can be conducted faster and, in highly contaminated areas, the analytical instrumentation is not subject to that contamination.

The EPA Site Sampling Technology Demonstration program can be used as a starting point for the marketing of RSSAR I. By working with the EPA staff at the National Exposure Research Laboratory (NERL) in Las Vegas, a good indication of emerging sampling technologies will be gained. Critical review of the RSSAR system, including the multitube sampling module and the particular concept of automated solid sorbent sampling and analysis, through the field testing process will provide indications of the potential markets, the range of applications, and problems with the system.

The data from the field test and concurrent market analysis will be used to develop a marketing plan for RSSAR I. From information gathered to date, RSSAR I appears to have a market when tens to hundreds of wipe samples are now taken. Environmental cleanup companies, industries that perform their own assessments and cleanup, and a wide range of government agencies and industries that desire an efficient way to implement both sampling and remediation quality control should find RSSAR I attractive.

Marketing of RSSAR I will build on MASS customers with a need for RSSAR I capabilities and the information base established in marketing MASS. RSSAR I will be included in the product line at trade shows, supported by product announcements in appropriate journals, and pre- and post-show mailings and facsimiles. Direct sales contacts with industry representatives, such as laboratory, environmental, health and safety, and QA/QC staff, will be made by telephone, facsimile, and direct mailing. After initial marketing efforts the marketing approach will be redirected, as necessary, based on results.

Rapid Surface Sampling and Archival Record System II

RSSAR II, which incorporates a full field analysis capability into the system, will be a specialty item in the family of sampling and analysis instruments. RSSAR II will provide a field (portable) analytical capability by interfacing RSSAR I with the EAI MOD-U-LAB. This module laboratory (Figure 34), is air transportable and can be configured with a wide range of analytical instruments and analytical support equipment (sample preparation, computer, power generator, carrier gas generator).

The MOD-U-LAB will be shown at trade shows. Leads will be generated from trade show traffic and from inquiries about other RSSAR family instrumentation. Marketing materials, such as advertising brochures, Internet home page information, and system specifications in a range of configurations will be prepared.

RSSAR Heated Sampling Heads

Although the preference is to market and sell RSSAR I as a sampling system, it may evolve that the heated sampling heads are in fact a standalone marketable product. As described previously, heated sampling heads appear to be a significant improvement over wipe samples in markets where tens to hundreds of samples are taken daily.

Figure 34. MOD-U-LAB

Environmental firms, industries with a need to periodically sample materials (i.e., after a minor spill and cleanup), government agencies with a periodic sampling need, and law enforcement (seeking evidence) appear to offer a market for heated sampling heads in conjunction with one-, two-, and four-tube solid sorbent sample collection devices or real-time monitors. At this point the heated sampling heads in the RSSAR system require more R&D before the commercialization potential can be assessed, the markets analyzed, and the marketing approach developed.

However, it appears that with the acceptance of the RSSAR I system, the viability of an array of appropriately priced heated sampling heads with interfaces to a sample collection and/or real-time analysis device would become evident.

Research and Development

A significant element in the commercialization of the RSSAR family of instrumentation is the continuing research and development program. The R&D in support of commercialization will follow two general lines. The first line is the continuous testing and preparation of improvements to existing products. For example, the MSTM has been redesigned for the MASS version, reducing the magazine size, stabilizing the sampling needles, improving the magazine opening, and enhancing the ATD-400 interface.

The products, beginning with MASS, will be re-evaluated based on customer feedback, in-house testing, and outside consultant input. As feedback is received and at scheduled period design reviews, system performance will be evaluated. Based on these reviews, product improvements and continuing R&D will be planned. The results of these R&D efforts will be incorporated into pre-planned periodic product improvements. Once every 12 to 18 months an enhanced version of a product will be introduced.

The second line of R&D that will be pursued in support of commercialization over the first two to three years will be adaptations of the technologies and the products for specific applications. The redesign of the heated sampling heads for broader applications is an example of this line of R&D. Redesigning the heads to make them tunable, user friendly, and capable of interfacing with a variety of sample collection systems are types of R&D that would be undertaken to provide a new product for commercialization.

Research and development will be planned on a yearly cycle, updated every six months for the next year. A minimum of 5% and a goal of 10% for R&D will be established as an integral part of business planning and the commercialization plans.

Bibliography

- Betz, W.R., Hazard, S.A. Yearick, E.M. (Supelco Inc., Bellefonte, PA 16823-0048) *Int. Labmate* (1990) 15(1), 41-44.
- Brown, R.S., Pettit, K., Price, D., Jones, P.W. *Chemosphere*, 1991, 23 (8-9), 1145-1150.
- Hart, K.M., Pankow, J.F. HRC CC, *J. High Resolut. Chromatog. Chromatog Commun.* 1987, 10 (9), 484-492.
- Hawker, D.W. *Environ. Sci. Technol.*, 1989, 23, 1250-1253.
- Lesage, S. Fresenius, *J. Anal. Chem.*, 1991, 339 (7), 516-527.
- Macguire, V., Svrcek, W.Y., Mehrotra, A.K. *The Canadian Journal of Chemical Engineering*, 1995, 73, 844-853.
- Perkin Elmer Thermal Desorption Applications No. 36, "Sampling and Analysis of Polychlorinated Biphenyls (PCBs) in Indoor Air using Thermal Desorption, Capillary Gas Chromatography and Mass Spectrometer Detection," Perkin-Elmer Corporation, Norwalk, CT, 1993.
- Puettmann, W. *Chromatographia*, 1988, 26, 171-7.
- Robbat, A. Jr., Liu, T.Y., Abraham, B., *Anal. Chem.*, 1992, 64(4), 358-364.
- Robbat, A. Jr., Liu, T.Y., Abraham, B.M., *Anal. Chem.*, 1992, 64(13), 1477-83.
- Sheldon, R.B., Penney, C.M., Barren, E., Feldman, S.F., Olson, D.R., Ortiz, A.L., Jr., and Berdahl, D.R. "Rapid Surface Sample and Archival Record (RSSAR) System, Phase 1 Final Report," GE Corporate Research and Development, March 1995.
- Sye, W.F., Chang, C.L., *Journal of the Chinese Chemical Society*, 1989, 36, 523-530.

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