**Final Report
of the
Integrated Design for Marketing and Manufacturing Team**

An examination of LA-ICP-AES in a mobile configuration

**sponsored by
Technology Integration Program
Environmental Technology Development
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Executive Summary

The Problem

The Department of Energy (DOE) has identified the need for field-deployable elemental analysis devices that are safer, faster, and less expensive than the fixed laboratory procedures now used to screen hazardous waste sites. As a response to this need, the Technology Integration Program (TIP) created a mobile, field-deployable laser ablation-inductively coupled plasma-atomic emission spectrometry (LA-ICP-AES) sampling and analysis prototype. Although the elemental screening prototype has been successfully field-tested, continued marketing and technical development efforts are required to transfer LA-ICP-AES technology to the commercial sector.

The Response

TIP established and supported a student research and design group called the Integrated Design for Marketing and Manufacturing (IDMM) team to advance the technology transfer of mobile, field-deployable LA-ICP-AES.

The Findings

The IDMM team developed a conceptual design (which is detailed in this report) for a mobile, field-deployable LA-ICP-AES sampling and analysis system, and reports the following findings:

- Mobile, field-deployable LA-ICP-AES is commercially viable.
- Eventual regulatory acceptance of field-deployable LA-ICP-AES, while not a simple process, is likely.
- Further refinement of certain processes and components of LA-ICP-AES will enhance the device's sensitivity and accuracy.

The Recommendations

Based on these findings, the IDMM team makes the following recommendations:

- Continue marketing research in order to identify marketplace trends and companies that are possible manufacturers or operators of mobile, field-deployable LA-ICP-AES analytical devices.
- Arrange field demonstrations and controlled comparisons with fixed laboratory analysis in order to establish and document that the requisite levels of accuracy, repeatability, and sensitivity can be obtained in a field-deployed LA-ICP-AES analytical device.
- Continue the development of the components and processes of LA-ICP-AES, such as dynamic focusing of the laser light, subsurface sampling capability, realtime calibration, and possible incorporation of mass spectrometry (which would increase detection limits and permit isotopic discrimination) in order to improve the marketability and regulatory appeal of the device.

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Preface

Organizational Relationships

At Ames Laboratory, operated for DOE by Iowa State University (ISU), the Environmental Technology Development Program (ETD) addresses the need for efficient new characterization technologies. Within ETD, the Technology Integration Program (TIP) designed, built, and demonstrated a prototype for characterization of contaminated sites. TIP developed and demonstrated a mobile sampling and analysis vehicle for *in situ* sampling of elemental compounds, including radionuclide contaminants. The TIP prototype is called the Mobile Demonstration Laboratory for Environmental Screening Technologies (MDLEST). TIP staff are now refining the MDLEST.

A group of Iowa State University faculty and students was funded within TIP to conduct a complete conceptual design study of the prototype technology developed at TIP and Ames Laboratory. This group was called the Integrated Design for Marketing and Manufacturing (IDMM) team. The core of the IDMM team was convened in early 1993. By summer 1993, a total of 13 students were involved in this practice-oriented academic experience. Most of the team's design, engineering and research work was done between mid-May and November, 1993.

IDMM Project Team Roster

Leader	Ralph E (Pat) Patterson III	Electrical Engineering	
ISU Advisers	Sanjeev Agarwal	Business Administration	
	Rebecca E. Burnett	English	
	Helen Rothschild Ewald	English	
	Ed Jaselskis	Construction Engineering	
Student Members	Darren Almond	Senior	Mechanical Engineering
	Lisa Blanchet	Senior	Chemical Engineering
	Peter Brust	PhD	Industrial Engineering
	Zia Haque	Masters	Electrical Engineering
	Scott Moreland	Senior	Computer Engineering
	Kwi Chuan Ng	Senior	Computer Engineering
	Matt Reid	Masters	Industrial Engineering
	John Sachs	Masters	Business Administration
	Doug Shanda	Senior	Electrical Engineering
	Sarina Tantri	Senior	Electrical Engineering
	Kelly Tilford	Masters	Construction Engineering
	Christianna I. White	Masters	English
	Craig Zeutzius	Senior	Industrial Engineering

Additional professionals rounded out the roster of IDMM advisers, reviewers, and resource people.

Independent Project Reviewers

Johanshir Golchin	Iowa Department of Natural Resources
Dick Gaertner	Institute for Physical Research and Technology
Al Bevolo	Technology Integration Program

Project Reviewers and Resource People

Arvid Eide	College of Engineering
Marvin S. Anderson	Technology Integration Program
David Baldwin	Ames Laboratory
Steve Braymen	Technology Integration Program
Art D'Silva	Ames Laboratory
Rick McIntosh	Technology Integration Program
David Martin	Materials Science/Engineering
Tom Noble	Technology Integration Program
Jeffrey D. Pfeiffle	Technology Integration Program
Joel Prail	Technology Integration Program
Dan Zamzow	Ames Laboratory

IDMM Team Purpose, Structure, Methods and Tasks

To accomplish the stated objective of performing a complete conceptual design study of the prototype technology, the IDMM team independently established the team purpose, structure, methods, and tasks. The purpose of the IDMM team was to take a fresh, and partially biased look at the MDLEST elemental analysis technology, modify the design, and determine its viability in the environmental marketplace. The team structure was non-hierarchical, with responsibilities shared among the team members. The IDMM team employed concurrent engineering methods to fulfill the purpose and accomplish the team's tasks. The IDMM tasks were to study the MDLEST technology, to perform marketing and engineering studies, and to prepare a high-level conceptual design of a mobile sampling and analysis vehicle for *in situ* sampling of elemental compounds, including radionuclide contaminants. The IDMM conceptual design is biased in that it is based on the MDLEST, but the team attempted to maintain an objective outlook on the limitations and benefits of each component within the system.

This report presents not only the IDMM conceptual design and reports on the results of both formal and informal investigations, but also recommends responses to problems the team identified as part of its investigation.

Part I

IDMM Project Overview

Chapter 1. Key Problems and IDMM Responses¹

1.1 Key Problems

The market for environmental screening technologies is driven by stringent federal regulations that specify sampling and analysis methods. These current methods of measuring inorganic elemental contaminants in soil are usually performed in off-site fixed laboratories rather than on site. On-site methods for measuring the levels of heavy metals and radionuclides are non-existent or inadequate. Current off-site methods and the lack of effective on-site methods as an overall problem can be separated into three key problems:

1. **Safety** Current methods expose workers to hazardous materials and produce secondary hazardous wastes.
2. **Time** Sample analysis by off-site fixed laboratories is time consuming.
3. **Cost** The high costs of off-site fixed laboratories reflect not only the direct costs of expensive laboratory equipment and personnel, but also indirect costs such as multiple field visits, idle machines and personnel while awaiting analytical results, and hazardous secondary wastes storage and disposal.

A field-deployable elemental screening device that is safer, faster, and less expensive than current methods has a high market potential; to date, this market potential has not been fully developed.

1.2 Responses to the Problems

The Integrated Design for Marketing and Manufacturing (IDMM) team researched the overall problem and the three key problems in order to develop a conceptual design to address the overall problem. The IDMM conceptual design is a self-contained mobile laboratory for on-site and *in situ* determination of elemental contaminants. The mobile laboratory is the "hardware" component of the conceptual design, and flexible sampling capability is an application component of the design. The laboratory and the flexible sampling capability together provide viable solutions to the overall problem of non-existent or inadequate on-site analytical methods.

In responding to the overall problem, the laboratory component of the IDMM design is built around Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES), which is an analytical process certified for fixed-laboratory determination of elemental contaminants. The IDMM design uses Laser Ablation (LA) as the sample acquisition method. A report detailing the LA-ICP-AES process is located in Chapter 5, Technical Process Overview, and a discussion of the flexible sampling capability is located in Chapter 6, Operating Protocols, Dynamic Sampling, and Data Integration. Together the IDMM recommendation for placing LA-

¹ While the entire IDMM team researched the problems and designed responses, credit for writing this chapter goes to Christianna I. White.

ICP-AES in a mobile configuration and associated flexible sampling methods directly address the problems related to safety, time, and cost.

1.2.1 Safety

Site characterization and screening safety issues are addressed by the flexible sampling capability of *in situ* and on-site sampling. The IDMM conceptual design uses a surface sampler to ablate minute quantities directly from a surface and process the sample with minimal operator handling.

The IDMM conceptual design provides on-site sampling capability by fixing the surface sampler to the outside of the mobile laboratory and introducing samples that are brought to the fixed sampling head from locations around the site. Both *in situ* and on-site sampling strategies eliminate the possibility of exposure of people off site to possible contaminants. *In situ* sampling virtually eliminates human contact with the samples, and on-site sampling minimizes sample handling and possible exposure.

Both *in situ* and fixed on-site sampling eliminate the safety problems associated with packaging and transporting contaminated samples to an off-site laboratory. Thus, using the flexible sampling methods of the IDMM conceptual design lessens the likelihood of safety problems.

1.2.2 Time

A recent (October 20, 1993) article in *Environmental Remediation Technology* discusses the time associated with analysis as currently performed by off-site laboratories.

Under current protocol, testing is handled by an off-site commercial laboratory. The usual time to get the test data back is three to six months, said Westinghouse Hanford spokesman Mike Berriochoa. "In the past few years, samples that we've sent out to commercial labs, we've struggled to get analyses back within 120 days," said Richard Roos. . . . Often, no work can be performed on the site until test results are known. Schedules are put on hold until results are returned and an informed decision can be made on how to proceed. (25)

In contrast, LA-ICP-AES in a mobile laboratory reduces the time from the present 120 days to minutes. The projected average sample cycle time for *in situ* sampling is 15 minutes, and on-site fixed location sampling will take even less time. More data points can be analyzed in a shorter period of time, and the analysis results are available immediately and can be used to guide characterization and remediation.

1.2.3 Cost

Time and cost are closely related. An on-site elemental analysis device that delivers near realtime results contributes to an overall lowering of operations costs. The IDMM conceptual design, as a refinement of a field-tested screening prototype, is likely to significantly decrease

the cost of site characterization and screening. Cost is addressed in the same *Environmental Remediation Technology* article: "If testing costs, which can run several thousand dollars per test, are added to the costs of inactive engineers and technicians, project costs soar" (25).

The IDMM team has concluded that the Department of Energy needs safer, faster, less expensive characterization and screening devices. The increased safety and reduced cost and time required for site characterization and remediation using an on-site, near realtime elemental screening device reflect market needs that have not been fully explored. LA-ICP-AES in a mobile configuration that incorporates flexible sampling strategies responds to these needs. In addition, IDMM market research shows that a potential market for this technology exists in the wider environmental consulting industry.

1.3 Resources Consulted

Four sources of information form the bases for the responses proposed by the IDMM team:

1. *Mobile Demonstration Laboratory for Environmental Screening Technologies (MDLEST) technology, specifically laser ablation-inductively coupled plasma-atomic emission spectrometry/mass spectrometry (LA-ICP-AES/MS) in a mobile configuration*— The IDMM conceptual design is based not only on the technology currently housed in the MDLEST, but also on the theoretical underpinnings and possible applications of LA-ICP-AES/MS in a mobile configuration. Many of the people who work with various aspects of the MDLEST shared information and offered feedback as the IDMM team formulated its conceptual design.
2. *Consultation with an Iowa Department of Natural Resources regulator and the Ames Laboratory spectrochemistry group that is researching LA-ICP-AES/MS*— The regulator offered guidance with regard to compliance issues, and the chemists offered guidance and review of the conceptual design process and product.
3. *A review of relevant literature*— This review included DOE and EPA documents, product information, and technical and academic literature about LA-ICP-AES/MS and heavy metal and radionuclide characterization and remediation.
4. *A market survey*— The market research was designed to evaluate the level of acceptance of the IDMM conceptual design in markets outside the DOE and to test enhancement options preferences.

1.4 Project Constraints

The IDMM team undertook this project in an environment that links academic research, the research laboratory, and the marketplace. The team sought information from companies, organizations, groups, and individuals known to be involved in characterization and remediation of contaminated waste sites. The IDMM team worked under constraints that prohibited exhaustive research into every possible manufacturer, supplier, or designer of each component of

the IDMM conceptual design. Instead, the team obtained information from representative designers, manufacturers, and suppliers. Therefore, any potential licensor of this or similar technology is advised to conduct a comparable product development study.

1.5 Report Structure

The second chapter in Part I, "The IDMM Conceptual Design," presents the IDMM conceptual design by articulating the design parameters and elaborating functional requirements that address each of the problems. This chapter includes illustrations and accompanying texts that describe the IDMM conceptual design.

Part II consists of a series of reports dealing with overall aspects of the IDMM project and the IDMM conceptual design. The chapters in Part II include a marketing report, a manufacturability report, a technical process overview, a report on dynamic sampling, data integration and operations protocols, and a report on the computer and controls system.

Part III consists of a series of technical reports on individual components of the IDMM technology such as power, spectrometers, various aspects related to laser ablation, and a report on volatile organic compounds.

References for each chapter immediately follow the text of the chapter. All calculations referred to in each chapter follow the references.

1.6 References

Improve Cleanup Time, Efficiency Are Linked to Field Screening Lab. 1993. *Environmental Remediation Technology*. 1, no. 3 (October 20): 25-26.

Chapter 2. The IDMM Conceptual Design²

In response to the ineffectiveness of current off-site sampling methods, the IDMM team developed a high-level conceptual design of a mobile sampling and analysis vehicle for *in situ* sampling of elemental compounds, including radionuclide contaminants. The design incorporates the advantages of LA-ICP-AES technology in a field-deployable mobile laboratory and utilizes an innovative sampling strategy for site screening and characterization. The combination of the field-deployable mobile laboratory and the dynamic sampling strategy provides faster, safer, and less expensive results than existing sampling and analysis techniques.

This chapter presents the IDMM conceptual design in three parts. The next section contains illustrations and descriptions of the mobile laboratory. The second section describes how the design meets the requirements for field deployment in the environmental marketplace. The final section discusses the dynamic sampling strategy associated with the mobile laboratory.

2.1 Descriptions and Illustrations

The components of the IDMM conceptual design and their arrangement in the mobile laboratory were all researched to ensure a high probability of a viable configuration. Because this is a conceptual design, much of the detail work (such as ventilation ductwork and electrical conduits) has been left for future consideration.

For ease of discussion, the design is discussed as an actual artifact even though a prototype of the IDMM conceptual design has not been constructed. First the vehicle platform is described. Then the compartments of the laboratory are placed on the vehicle platform. Finally, the laboratory equipment and support system components are located within each of the compartments.

2.1.1 The vehicle platform

The IDMM mobile laboratory is mounted on a 26-foot truck chassis. The general characteristics for a vehicle of this type are given in Table 2.1 below. This vehicle was chosen for the platform of the mobile laboratory because it offered the best mobility while still satisfying the weight and space requirements of the laboratory.

² While the entire IDMM team researched the conceptual design, credit for writing this chapter goes to Craig Zeutzius, Darren Almond, and Christianna White; credit for the illustrations goes to Jeffrey D. Pfeifle (TIP staff) and Darren Almond.

Wheel base:	178.0"
Vehicle length:	312.0" (26')
GVWR:	14,500 lbs.
Engine:	7.4 L V8 (240 HP)
Transmission:	4-speed automatic w/ overdrive
Fuel tank:	40 gallon
Payload area:	8' x 16' x 6.5'
Payload capacity:	5500 lbs.

Table 2.1 Vehicle platform specifications.

2.1.2 Compartments

This section describes the seven basic compartments in the payload area of the vehicle that comprise the mobile laboratory. The compartments of the mobile laboratory are listed from the front to the rear of the vehicle. The letters correspond with labels in Figures 2.2, 2.3, 2.4 and 2.5.

- A generator bay
- B overhead storage
- C entrance way/storage
- D argon dewar closet
- E air conditioner compartment
- F instrument room
- G workspace

The generator bay is not enclosed. The rest of the compartments are within what will be referred to as the shell of the mobile laboratory. References will be made to doors and panels that allow entrance to the compartments and/or access to various components. The components of the laboratory will be described in more detail in section 2.1.3, Equipment and components.

2.1.2.1 Generator bay (A) The generator bay is located immediately behind the cab of the vehicle. This compartment houses the generator and the batteries for starting the generator and providing dc power to the laboratory. Although this compartment is not completely enclosed it is somewhat sheltered from the environment by the cab and laboratory shell.

Both the passenger and driver's sides of the compartment are open to the outside air to provide cooling and allow access to the generator for service. The engine of the generator is serviced through a pop-out panel in the front wall of the laboratory shell. In the event of catastrophic failure, moving the overhead storage compartment would facilitate replacing the generator.

2.1.2.2 Overhead storage (B) The overhead storage compartment is located directly above the generator bay. This compartment is designed to house relatively light items. This compartment is hinged at the roof to allow the entire compartment to flip up onto the roof for access to the generator bay. This compartment is accessed from the entrance way/storage area.

2.1.2.3 Entrance way/storage (C) The entrance way/storage compartment is located immediately behind the generator bay on the passenger's side of the vehicle. This compartment is the only entrance into the laboratory shell when the mobile laboratory is operating. Access is through a door on the passenger's side of the vehicle. This compartment provides access to the generator through a pop-out panel, the overhead storage area, the argon dewar closet through a pair of cabinet doors, and the instrument room. This compartment receives no direct climate control from the air conditioning system since it contains no sensitive equipment and personnel are not inside during operation of the laboratory.

2.1.2.4 Argon dewar closet (D) The argon dewar closet is located directly behind the generator bay on the driver's side of the vehicle. This compartment is accessed through a door on the driver's side of the laboratory shell and also from the entrance way through a pair of cabinet doors. The cabinet doors allow the operators to reach the argon dewar connections while replacing the dewar.

2.1.2.5 Air conditioner compartment (E) The air conditioner compartment is located directly beneath the argon dewar closet on the driver's side of the vehicle. This compartment is accessed through an outside panel on the driver's side of the vehicle. The return and discharge air hookups for the air conditioner are within this compartment.

2.1.2.6 Sensitive instrument compartment (F) The large room in the center of the laboratory shell is the main instrument compartment. This room houses all of the analytical equipment. The instrument room is climate controlled because the equipment is sensitive to fluctuations and extremes of temperature and humidity. This is the only compartment within the laboratory shell that will receive climate control. This decision was made to reduce the size of the air conditioner that was required.

There are two ways to access the instrument room. Conventional access is through a door from the entrance way. The room can also be accessed through a large panel at the rear of the room. This panel can be removed for installation and/or major servicing of the equipment.

In order to prevent contamination and to maintain a stable climate within this compartment, no one will be allowed into this room during a sampling operation. The instrumentation and equipment in this mobile laboratory will be automated to the fullest extent possible to alleviate the need for direct human interaction with the equipment in this room.

2.1.2.7 Workspace (G) The operator workspace is at the rear of the vehicle. This is where all of the sampling and interaction with the equipment occurs. This area is accessed through the two large doors at the rear of the vehicle. These doors latch to the side of the vehicle during operation.

The wall separating the instrument room from the workspace contains two large flat screen monitors that provide the graphic interface between the users and the equipment. A window is also located in this wall to allow the operators to look into the instrument room. The workspace area also houses the surface sampler and a storage cabinet.

2.1.3 Equipment and components

This section identifies the major components that comprise the mobile laboratory. These components, with their respective dimensions and weights, are shown in Table 2.2. Then the compartments of the mobile laboratory are described with regard to placement of all of the analysis equipment and support systems.

Equipment	Dimensions (in.)	Weight (lbs)
	L x W x H	
Propane generator	84 x 27 x 51	1500
Air conditioner	44 x 21 x 16.5	200
Laser power supply	28 x 25 x 28	350
Spectrometer	49.7 x 30 x 36	850
Chiller	23.5 x 14.5 x 24.5	250
Computer racks (2)	18 x 18 x 36	200
Surface sampler	20 x 18 x 24	60
Propane tanks (2)	16 (D) x 36 (H)	100
Argon dewar	24 (D) x 36 (H)	500

Payload Capacity = 5500 lbs.

Total Weight = 3910

Table 2.2 Equipment dimensions and weights.

The propane generator is located in the generator bay immediately behind the cab of the vehicle. It is mounted directly to the chassis using shock absorbing mounts. The generator is

Figure 2.2 Generator, propane tanks, breaker panel

oriented so that the engine is located on the passenger's side of the vehicle and the generator coils are located behind the driver. The propane to run the engine is in two cylindrical tanks which are located in the entrance way/storage area. These tanks could be likened to the tanks on a propane-powered forklift. The breaker panel (power distribution center) is located on the front wall of the entrance way/storage area.

The argon dewar is located in the argon dewar closet on the driver's side of the vehicle. An electric winch is located within this closet to aid in the removal and installation of dewars. The 27,000 Btu/Hr recreational vehicle central air conditioner with an aftermarket heating element is located in the air conditioner compartment beneath the argon dewar.

Figure 2.3 Argon, A/C, batteries, winch, intake/exhaust

A 150 cu. ft/min filtered intake air blower, which supplies fresh air to the air-conditioned room, is located on the roof of the mobile laboratory. The filtered exhaust port of the plasma torch is also located on the roof of the vehicle.

The atomic emission spectrometer and supporting chiller, the laser power supply, and two computer racks are located within the instrument room. The laser power supply and the spectrometer are positioned in the center of the vehicle to benefit the transverse weight distribution of the vehicle. Although the room is somewhat cramped, a two-foot walkway

remains between the spectrometer and the laser power supply. This was deemed to be sufficient because the operators would not be working in this room during a sampling operation.

Figure 2.4 Sensitive instruments compartment.

The surface sampler, sample introduction device, and computer interface equipment are in the workspace area at the rear of the vehicle. An umbilical that supplies the surface sampler with power, argon gas, and computer control commands is rolled onto a spool that is mounted on the rear wall of the vehicle. The only major feature that is not shown in these views is a ladder that is attached on the left rear door of the vehicle. This ladder allows an operator to climb to the top of the vehicle to change the plasma torch exhaust HEPA filter as needed.

2.2 Design Requirements

To apply LA-ICP-AES technology to on-site sampling, a design for a mobile laboratory and a dynamic sampling strategy viable for field deployment were developed by the IDMM team. The following sections explain the design requirements necessary for field deployment of a mobile laboratory and the aspects of the IDMM conceptual design that satisfy those requirements. The IDMM team considered regulatory, mobility, flexibility, reliability, system operation, and maintenance requirements.

Figure 2.5 Operator workspace

2.2.1 Regulatory requirements

The mobile laboratory must meet all the regulatory requirements regarding environmental screening and characterization. Numerous federal and state regulations govern the environmental cleanup industry. These regulations not only vary from state to state, but also vary among hazardous waste sites. The IDMM team investigated these regulatory requirements to design a mobile laboratory that would be in compliance with the regulations. However, because of the magnitude and complexity of the regulatory structure, a few areas may have been inadvertently overlooked.

The mobile laboratory must be able to detect elemental contaminants at concentration levels dictated by the official in charge of a particular hazardous waste site. Because these requirements differ for each site, the goal of the IDMM mobile laboratory design is to provide analysis approaching concentration levels comparable to those found by off-site certified laboratories that use a USEPA-approved technology, inductively coupled plasma-atomic emission spectrometry (ICP-AES). While most off-site laboratories use conventional sample preparation techniques, the IDMM design incorporates laser ablation as the sample acquisition method.

ICP-AES is an approved analytical method under the analytical support levels system established by the USEPA. The USEPA's five analytical support levels guide the appropriate use of analytical methods at a particular site. The five levels are described fully in *Data Quality Objectives for Remedial Response Activities: Development Process* (EPA 1987). The IDMM team consulted this and other resources (also see Chapter 3, Marketing, section 3.4.1) to determine the likely analytical level of the IDMM mobile laboratory and concluded that LA-ICP-AES in a mobile configuration would most likely be considered analytical support methods in Levels I and II. Level I, field screening analysis, has as its objective "to generate data which are generally used in refining sampling plans and determining the extent of contamination at this site" (EPA 1987, B-7). Level I includes requirements for on-site, realtime data acquisition and analysis that is primarily qualitative. Level II analytical support, which is field analysis, "is designed to provide real-time data for ongoing field activities. . . . Level II analysis can also be utilized effectively when a phase approach is used for field sampling. In a phased sampling effort, results of the first phase guide the development of subsequent phases, and thus, real-time data are important" (EPA 1987, B-6).

The accuracy, reliability, and the detection limits of the analytical equipment on the mobile laboratory determine whether this laboratory configuration can be certified by federal and state environmental agencies as the new way of screening and characterizing a contaminated site. This certification would allow the characterization of a contaminated site to the level certified for elemental contaminants at a fraction of the time and cost of current conventional practices. However, this certification can only be obtained with proven performance under a variety of conditions in the field.

One of the features of this mobile laboratory is the ability to establish an electronic, relatively tamper-proof chain of custody of *in situ* samples. The chain of custody of a sample is the meticulous tracking of a sample from when it is taken from the ground until it is analyzed at the laboratory. By locating and labeling *in situ* samples using a global positioning system, and by integrating that data with the analysis results, samples that are analyzed at the site using the mobile lab are tracked electronically with a minimal chance for human error.

To preserve data quality, the mobile laboratory must eliminate the possibility of sample cross contamination. The main site of possible cross contamination that the IDMM team attempted to investigate was the argon transport tubing. This investigation relied solely on the results of tests of the MDLEST (which is composed of essentially the same equipment as the IDMM conceptual design) and not on independent testing by the IDMM team. Based on results obtained from two TIP tests at contaminated sites in Fernald, Ohio, and Gunnison, Colorado, cross contamination introduced through the transport tubing is not a problem.

The mobile laboratory must be easily decontaminated upon completion of its work at a contaminated site. To facilitate decontamination, the mobile laboratory is designed so that the portions of the vehicle that are exposed to contamination can be easily cleaned using pressurized water. Except for the transport tubing and the plasma torch exhaust, the instrument room of the mobile laboratory should not require any decontamination. In the case of the plasma torch,

results from the two TIP tests indicate no need for concern. In fact, the HEPA filter at the end of the plasma torch exhaust duct, which is designed to trap any particulates in the air stream, shows no signs of contamination above natural background levels.

2.2.2 Mobility requirements

The mobile laboratory must be able to transport LA-ICP-AES technology from site to site, around a site, and to the sample location. Since most contaminated sites are not large enough to utilize a mobile laboratory for its entire projected three-year life cycle, site-to-site travel would be required. To facilitate site-to-site travel, the laboratory design uses a standard truck chassis and cab, which comply with road travel and safety regulations.

For *in situ* sampling, the laboratory must be able to get close to the sampling location. On-site transport is accomplished by controlling several aspects of the design. First, the shocks are specified for off-road travel. Second, weight and size of the mobile lab are minimized to prevent the laboratory from sinking in soft ground or being unable to move up inclines. Third, the weight on the chassis is well balanced and widely distributed on the ground by using double rear tires and wide front tires. Balancing the weight should prevent the vehicle from sinking into the ground or tipping over on rough terrain.

Once the mobile lab is near the *in situ* sampling location, the next step is to position the surface sampler at the sample site. The IDMM conceptual design uses a surface sampler that will be carried to the sample site by the operators. The surface sampler has handles located on the sides for easy lifting and carrying.

The surface sampler is powered and supplied by an umbilical attached to the mobile lab. Because the surface sampler is manually carried, its weight and the weight of the umbilical are minimized. Minimizing the weight of the surface sampler has been achieved by reducing the amount of optics used, selecting a light-weight laser head and laser support system, and designing the structure of the surface sampler to be as light as possible. The umbilical weight has been reduced by placing a closed-loop coolant system and finned heat exchanger in the surface sampler to cool the laser. This eliminates the need to transport water through the umbilical to cool the laser, and only slightly increases the weight of the surface sampler.

2.2.3 Flexibility requirements

The sampling methods of the mobile laboratory must be flexible to accommodate various sampling strategies and to enable operators to utilize the design for rapid sampling, subsurface sampling, and *in situ* sampling. Sampling flexibility has been obtained in the IDMM conceptual design by having two distinct modes of operation, fixed on-site sampling (rapid sampling mode) and *in situ* sampling. By matching the strengths of these methods with the needs of characterization, a hazardous waste site can be mapped more rapidly and efficiently. Both the *in situ* and rapid sampling modes are explained in detail within the context of the dynamic sampling strategy, which is found in section 2.4.

2.2.4 Reliability requirements

All instrumentation in the mobile laboratory must be able to withstand the effects of extensive travel, anticipated worst case operation requirements, and conditions of the operating environment. To diminish the effect of travel, all sensitive instrumentation is shock mounted and equipped with lock down devices. These devices protect the instrumentation from vibrations and jarring of travel. Problems with laser misalignment are minimized by reducing the amount and complexity of optics required to deliver the laser energy to the soil. This is achieved by placing the laser head on the surface sampler and directly firing at the soil rather than transmitting the laser beam through fiber optics.

In order to increase the reliability of the mobile laboratory, components have been selected to meet anticipated worst case operation requirements. The generator is sized to ensure it has the capacity to meet the peak power demands of the system, preventing damage to the equipment or faulty readings due to power inadequacies. When specifying the laser, no duty cycle limitation is required. Because the laser can operate nearly continuously for extended periods of time, problems arising from analyses of large numbers of samples are minimized.

The instrumentation is protected from the operating environment and contamination by sealing it in two environmentally shielded "cells." The two cells have either limited filtered air circulation or no outside air circulation. The primary instrumentation cell is the area of the mobile laboratory containing the spectrometer, computers, laser power supply, and chiller (Shown as F in Figure 2.1, page 7). Since this area is not accessed during on-site operation, it is possible to seal the cell to prevent temperature fluctuations that could cause problems for the spectrometer. Temperature and humidity of this cell are controlled by an air conditioning/heating system located on the vehicle, but outside of the cell.

The second instrumentation cell is located on the surface sampler. This cell contains the laser head, rastering system, optics, pulse forming network, and closed-loop coolant network. The instrumentation inside of this cell is not temperature or humidity sensitive, except for the laser head, which is cooled during operation by a closed-loop heat exchange system. A 500 W finned heat exchanger is used to transfer the heat generated by the laser through the metallic fins and into the surrounding air. If the ambient air temperature drops below 20°F, a resistive heating element heating system prevents damage to the laser that might result from the coolant freezing. This auxiliary heating system is powered from the mobile laboratory through the umbilical.

2.2.5 System operation requirements

The mobile laboratory is designed to reduce the possibility of harm to the operators, facilitate operation in a hazardous environment, and minimize the amount of specialized training required for system operation. Operator safety was the top priority in the IDMM conceptual design. In addition to complying with the regulatory requirements for on site screening and characterization, two aspects of the design greatly increase operator safety. These two design

aspects are the operator workspace at the back of the vehicle and the placement of the laser head on the surface sampler.

The mobile laboratory was designed so that the operator working at the rear work station is in visual contact with the operator at the sampling site. This increases communication between operators, which reduces the likelihood of injury during on-site operation.

The second aspect of the design that improves operator safety is the positioning and operation of the laser head. For a more complete discussion of operations protocols, see Chapter 6, Operation Protocols, Dynamic Sampling and Data Integration. The laser head is located in an environmentally sealed cell on the surface sampler. This cell must be completely sealed in order for the system to operate, which eliminates the possibility of operator contact with laser energy during normal operation. The laser energy is focused and discharged directly at the soil, which reduces the potential for the laser energy to be misdirected by an optical alignment problem. Also, by focusing the laser directly at the soil, if an energy pulse is fired mistakenly into the surroundings, it will become defocused, reducing the possibility of serious injury. If, during sampling, the surface sampler breaks contact with the surface plate, laser operation is immediately stopped to prevent the laser from discharging into the environment.

The operation of the mobile laboratory requires accommodation for usage in a hazardous environment. This has been accomplished by automating sensitive instrumentation adjustments that could not be performed with a gloved hand. The computer control system is also designed to be controlled by a person wearing thick gloves. Because the operator will wear gloves, keyboard operation may not be possible. A graphical user interface (GUI) is used in combination with a joy stick or other control device to allow the operator to easily control the computer system while wearing protective clothing (see Chapter 7, IDMM Computer and Control System, section 7.2).

The IDMM conceptual design is designed so that only two operators are needed to control the system. Subsystem specialization was avoided by automating complicated instrumentation and by specifying the systems that are not automated to require little specialized training. The two areas that require direct operator interface are the computer control systems and the surface sampler. The computer control system is designed to be user friendly, with several monitoring screens and a GUI providing the information needed for systems operation. The surface sampler requires direct human interaction as a safety precaution when firing the laser. However, the rastering system and laser alignment are fixed and require little specialized training to adjust if adjustment is needed.

2.2.6 Maintenance requirements

Because a mobile laboratory operating in the field will have little technical support equipment, all general maintenance must be able to be performed on site with little specialized training. Instrumentation has been selected that has easily replaceable parts, and the high risk instrumentation, such as the spectrometer, has been positioned for easy access for maintenance.

The laser flash lamp can be easily removed and replaced from the laser head on site by an operator who has had minimal laser training. In addition, extra electronic boards (such as those for the rastering control system) are carried with other supplies so that if problems occur with a board in operation on site, it can be replaced and sampling can continue.

2.3 Dynamic Sampling Strategy

If the capabilities of LA-ICP-AES technology are to be fully utilized on site, the mobile laboratory must be able to fulfill the demands of a dynamic sampling strategy. Design requirements for implementing the dynamic sampling strategy are discussed in this section. The sample strategy involves the operation of the mobile laboratory in two distinct modes, the *in situ* sampling mode and the fixed on-site or rapid sampling mode.

The initial screening of a hazardous waste site often consists of taking samples over a specified grid that overlays the site. This task can be readily accomplished by the mobile laboratory in the rapid sampling mode. The rapid sampling mode consists of collecting small soil samples in containers that are compatible with the sample introduction device in a fixed location at the rear of the vehicle. The small sample containers in the sample introduction device are mated with the surface sampler and then analyzed. In no more than ten minutes, the next sample can be introduced and analyzed.

During the rapid sampling mode of operation, the vehicle remains stationary to allow a large number of samples to be taken without fear of errors due to the jostling of the equipment during the movement from point to point. However, this does not mean that the vehicle can not be initially positioned in a strategic location that would allow the greatest number of samples to be collected in the shortest amount of time.

This rapid sampling mode of operation also allows for the introduction of subsurface samples. All that is required for subsurface or "downhole" sampling is that equipment such as a cone penetrometer bring up a subsurface sample. Portions of the column that are retrieved by the cone penetrometer are then put in the sample containers and taken to the truck to be analyzed. The only added concern to the operators is that they keep track of the depth at which the sample was taken to comply with chain of custody requirements.

Once the initial screening is complete, the results of the sample analysis show where potential "hot spots" of contamination are located. Intensive sampling is done around these "hot spots" to get a better indication of the extent of the contamination. For surface analysis, this intensive sampling can be easily conducted by the mobile laboratory in the *in situ* mode.

The *in situ* mode of operation is a unique feature of this mobile laboratory. The same surface sampler that is used to analyze samples in the rapid sampling mode is removed from the back of the truck and placed on the ground at the sampling location. The only preparation required is the scraping away of surface vegetation and the placement of an aluminum ring plate that helps to provide a seal for the ablation process. Once the surface sampler is in place, the

surface soil can be analyzed without a sample being taken from the ground. If the sampling locations are in close proximity to one another, as they are in an intensive sampling scenario, a large number of samples can be analyzed in a relatively short amount of time. By using the information obtained from the *in situ* samples and relating it to the analyzed grid points, a future sampling site can be determined.

In addition to the benefit of reducing the amount of time required to obtain results, the *in situ* sampling mode also reduces the risk to the operators. The *in situ* sampling mode will be used primarily at locations which are known to have a level of contamination that is of concern. This knowledge is obtained from the initial screening. The fact that none of the surface soil is removed from the ground reduces the risk to the operators and reduces the amount of secondary waste.

The IDMM team believes that this sampling strategy would be an effective application of a field-deployable mobile laboratory utilizing LA-ICP-AES technology. The team acknowledges that differences in site screening and characterization plans would most likely cause changes in this sampling strategy. However, the design of the mobile laboratory allows for changes in the sample strategy to be easily made as needed.

2.4 References

EPA. 1987. *Data Quality Objectives for Remedial Response Activities: Development Process* EPA/540/G-87/003. Annandale, VA: CDM Federal Programs Corporation.

Part II

Reports on the Whole IDMM Conceptual Design

Chapter 3. Marketing³

The IDMM team began this project by looking at the Department of Energy's (DOE) needs for a mobile field screening device that can detect elemental inorganic contaminants in soils. Our sponsors at the Technology Integration Program (TIP) demonstrated the capability of taking laboratory instrumentation to the field. They wanted the IDMM team to create a design concept that could be made commercially available to the DOE.

This chapter explores the following topics:

- The problem
- IDMM design concept
- IDMM design objectives
- Marketing research
- Potential market size
- Competing technologies
- Conclusions

3.1 The Problem

Heavy metal and radionuclide analysis is performed almost exclusively in fixed off-site laboratories. There aren't any reliable mobile field screening devices available for this market. Off-site laboratories bring together a number of technologies to analyze samples. The capability of using these technologies allows an off-site laboratory to analyze samples to the lowest possible detection limits and perform extensive quality checks. The drawbacks of the current methodology are related to time, cost, and safety.

3.1.1 Time

It normally takes three months to get sample analysis results. Figure 3.1 shows a typical breakdown of this time. Twenty-four hour turnaround of analysis results is available for a very high price. To provide twenty-four hour turnaround, the fixed laboratory assigns a person to expedite the sample through the laboratory.

3.1.2 Cost

The current method of analyzing soil samples incurs extra costs due to the expensive analytical techniques and the large amount of material handling involved.

³ While the entire IDMM team researched the conceptual design, credit for writing this chapter goes to John Sachs and Kelly Tilford; credit for the figures in this chapter goes to John Sachs.

Figure 3.1: Conventional Analysis Timeline (typical)

3.1.3 Safety

There is a some risk related to shipping contaminated samples. Excessive material handling exposes workers to contamination.

3.2 IDMM Design Concept

The DOE and the EPA want mobile screening devices that can detect heavy metals and radionuclides in soils and water. The IDMM design is intended to fill this market niche. The IDMM mobile laboratory and dynamic sampling methods are better than off-site laboratories because they are faster, cheaper and safer. The IDMM mobile laboratory design also fills the requirements for analytical capabilities and environmental operating issues.

3.2.1 Time

The IDMM design can complete a sample analysis in under ten minutes with identification of up to 24 different elemental contaminants. Four samples per hour could be analyzed by *in situ* sampling and eight samples per hour could be analyzed for fixed on-site sampling (sheet showing the IDMM cost projections is at the end of this chapter). This would allow field decisions to be made on a realtime basis as part of a characterization or remediation process.

3.2.2 Cost

The IDMM mobile laboratory could process the same number of samples for less money through savings of material handling and shipping. An ICP metals analysis performed by a typical commercial laboratory would cost \$200/sample. The \$200 sample analysis price doesn't include obtaining the sample and shipping it to the laboratory (Winge 1990). The estimated cost of operating the IDMM design would be \$137.52 per sample for *in situ* sampling and \$58.34 for fixed on-site sampling (information on the projected cost figures is at the end of this chapter).

The IDMM design analysis technique would also improve the productivity of scientific staff, appeal to regulatory personnel, and fully utilize on-site heavy equipment.

3.2.3 Safety

The samples can be obtained and analyzed without direct human contact in the *in situ* mode, and in the fixed on-site mode there is no need for sample shipping. Either way this screening technique greatly reduces waste as a byproduct of the analysis process.

3.2.4 Analytical capabilities

The IDMM design has the potential of determining more than 70 elements (up to 24 at a time) at concentrations ranging over nine decades (parts per billion to percent) with a precision of plus or minus ten percent (D'Silva, et al. 1992). The analytical technique (ICP-AES) is used in over 5,000 laboratories through the world for trace elemental analysis (Fassel 1979). ICP-AES is accepted by the EPA and is the most widely used analytical technique for simultaneous multi-element determination.

	IDMM design	Off-site laboratory ICP metals	Off-site laboratory ICP with CLP
Contaminants detected	Heavy metals and radionuclides	Heavy metals and radionuclides	Heavy metals and radionuclides
Detection limits	20–750 ppb ¹	2–75 ppb ²	2–75 ppb ²
Samples per hour	4 <i>in situ</i> 8 fixed	N/A	N/A
Results turnaround	7 minutes	24 hours at best. normally 3 months	24 hours at best. normally 3 months
Costs	\$137.52 <i>in situ</i> \$58.34 fixed ³	\$200 for lab analysis only ⁴	\$400 for lab analysis only ⁴

¹ Detection limits for ICP reflect a factor of 10 to account for laser ablation and *in situ* calibration

² The estimated instrumental detection limits as shown are taken from Inductively Coupled Plasma-Atomic Emission Spectroscopy-Prominent Lines. EPA 600/4 79 017. They are given as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies.

³ See Attachments at the end of the chapter.

⁴ Winge 1990

Table 3.1 Comparison of IDMM design with off-site fixed laboratories.

3.2.5 Operating environment

The IDMM design can operate in a wide range of weather conditions. It is equipped with a dedicated air conditioning/heating system to handle extremes of -10°F to 140°F. The IDMM design can operate under soil moisture conditions from nearly saturated to dry.

3.3 The Design Objectives

The IDMM team structure and schedule called for parallel design and marketing research efforts. Early in the project, the parameters of the IDMM design were set to fulfill the screening of inorganic contaminants in soils at Hanford. The decision was based on the following criteria:

- The DOE supported the IDMM project.
- Hanford is a significantly contaminated DOE facility, with plutonium production dating back to 1943.
- The MDLEST (Mobile Demonstration Laboratory for Environmental Screening Technologies) was scheduled to demonstrate at Hanford in the early summer of 1993 (it was later canceled). This would have provided a unique opportunity to get first-hand information for design decisions.

The IDMM design was constrained more by TIP's LA-ICP-AES technology than by market needs. Whenever possible, the IDMM team considered only commercially available, off-the-shelf, components for this system; these components greatly influenced the capabilities, size, and cost of the IDMM design. The team researched competing technologies to ascertain whether LA-ICP-AES in a mobile configuration is a sound technology for characterization of contaminants in soil and water.

The IDMM design is not a total replacement of current technology (off-site laboratories) but it addresses DOE and EPA characterization and screening needs.

3.4 Marketing Research

The marketing research performed by the IDMM team consisted of two activities, a survey of relevant literature, primarily Department of Energy documents, and a concept study.

3.4.1 Survey of selected Department of Energy documents

The purpose of the literature survey was to identify the functional requirements of the DOE related to the IDMM conceptual design. The DOE has produced a number of needs analysis reports for the environmental cleanup of former radioactive fuels production facilities. In addition to reviewing these DOE reports, the team also contacted personnel at Hanford to get expert input.

The DOE is looking for better technologies to reduce their overall remediation effort. By "better," we mean primarily faster, cheaper, and safer methods. We also addressed the necessary analytical capabilities and the operating environment of a mobile laboratory in the field.

3.4.1.1 Faster The system should get the results of each analysis within 10 minutes after initiating the process. This would allow 30 to 40 samples to be analyzed each day.

- "Emphasis will be placed on field deployable instruments for on-site and/or on-line analyses to provide real-time analytical capabilities for screening level and/or decision quality data" (DOE memorandum, Call for Technical Task Plans for FY 94 1993, 12).
- "The techniques must deliver near real-time data (less than 10 minutes per sample) with sufficient sensitivity to detect contaminants of interest at or below the regulatory limit" (DOE memorandum, Call for Technical Task Plans for FY 94 1993, 3).
- "The system should be capable of providing new measurements every 10 minutes" (Consolidated Listing of Characterization Needs. 1992, 17).
- The system should have the capability of analyzing thirty to forty samples per day (Faulk 1993).

3.4.1.2 Cheaper The system should reduce the direct cost of sampling and analysis. The system should also provide for faster turnaround of analysis results and reduce the handling of contaminated material.

- "Reduce data collection costs and decreased field time are highly desirable" (DOE memorandum, Call for Technical Task Plans for FY 94 1993, 7).

3.4.1.3 Safer The system should reduce the amount of exposure of workers to contaminants and all but eliminate the need of contaminated samples leaving the site.

- Operate *in situ* so that soil isn't moved from its location (DOE memorandum, Call for Technical Task Plans for FY-94 1993)
- Reduce the number of samples taken to characterize a location, reducing handling of samples and potential for personnel exposure (TNA II 1993).

3.4.1.4 Analytical capabilities The analytical capabilities of the system must accurately determine amounts of contaminants down to their background levels. The system should be able to view a wide spectrum of heavy metals and radionuclides in both soil and ground water. The system should be able to be deployed with a minimally-intrusive method of gathering subsurface soil samples. The system should have visual display and hard copy reporting capabilities.

- "Analytical characterization technology is needed to measure volatile organic compounds (VOCs); heavy metals, i.e., Hg, Pb Cr^{VI}, As, etc.; anionic species, i.e., cyanide, nitrate, sulfate, chloride, phosphate, etc.; and radionuclides, i.e., Pu, U, Am, ³H, etc. The matrices of interest are soil and ground water" (DOE memorandum, Call for Technical Task Plans for FY-94 1993, 3).
- "Must provide accurate quantitative determinations of the contaminant(s) of interest at the level(s) equivalent to the EPA toxicity (or other applicable DOE or NRC regulatory) level(s) for the contaminant(s)" (Consolidated Listing of Characterization Needs 1992, 17).
- "Subsurface probes associated with operation of the system should be capable of deployment with a cone penetrometer or other minimally intrusive system. A system that uses a single subsurface probe for measurement of multiple contaminants is preferred

over systems that require a dedicated probe for each contaminant" (Consolidated Listing of Characterization Needs 1992, 17).

- "The master station should be capable of providing visual and hard copy displays of the concentration isopleths for each and all of the contaminants being measured" (Consolidated Listing of Characterization Needs 1992, 17).
- Automated systems should eliminate tracking and archiving of extraneous data that has no bearing on the record of decision for the location (TNA II 1993).

3.4.1.5 Environmental The system should be able to operate in a wide variety of climates and soil conditions.

- "The soil at most of the sites of interest consists of alluvial deposits containing sands, gravel and cobbles, or sands, gravel, and alternating clay layers; one non-arid site (SRS) has unconsolidated sands, clayey sands and sandy clays" (Consolidated Listing of Characterization Needs. 1992, 5).
- The Hanford site is located in the southeastern corner of Washington state. It covers an area of about 560 square miles. The average minimum and maximum temperatures in July are 61°F and 90°F. The average minimum and maximum temperatures in January are 21°F and 37°F. This desert-like climate in the summer can get hotter than 100°F and the winters can get as cold as 10°F (DOE/RL-92-27, 1992; Faulk 1993).

3.4.2 Concept study

The purpose of the concept study was to gain insight into how the IDMM conceptual design might fill market niches outside the Department of Energy and to test to what extent the potential users valued the attributes of the IDMM design. The attributes of the IDMM design tested by the concept study are increased mobility, *in situ* sampling capability, fixed on-site semi-automatic sample feeder, a seven-minute sample cycle, a two-person crew, and a self-sufficient mobile platform. The concept study was also designed to test potential areas of enhancement through rating preferences of options.

There were three steps to the development of the concept study: (1) identify the audience, (2) develop the presentation, and (3) develop the survey. After these steps were complete, we went to the intended audience, delivered the presentation, discussed possibilities of the IDMM design, and administered the survey.

3.4.2.1 Audience The audience for the concept study was defined as potential customers or users of the IDMM design:

- Manufacturers of the technology, who would adopt the technology and provide it to the market place.
- Environmental consulting engineers, who would recommend what techniques would be used for screening and characterization. They could either purchase the system or purchase the services from a third party.
- Analytical laboratories, who would provide the services to the field.

- Owners of the "dirty" property, who are cited by the regulators as having a potentially contaminated site.
- Government regulators, who are charged with overseeing the environmental clean up and who decide what technologies are acceptable.

Of these potential customers, we targeted the environmental consultants and governmental regulators as the audience for the concept study because these two groups are likely to have the greatest voice in determining what methods will be used in the clean-up process.

To provide input from regulators in two different regions, we made two trips, one to Kansas City (EPA Region VII) and another to Chicago (EPA Region V). We also met with representatives of eight environmental consulting engineering firms, four in each city. These firms represent larger companies that have offices throughout the country. They include Dames and More, Layne Geosciences, PRC Environmental Management, Metcalf and Eddy, Black & Veatch, Fluor Daniel, ICF Kaiser Engineers, and Consoer Townsend & Associates.

3.4.2.2 The presentation We needed a method of quickly presenting the IDMM design to the potential customers. As a result, we developed a fifteen-minute overhead-based presentation. The overheads covered a description of the IDMM project, the LA-ICP-AES description, IDMM design attributes, description, and design options.

After the presentation, we distributed the survey questionnaire and encouraged the audience to respond, which gave us immediate feedback by which to judge the acceptance of the IDMM design. Three handouts were included with the presentation: a list of attributes and options; a list of detection limits for elemental contaminants, and the system's expected lowest detection limits in parts per billion (ppb); and a cost sheet with a breakdown of fully amortized costs-per-sample. The handouts follow this chapter.

3.4.2.3 Initial response to presentation Initial responses were noted by the presenters as comments from the audience during and following the presentation. These responses are grouped in the regulatory perspective and the consultant's perspective.

Both EPA offices were interested in our system's capabilities and showed strong interest in doing demonstration activities. The regulators expressed the following concerns:

Quantitative analysis: They wanted us to address the soil matrix issues of *in situ* analysis. They want us to determine a method of quantifying the contaminants in soils that is reliable and capable of working in varying soils. The results don't need to be as accurate as fixed laboratory results, but at least within an order of magnitude.

Field Procedures: They wanted us to establish field procedures for the use of this system and quality assurance protocols to verify that the system is working properly.

Price: There was some concern mentioned about the price and size of this system.

In general, all the consultants were interested in soil sampling and analysis capabilities. The consultants expressed the following concerns:

EPA acceptance: The consultants wouldn't use the system unless it was accepted by the EPA. Its use in the field would depend on the level of acceptance. In Chicago, they were interested in analyses that were defensible in court. The consultants in Kansas City weren't as concerned with court defensible data. Preferences may vary by region, and the IDMM design may prove more successful in a Kansas City market.

Increased Capabilities: The consultants would like a system that could analyze more than just heavy metals, and could do subsurface analysis. Organic analysis and subsurface sampling capabilities were two most requested attributes that the IDMM design lacked.

Price: The consultants wouldn't be interested in a system that they couldn't amortize over more than one or two jobs. Most of the consultants expressed a ceiling of \$100,000 for field screening devices. However, PRC Environmental expressed interest in possibly purchasing a system.

3.4.2.4 Survey The concept study survey is based on an itemized rating scale from one to ten, with one as not important and ten as very important. A copy of the survey can be found at the end of this chapter. There were 37 respondents to the survey (22 from Region V and 15 from Region VII). Of those, 10 were regulators and 27 were consultants.

The survey was designed to answer the following questions:

- What attributes do our potential customers value the most?
- What areas of enhancement do our potential customers favor?
- Are our potential customers price sensitive with respect to detection limits?
- What forms of reporting do our potential customers prefer?

Attribute importance gave us the most significant findings from the survey. It proved to be the best gauge of the respondents perceptions of the IDMM design. The attribute measurement questions appear on the first page of the survey. There are four major topics: safer, faster; better, and cheaper. The rating of the four major topics wasn't effective since it was too vague to our respondents. However, the specific attributes listed in Table 3.2 and their ranking provided some interesting information.

We used perceptual mapping to find the number of dimensions that consumers perceive our product possesses, the names of these dimensions, and the location where consumers prefer a product to be on those dimensions.

Survey Attribute Statements	Kansas City	Chicago	Regulators	Consultants	Total
A No contamination leaves the site	8.0	7.1	6.7	7.3	7.2
B Operators spend less time on the site	7.9	6.8	7.3	7.1	7.1
C Operators handle fewer contaminated samples	6.8	6.8	6.8	6.4	6.5
D Seven minute sample cycle time	8.4	6.6	6.2	7.6	7.2
E One visit to the site	9.0	8.2	8.6	8.2	8.3
F Integrate sampling and remediation	6.9	8.2	7.2	7.9	7.7
G Low detection limits	7.0	7.0	8.0	6.6	7.0
H Fewer chain of custody problems	6.5	6.1	5.9	6.3	6.2
I Faster turnaround of information	8.3	8.0	7.6	8.4	8.2
J Highly mobile	8.1	6.9	7.0	7.3	7.3
K Intelligent sample location selection	7.6	7.6	7.4	7.6	7.5
L Fewer visits to the site	8.8	7.7	8.0	7.9	7.9
M Cost per sample	8.1	7.4	7.2	7.9	7.7
N Multi-element analysis	8.0	7.5	7.4	8.1	7.9
O Improved cash flow	6.0	6.5	6.2	6.3	6.3

Table 3.2 Survey attribute mean results

The survey data was analyzed using a multi-discriminant statistical model. The results of the rotated standardized discriminant function coefficients based on rotation of the structure matrix are displayed in Figure 3.2. Both the X and Y discriminant functions are significant to the .95 confidence interval. The attribute means that are aligned closest to the axes will define the function that axis represents. In our model, the X axis is best defined by F & I (fast turnaround of sample analysis) and G (low detection limits). The Y axis is best defined by O (improved cash flow) and J, N, & E (efficient sampling) (see Figure 3.2).

Note the differences between the regulators and the consultants. This is understandable because each has different agendas. The difference between Chicago and Kansas City was surprising. Before visiting the different regional offices we assumed that there were no differences between regions.

The regulators are very concerned about low detection limits as displayed in Figure 3.3. They also aligned strongly with the improved cash flow. This was surprising at first since the regulatory community is usually not price sensitive. But they seem to be influenced by the financial concerns of the contractors in the environmental business.

Consultants are more preoccupied with efficient sampling and fast turnaround of sample analysis. The consultants are only interested in using the methods that work best for them and are approved by the regulators.

Figure 3.2 Multidimensional scaling map of system attributes

Chicago seemed more interested in improved cash flow than Kansas City. In Chicago they were preoccupied with being able to legally prove the level of contamination. In Chicago, the consultants and the regulators appeared to have a more adversarial relationship. This shows up on the perceptual map by the distance between Chicago and the regulators in respect to low detection limits.

Kansas City seemed to be more aligned with the EPA in a cooperative venture. This cooperation shows in the concern for low detection limits.

Enhancements are addressed as options in the survey. This group of attributes will help us to explore areas for future enhancements for the IDMM design. In the presentation we only talked about these attributes as options without any consideration of prices for these options. Table 3.3 displays the mean ratings of the option attributes.

Figure 3.3. Perceptual Map - IDMM design attributes.

Table 3.3 shows that the audience is more interested in organic and subsurface analysis than accurate positioning of the sample or isotopic determination.

Options Attributes	Kansas City	Chicago	Regulators	Consultants	Total
Subsurface sampling capabilities	9.5	7.6	7.6	8.6	8.3
Organic sampling capabilities	9.8	8.1	7.9	9.2	8.8
Accurate positioning of the sample	6.8	6.7	6.9	6.7	6.7
Isotopic determination	7.4	5.4	5.6	6.4	6.2

Table 3.3 Options attributes mean results

The price sensitivity portion of the survey was completely inconclusive. One respondent commented that at \$900,000 a savings of \$150,000 isn't that meaningful. The consultants were only interested in detection limits as defined by the EPA, and the EPA is interested in detection limits that can see down to background levels.

The report formats section of the survey dealt with reporting preferences. Table 3.4 has the mean results of these attributes. Table 3.4 shows that our audience is more interested in instant reporting of sample analysis to aid in sample selection and graphical contaminant maps than hard copy report and tabular output of data.

Reporting Formats	Kansas City	Chicago	Regulators	Consultants	Total
Graphical contaminant maps	8.5	7.9	7.4	8.3	8.1
Tabular output of data	8.2	7.0	6.9	7.6	7.4
Instant reporting to aid in sample location selection	9.1	8.5	8.1	9.0	8.8
Hard copy reports	7.3	7.5	7.7	7.4	7.5

Table 3.4. Reporting formats mean results

3.5 Potential Market Size

Table 3.5 shows the 1992 revenue and 1991-92 growth of the environmental industry.

Industry Segmentation	1992 Revenue (\$Billion)	1991-1992 Growth
Analytical Services	1.8	3%
Solid Waste Management	28.2	3%
Hazardous Waste Management	14.6	7%
Asbestos Abatement	3.1	3%
Water Infrastructure	13.0	4%
Water Utilities	21.8	3%
Environmental Consulting	14.2	6%
Resource Recovery	16.0	12%
Instrument Manufacturing	1.8	6%
Air Pollution Control	5.4	2%
Waste Management Equipment	11.5	4%
Environmental Energy Sources	2.2	11%
Total	133.7	3.9%

Table 3.5. U.S. Environmental Market Segments (Environmental Business International, June 1993) HMCRI FOCUS July 1993

Table 3.6 gives projected growth figures for the global environmental industry.

	1992 (\$ billion)	Projected Growth (%)	1997 (\$ billion)
United States	134	6	180
Canada	10	11	17
Mexico	1	15	2
Latin America	6	12	10
Western Europe	94	7	132
East Europe/ex USSR	14	14	27
Japan	21	8	31
Australia/New Zealand	3	9	5
Southeast Asia	6	16	13
Rest of the World	6	8	9
Total	295	8	426

Table 3.6 Global environmental industry: Projected growth over 5 years
(Environmental Business International, San Diego) New Technology Week, Aug. 16, 1993.

Using the figures from Tables 3.5 and 3.6, we can project that by 1997 the United States will spend \$180 billion on environmental cleanup while world-wide spending for environmental cleanup will be \$426 billion. If we assume that the demand for heavy metal analysis is constant, then world demand could support between 350 and 475 IDMM mobile laboratories. This estimate is based on the following projections.

The IDMM design is capable of between 4,000 to 9,600 samples per year depending on the type of sampling performed (*in situ* or fixed on-site sampling). Regardless of the sampling method employed, it will cost about \$550,000 a year to maintain one working mobile laboratory in the field. This includes a three year pay back on capital, three year loan at 10%, 125 to 150 day operation in a year at eight hours per day, crew of two, and operating expenses (an estimated sampling cost summary follows this chapter). These costs do not include expenses for maintaining a crew in the field such as lodging, food, and transportation.

We have calculated that between 150 and 200 of these mobile laboratories could be utilized in the United States. This is the equivalent of three to four systems per state. If 200 of these mobile laboratories were deployed, they could generate up to 1.96 million sample analyses per year. It would cost \$110,000,000 to support 200 mobile laboratories in the field. That would amount to a little over 6% of the dollars spent on analytical services portion of the market for 1992 (see Table 3.5). Because of the fast turnaround of analysis results that current off-site laboratories can't provide, additional market opportunities would be available in the remediation of contaminated sites. This should create a greater demand for this method of analysis.

3.6 Competing Technologies

An essential part of the IDMM study was to determine if any other technologies, presently available or under development, could displace LA-ICP-AES from the environmental screening market. To be considered a serious competing technology, the method would have to provide comparable analytical results in a less expensive configuration, or could cost nearly the same and be easier to use.

At present, the regulatory requirements for screening level technology are the driving mechanism for the need for such a device. As explained in Chapter 2, The IDMM Conceptual Design, section 2.2.1, LA-ICP-AES is likely to provide Level I and II screening capability (EPA 1987). These levels give approximate contaminant concentrations that help guide conventional sampling efforts in a present/not present level of sensitivity.

Several types of instrumentation were identified as competing technologies. A brief review of textbook (Ewing 1990) and manufacturers' product literature showed that X-ray fluorescence is the most promising competing technique for screening of elemental contaminants in soil and water. For water analyses alone, technologies identified include *in situ* laser fluorescence and atomic absorption spectroscopy.

3.6.1 X-Ray fluorescence (XRF)

X-ray fluorescence works by bombarding a soil sample with x-rays, causing specific elements in the soil to fluoresce. The emissions given off by each element are sensed by a detector and analyzed for specific elements (characteristic wavelength) and their concentrations (signal intensity). Some elements react differently, dependent on the excitation source. The x-ray source can be interchanged to target specific contaminants for analysis (Outokumpu Instruments 1992; Asoma Instruments 1992; HNU Systems 1991). Stated detection limits are typically in the 100–200 mg/kg range. The EPA has accepted Energy Dispersive XRF as a Level II screening tool (EPA 1987). Several XRF detectors are commercially available, but product literature seems to favor a high resolution Si(Li) detector as the most effective. Software packages shipped with the instruments are coupled with portable computers to provide data logging, data reduction, and data plotting in a realtime field setting. XRF can be used for *in situ* surface soil sampling, on-site soil sampling from soil borings, sludge analysis, ground water analysis, and air particulate filter paper analysis.

While XRF is a promising tool as a screening technology, practitioners rate the actual performance of this method in a field setting as poor and unreliable (Baldwin 1993; Rossabi 1993). The tool suffers from soil matrix interference effects and limitations on detection related to the excitation source. Further development of the capabilities of this instrument will be required to achieve greater than Level II screening capability.

3.6.2 *In situ* laser fluorescence

Researchers working independently at North Dakota State University (Gillispie and St. Germain undated) and the U.S. Naval Ocean Systems Center in San Diego (Liebermann, et al. 1990) have employed fiber-optic based chemical sensors for analysis of organic compounds in water. The naval researchers are also working on a system for analysis of metals in water.

Laser fluorescence spectroscopy uses laser light delivered through a fiber-optic cable to the soil or groundwater. Response emissions from contaminants in the medium are then returned to the spectrometer by a return fiber-optic cable. Wavelength and intensity of the response spectra indicate type and relative amount of contaminant present. These systems claim resolution in the parts-per-trillion range for some elements and less sensitivity for others (Liebermann, et al. 1990). Both systems suffer from interference effects of other elements present, but provide methodologies to minimize their effects. Liebermann et al. (1990) indicate the planned adaptation of laser fluorescence to a cone penetrometer system and present a schematic design.

3.6.3 Atomic absorption

No manufacturers were identified as producers of field-portable atomic absorption (AA) units. Patrick Splichal, an environmental scientist with PRC Environmental, Inc., in Kansas City, reported that PRC had adapted a laboratory instrument for use in the field. He reported mixed results and less demand for the system than anticipated. This system appears to have limited field use because of the required support systems (such as furnace cooling systems) and because it analyzes only one element at a time, requiring a setup change to look for a different element. Additionally, a review of environmental product literature, such as *Pollution Equipment News*, found no references to portable AA unit manufacturers.

3.7 Marketing Conclusions

Based on the survey of relevant literature, the IDMM team concluded that the IDMM design addresses the majority of DOE's characterization needs. These needs are based on more efficient methods of analysis of inorganic contaminants in soil and water. We believe that the IDMM design is the best solution available today or in the near future to analyze inorganic contaminants in soils and water.

Through the concept study, we demonstrated the demand for an IDMM design in markets outside the DOE. Kansas City is utilizing non-CLP analysis of metals and could more easily accept the IDMM design once identified weaknesses—quantitative analysis, field procedures, EPA acceptance, increased capabilities, and system price—are addressed. Chicago is using only CLP data analysis for metals. They are interested in data that can be court defensible. It is going to be much harder to sell the use of a screening device to the Chicago region because of the need for court defensible data. Dialogue with and survey results from regulators and consultants in Kansas City and Chicago gave us information to conclude that not

all the EPA regions operate the same way. Therefore, further study is needed to understand the acceptability of the IDMM design throughout the ten EPA regions.

We recognize that the EPA acceptance of the IDMM design is necessary to make it a valuable tool to the DOE. There aren't any devices today that qualify as EPA Level II field screening for inorganics. EPA Level III laboratory screening is performed today by ICP procedures. ICP-AES is the heart of the IDMM design. In order to gain EPA acceptance of LA-ICP-AES, we need to provide better quantitative analysis and quality assurance protocols.

EPA acceptance of a field deployable LA-ICP-AES is a lengthy process, but eventual acceptance seems likely. Both Kansas City and Chicago EPA offices are interested in demonstration projects. They suggested contacting EPA Environmental Monitoring Systems Laboratory in Las Vegas and the EPA Environmental Remediation Systems Laboratory in Cincinnati to work with them in addressing the weaknesses that were identified earlier.

System price is going to be a big issue. Both the EPA offices and the consultants felt the price was too high, even though the cost per sample was reasonable. The consultants wouldn't be interested in a system that they couldn't amortize over more than one or two jobs. Most of the consultants expressed a ceiling of \$100,000 for field screening devices. This means that we would either have to get off-site laboratory owners interested in this system or find new parties that would be interested in providing this service to the consultants and remediation contractors.

The EPA and the DOE have a lot of environmental cleanup activities that are going to continue for the at least next quarter century. There will be enough activity that we see a market that would support three to four of the IDMM mobile laboratories per state. That would amount to 150 to 200 mobile labs operating in the field at any one time over the next twenty-five years. International markets could easily more than double that number.

3.8 References

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Marketing presentation handout: Attributes and options

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SEEKER™

Elemental Contaminant Screening

- ☐ Mobile system
- ☐ Self sufficient
- ☐ Two person crew
- ☐ Surface sample gathering techniques
 - ☐ in-situ sampling on surface up to 100 feet from truck
 - ☐ fixed semi-automatic sample feeder
- ☐ Real time results

Options

- ☐ Subsurface sampling capabilities
 - ☐ in-situ subsurface sampling head
 - ☐ gather sample to fixed sample station
- ☐ Organic sampling capabilities
- ☐ Accurate location of sample
- ☐ Lower detection limits
- ☐ Isotopic determination
- ☐ Decision support tools
 - ☐ geostatistical location selection
 - ☐ modeling

Marketing presentation handout: Detection limits

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Common Inorganic Contaminants

Element	Detection Limits AES system(ppb)
Aluminum	100
Antimony	200
* Arsenic	300
* Barium	5
Beryllium	5
Boron	5
* Cadmium	20
* Chromium	30
Copper	10
* Lead	250
Manganese	10
* Mercury	300
Molybdenum	30
Nickel	40
* Selenium	30
* Silver	30
Sodium	10
Strontium	2
Thallium	300
Vanadium	10
Zinc	10

*** indicates RCRA Heavy Metal**

Assume a sedimentary soil using a Atomic Emission Spectrometer.

Marketing presentation handout: Cost sheet

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Estimated Sampling Cost of IDMM LA-ICP-AES System

	<u>In-Situ Sampling</u>	<u>Fixed On Site Sampling</u>
Cost of Mobile Lab	\$900,000.00	\$900,000.00
Interest at 10%	\$150,294.00	\$150,294.00
Service Life (Years)	3	3
Duty Cycle (Days/Year)	125	150
(inclement weather, breakdown, calibration, transportation time, and field conditions)		
Samples per hour	4	8
Samples over Life	12,000	28,800
Equipment amortization/sample	\$87.52	\$36.47
Crew size	2	2
Annual salary per technician	\$30,000	\$30,000
Personnel overhead*	150%	150%
(benefits, training, liability insurance, administration)		
Direct Labor Expenses/sample	\$37.50	\$15.63
Operating expenses (\$/hr.)	\$50.00	\$50.00
(consumables, maintenance, etc.)		
Operating expenses/sample	\$12.50	\$6.25
Total costs/sample	\$137.52	\$58.34

The above figures are conservative.

* Living expenses away from home for the crew are not included in the above information.

Marketing survey

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We would like you to rank each group on the lines provided on the right (1 is not important and 10 is very important). Then rank the "safer, faster, better, and cheaper" on the left the same way (1 to 10). Continue on with the second page ranking by each topic the same way (1 to 10).

A. System Advantages

_____ Safer

- ☐ No contamination leaves the site _____
- ☐ Operators spend less time on the site _____
- ☐ Operators handle fewer contaminated samples _____

_____ Faster

- ☐ Seven minute sample cycle time _____
- ☐ One visit to the site _____
- ☐ Integrate sampling and remediation _____

_____ Better

- ☐ Low detection limits _____
- ☐ Fewer chain of custody problems _____
- ☐ Faster turn around of information _____
- ☐ Highly mobile _____
- ☐ Intelligent sample location selection _____

_____ Cheaper

- ☐ Fewer visits to the site _____
- ☐ Cost per sample _____
- ☐ Multi-element analysis _____
- ☐ Improved cash flow _____

Marketing survey (continued)

B. Options:

- ☐ Subsurface sampling capabilities _____
- ☐ Organic sampling capabilities _____
- ☐ Accurate positioning of the sample _____
- ☐ Isotopic determination _____

C. Detection Limits:

- ☐ Current listed limits unit price is \$900K _____
- ☐ Reduce price \$150K and increase limits by 50 _____
- ☐ Increase price \$150K and decrease limits by 50 _____

D. Reporting preferences:

- ☐ Graphical contaminant maps _____
- ☐ Tabular output of data _____
- ☒ Instant reporting to aid in sample location selection .. _____
- ☐ Hard copy reports _____

E. Other (Please write in any other comments you may have below):

Chapter 4. Manufacturability of the IDMM Conceptual Design⁴

Based on an initial production volumes of between 10 and 100 units, the IDMM conceptual design would most likely be produced in a "fixed position" manufacturing set-up (i.e., with the platform truck remaining stationary and the subsystems and components brought to the platform and installed).

It is anticipated that the platform will be produced by a specialized vehicle manufacturer and that a new or existing organization specializing in producing specialty mobile laboratories or vans (e.g., Ellis and Watts, Calumet Coach Company, etc.) with access to the experience and expertise of the Technology Integration Program (TIP) staff through a technology license agreement will assemble the subsystems, install, and calibrate the instrumentation, and finally test the entire system. The instrumentation, subsystems, and wiring are designed to allow for easy assembly with little or no special tooling required. Also, given the relatively low production volumes, the sequencing and scheduling of the installation of instrumentation and subsystems would most likely be carried out during production.

4.1 Lead Time for the First Unit

The length of time to produce the first unit depends on which tasks can be completed in parallel and which must be completed in series. The following four major phases must be completed before the first unit is produced:

1. finish development and detailed design
2. manufacture the platform
3. purchase and receive all necessary components and instrumentation
4. install subsystems and instrumentation on the platform, calibrate and test.

4.1.1 Development and design

The TIP staff has provided the following estimates for the length of time to fully develop the current MDLEST into a market ready design.

Complete programming for a fully automated system	25 weeks
Layout and select components for automation of system	12 weeks
Refine and reprogram and test computer system	2 weeks
Detail the current MDLEST into IDMM concept design	8 weeks
Design electronics into PC boards for manufacturing	4 weeks
<u>Complete new design of the surface sampler</u>	<u>12 weeks</u>
Total	63 weeks

⁴ While the entire IDMM team researched aspects of manufacturability, credit for writing this chapter goes to Peter Brust.

It is probable that many of the above tasks may be completed in parallel. Taking this into account, a rough estimate of actual development lead time is approximately 38 weeks.

While the employment of other fully trained and experienced engineers and technicians in addition to the TIP personnel could shorten this time somewhat, the 38-week period will be used in the remainder of the chapter.

4.1.2 Platform production

The production of the platform will be carried out by a specialized vendor of custom vehicles. Contacts with representatives of Dodgen Industries indicated that their firm could readily construct a suitable platform for the mobile lab. This would include the cab, chassis for 26-foot truck, truck box and doors, generator, air conditioning, heating, major wiring and lighting. Installation of shock mounting and the alarm and fire prevention systems is optional work that might be performed by the vehicle vendor.

Dodgen Industries estimated the time needed to complete one unit at 300 labor hours. Assuming that 2 to 3 people work in tandem, this translates into a lead time of approximately 3 weeks. The cost estimate for this job was quoted as approximately \$75,000, not including the optional work.

4.1.3 Instrumentation procurement

The lead times involved in purchasing and receiving the necessary instrumentation and components from the various vendors are very difficult to determine. Not only is it difficult to find and qualify the needed suppliers, but also delivery of scientific instrumentation and components is usually very stochastic (e.g., spectrometers and custom lasers are usually produced in response to an order instead of carried as inventory). Making the assumption that qualified vendors can be found and that they meet their delivery schedules, the instrumentation and components can be scheduled to arrive prior to the time they are to be installed on the platform. Therefore, instrumentation procurement should not add to the lead time of the first unit.

4.1.4 Instrumentation installation and testing

The tasks of installing the subsystems and instrumentation on the platform, calibrating, and testing will most likely be done by trained specialists such as TIP staff members. TIP staff estimate that it would take 340 labor hours to install, calibrate, and test the instrumentation. Since some of the work must be done in series, it was further estimated that a minimum of 3 weeks would be needed to finish the work. If production volumes permit, this work may be passed along to technicians who are less skilled than the specialists at TIP.

Summing the lead times to complete the four tasks outlined above gives the following estimate:

Finish development and detailed design	38 weeks
Manufacture the mobile platform	3 weeks
Purchase and receive all necessary components and instrumentation	0
Install subsystems and instrumentation on the platform, calibrate and test	3 weeks
Total	44 weeks

4.2 Production Rates for Additional Units

Once the first unit has been produced, the subsequent production time of additional units is only a fraction of the lead time of the first unit.

The second unit produced will most likely incorporate several engineering changes. These minor changes will improve on the initial design and take advantage of the lessons learned in the production of the first unit. A very rough estimate of the redesign time for engineering changes is 4 weeks (based on 10% of the initial design time). The time to produce the platform will remain at 3 weeks, as will the installation of the instrumentation. Hence, the time to produce the second unit is approximately 10 weeks.

The production of additional units should be enhanced by the effects of a learning curve. Based upon the experience gained during the production work of prior units, each additional unit should take less time to complete. The aircraft industry has determined that for fixed position manufacture of complex assemblies the direct labor needed to complete a task will be reduced by approximately 20% every time the production rate doubles (i.e., the fourth unit produced will take only 80% as long as the second unit). This learning curve would reduce to 2.4 weeks the time needed to assemble the fourth lab. If demand warrants, it is also possible to have the platforms produced in parallel with the installation of the instrumentation, further reducing the production time. If this is indeed the case, it is conceivable that the 32nd unit can be produced in 1.25 weeks. This would correspond to a production rate of approximately 40 units per year. However, these projections are based on the assumption that the instrumentation and components will be available when they are needed.

4.3 Production Costs

The costs involved in the manufacturing of the mobile laboratory can be broken down into two major categories, direct costs and indirect or overhead costs.

4.3.1 Direct costs

These are the estimated direct, variable cost of manufacturing one unit:

Platform (includes list as above)	\$75,000
Technical labor (340 hours) @ \$35 per hour + benefits (50%) ^a	17,850
Shock mounting labor and materials	5,000

Spectrometer	\$125,000
GPS	35,000
2 umbilical	2,000
Automated sample handler	1,500
Laser and 2 flash lamps	35,000
Surface sampler and raster system	18,000
Computer and controls equipment ^a	23,150
Fire safety system	2,300
Alarm system	1,000
HEPA filters	4,000
Miscellaneous Hardware	<u>1,000</u>
Total	\$345,800

^a Includes assembly, testing, calibration

^b A detailed cost estimate for the computer and controls system can be found in Chapter 7, section 7.8.

These costs do not include any quantity discounts or the possible reduction in labor hours due to the learning curve. For larger production volumes, the actual direct costs could be substantially lower.

Since standard tooling will be used, little or no capital equipment is needed. Except for an estimated \$30,000 for test and evaluation equipment, capital equipment costs are irrelevant if it is assumed that the manufacture is to be done by an existing company. Given this assumption, the long term cost of capital is negligible. However, if a new, "start up," firm will produce the labs, much larger capital outlays will be required and the cost of capital will become a relevant factor. The financing of operating expenses also depends upon the nature of organization involved. Any short term interest expenses will be determined by the availability of working capital, cash flow, credit lines, etc.

The amortization of the research and development (R&D) costs is another matter altogether and is dependent upon production volumes. The decision of whether and how to allocate R&D costs to the product is a business decision that needs to be made by the proper individuals.

4.3.2 Indirect costs

It is difficult to estimate indirect costs even in the best of circumstances. Indirect costs would include both fixed and variable items such as order tracking, purchasing, payroll, facilities rent, insurance, utilities, documentation, and indirect materials. The method and bases for allocating indirect costs are different for every organization.

At present, it would be unwise to determine an indirect cost rate based on direct costs since the organization that would produce mobile laboratories based on the IDMM conceptual design is not well defined.

Chapter 5. Technical Process Overview⁵

Laser ablation-inductively coupled plasma-atomic emission spectrometry (LA-ICP-AES) analysis is the primary technology of the IDMM design. Although LA-ICP-AES is an active and well-researched field, only those technical characteristics of the composite process that have a direct bearing on IDMM design choices are discussed in this chapter.

ICP-AES is a standard procedure for elemental analysis that was developed by Ames Laboratory scientists in the 1960s. In conventional ICP-AES, the sample is introduced into the ICP torch by aqueous sample nebulization. However, in LA-ICP-AES, high-power laser pulses directed at the surface of the sample create micrometer-sized particles for analysis. These particles are entrained in an argon gas flow and transported to an ICP torch where they are dissociated, ionized, and excited to higher electronic states. The emissions that occur when the ions relax to lower electronic states are analyzed by an atomic emission spectrometer to identify and quantitate the elemental composition of the sample.

This chapter presents an overview of laser ablation, particle entrainment and transport, and inductively coupled plasma-atomic emission spectrometry.

5.1 Laser Ablation

Laser ablation is a recently developed method of creating particles with a diameter of 10 μm or smaller for direct injection into the ICP torch, eliminating the approximate eight-hour preparation time required by aqueous nebulization. Although a significant time savings may be achieved, care must be taken to ensure that the laser ablated particles are sufficient in number, size, and uniformity to be truly representative of the sample. Non-selective creation of uniformly constant particles is essential for accurate elemental analysis.

Although the physical process of laser ablation is not completely understood, according to conversations with David Baldwin, Ames Laboratory chemist, and from Radziemski and Cremers' book, *Laser-Induced Plasmas and Applications* (1989), ablation appears to result from a combination of both the heating and fracturing (shock) effects of short (Q-switched) laser pulses of high power density focused on a sample surface. The following parameters may be controlled to optimize these effects to create the requisite particles: Q-switched laser pulses, power density, focusing, wavelength, pulse duration, repetition rate, multiple ablation, and rastering.

⁵ While the entire IDMM team researched the conceptual design, credit for writing this chapter goes to Ralph E (Pat) Patterson III.

5.1.1 Q-Switched laser pulses

Lasers may be operated in either the Q-switched or free-running mode. While free-running lasers are capable of generating high power densities and ablating large quantities of material, they lack the shock effect needed to create particles of the size and uniformity required for accurate analysis. On the other hand, Q-switched lasers produce the required shock effect by generating very short pulses of high power density. Therefore, only Q-switched lasers should be considered for LA-ICP-AES in the IDMM conceptual design. (See Chapter 14, Laser Requirements and Selection.)

5.1.2 Power density

Laser power density is a critical factor in achieving non-selective, uniform ablation. Non-selective, uniform ablation is achieved when all constituents of the sample absorb energy equally. Unfortunately, the coefficient of reflectivity (the ability of an element to absorb rather than to reflect incident laser energy) is an elemental property and varies greatly with the different elements that may be present in a sample. However, according to conversations with Albert Bevolo, Ames Laboratory Senior Physicist, Baldwin, and Radziemski and Cremers (1989), the coefficients of reflectivity of all elements tend to become uniform as the elements enter the plasma state. Laser power densities above approximately 10^9 W/cm² are sufficient to induce a plasma state for all elements and facilitate non-selective, uniform ablation.

Selective, or non-uniform, ablation may result, in part, because contaminant particles appear to adhere to the surface of the matrix of the sample material. If ablation is performed with insufficient laser power density, the contaminant particles tend to be stripped from the surfaces of the sample matrix without adequate ablation of the underlying matrix material. Such selective ablation leads to unrepresentatively high concentrations of contaminant particles and inaccurate quantitations. Preliminary tests run by the spectrochemistry group at Ames Laboratory on a range of contaminants and matrices indicate that this selective ablation property disappears at power densities above 5×10^9 W/cm².

It should be noted that these results were obtained under ideal laboratory conditions by highly trained research personnel. Since the IDMM system will be operated under non-ideal, field conditions by personnel with technician-level training, good engineering design practice dictates that a safety factor be applied to the laser power density specification to ensure non-selective, uniform sample ablation. Undoubtedly, a safety factor of two is more than sufficient to compensate for routine field operations. Therefore, the IDMM conceptual design should be capable of delivering a minimum power density of 10^{10} W/cm² to the surface of the sample.

5.1.3 Laser focusing

The laser power density delivered to the surface of the sample is a function of the output power of the laser and of the surface area illuminated by the laser energy. For a given laser output power, power density may be increased by decreasing the illuminated area, i.e., by decreasing the diameter of the laser beam. The diameter may be decreased either by focusing the beam to the required diameter at the surface of the sample or by re-collimating the beam emerging from the

laser to a parallel beam of the required diameter. Re-collimating to a narrow, parallel beam eliminates the need to maintain focus as the sample surface elevation changes. However, some of the elements of the system may not be able to withstand the power densities required for non-selective, uniform ablation. Laser energy at the required power density of 10^{10} W/cm² would tend to burn the quartz window of the ablation cell and would certainly burn any ablated particles that might adhere to the quartz window during ablation. Therefore, the laser energy must be focused to the required diameter only at the sample surface.

In addition to enabling the required power density of 10^{10} W/cm², the diameter of the focused laser also affects the fracturing qualities of the laser pulse. A small diameter tends to enhance the fracturing effect by concentrating the energy in a small area and by increasing the effective temperature gradient between the laser spot and its surroundings.

While a further decrease in the diameter of the laser focus continues to increase the incident power density, little improvement in ablation uniformity is anticipated above the power density of 10^{10} W/cm². Also, the quality and accuracy of the optics components, coupled with diffraction effects, impose a practical lower limit on the focus diameter. A minimum focus diameter of approximately 100 μ m can readily be achieved with standard grade optics. Therefore, the IDMM conceptual design should be capable of delivering the required power density of 10^{10} W/cm² to the surface of the sample with a focus diameter of not less than 100 μ m.

5.1.4 Wavelength

The coefficients of reflectivity for various materials (not in a plasma state) vary with the wavelength of the incident laser energy. At the shorter wavelengths, such as those in the ultraviolet (UV) region, these coefficients decrease, causing a more uniform absorption of energy and thus less selective, more uniform ablation (Baldwin; Bevolo; Radziemski and Cremers 1989). However, generation of UV wavelengths (using frequency triplers) is somewhat difficult at the power required for uniform ablation, which mitigates against this option.

The coefficients of reflectivity for materials in a plasma state vary little with the wavelength of the incident laser energy, provided the wavelength is below that corresponding to the plasma frequency. The wavelengths corresponding to the plasma frequencies for materials of interest occur above 1064 nm, a common, easily-generated laser wavelength. It is easier to generate 1064 nm laser pulses at the energy required to produce a plasma state than it is to generate UV pulses at the lower energy. Further, some optical components, such as quartz (which may be used in the ablation cell window and the ICP torch), more readily absorb energy of UV wavelengths. Indeed, several commercial systems employ 1064 nm lasers for ablation. Therefore, a laser wavelength of 1064 nm is recommended.

5.1.5 Pulse duration

For a given laser, the pulse duration may have to be adjusted to achieve a power density of 10^{10} W/cm². In addition, pulse duration plays a small role in producing the ablation fracturing effect. Part of this effect is due to the large temperature gradient created by the deposition of a large

quantity of energy in a small area on the surface of the sample. A short deposition time enhances the creation of a large gradient and, hence, contributes to non-selective, uniform ablation. Experience of the Ames Laboratory chemistry group indicates that laser pulses of 20 ns duration (or shorter) produce adequate results even at power densities somewhat less than 10^{10} W/cm².

5.1.6 Repetition rate

For a given laser, the pulse repetition rate may have to be adjusted to achieve a power density of 10^{10} W/cm². In addition, the necessity of creating a sufficiently large number of particles, uniformly distributed over time, must be considered. Observations by Ames Laboratory personnel with the MDLEST instrumentation indicate that a minimum repetition rate of 20 pulses/second is more than sufficient to meet the requirements for AES analysis. However, if mass spectrometry (MS) analysis is employed, a higher repetition rate may be desired to reduce the apparent pulsing of the particle input over time. A more uniform particle input rate should improve the MS results since the mass spectrometer is a time-dependent, sequential (rather than concurrent) instrument (IS5106 1994).

5.1.7 Multiple ablation

When an area is ablated repetitively, the number of resulting particles appears to decrease with each successive ablation. This decrease in ablation efficiency may result from several causes. First, as material is removed by successive ablations, the laser is effectively defocused, resulting in a lower power density. Second, successive ablations may change the compaction characteristics of the surface of the sample, lessening the fracturing effect of the laser pulses. Finally, though less likely, a physical or chemical change (see the discussion of possible surface stripping of contaminants in section 5.1.2 above) may occur, which may lessen the ablation efficiency. For these reasons, it is necessary to move, or raster, the laser pulses over the surface of the sample.

5.1.8 Rastering

Rastering the laser pulses over the surface of the sample not only alleviates the multiple ablation problems discussed above, but also yields a more representative result by averaging data from a larger surface area. The rastering speed and precision required to accomplish these objectives are quite modest; it is sufficient merely to prevent the overlap of successive pulses. The rastering speed required to prevent overlapping is a function of the laser repetition rate and focus diameter. A buffer space between successive pulses of approximately ten percent of the focus diameter should provide a sufficient separation to prevent any likelihood of overlap. As the focus diameter is likely to be greater than 100 μ m, a rastering precision of 5 μ m, half the 10 μ m minimum buffer, is more than adequate. For a system with a larger focus diameter, this requirement may be relaxed proportionately. See Chapter 10, Rastering Requirements, for details of the IDMM rastering design.

5.1.9 Disclaimer and recommendation for further development

The discussion of power density, focusing, and wavelength effects above is based primarily on theory and has not been thoroughly investigated in the laboratory and has not been tested in a field setting at all. Good results have been obtained with the MDLEST in a field setting (IS-5099 1993) with considerably less than the 10^{10} W/cm² power density specified above. In the MDLEST, laser pulses with a power density of approximately $1-3 \times 10^8$ W/cm² at 532 nm wavelength and a repetition rate of 30 pulses/second are delivered to the surface of the sample by an optical fiber. It is the opinion of the IDMM team that, while good results have been obtained with the MDLEST by the highly trained team of scientists and engineers of TIP, the specifications given above for the IDMM conceptual design should provide a greater probability of success for personnel with lesser background and experience. Before implementation of the IDMM conceptual design, it is recommended that tests be conducted using the IDMM specifications to confirm that the design is sound and that uniform, non-selective results can be obtained by technician-level personnel.

5.2 Particle Entrainment and Transport

Laser ablated particles created within an ablation cell are entrained in an argon gas stream and are transported to an ICP torch where an argon plasma is formed. Results of Ames Laboratory studies indicate that the following factors are involved in the entrainment and transportation of these particles: ablation cell design, gas flow rate, and transport tube characteristics.

5.2.1 Ablation cell design

Laser ablation takes place within a specially designed ablation cell. The laser beam enters the ablation cell through a quartz window in the top of the cell. The bottom of the cell is designed to seal tightly to the ground (in *in situ* sampling) or to the sample introduction system (fixed, on-site sampling) to minimize the loss of argon gas. The argon gas flow pattern within the ablation cell must be carefully designed to facilitate efficient entrainment of correctly sized particles and to smooth the ripple in the particle concentration caused by the laser pulses. The argon inlet and exit ports also must be sized and located properly to enhance these actions. The design of the ablation cell is critical in providing a homogeneous mix of particles in sufficient quantities for accurate analysis, especially if mass spectrometer analysis is employed. The IDMM team strongly supports the continuing development and refinement of the ablation cell by TIP personnel.

5.2.2 Gas flow rate

The argon gas with the entrained particles flows from the ablation cell through the transport tubing to the ICP torch where an argon plasma is formed. The gas flow rate in this tubing is constrained by the requirements of the ICP torch to values between 0.5 and 2.0 l/min. Flow rates of less than 0.5 l/min carry an insufficient number of particles resulting in lower emissions and a poor signal-to-background ratio in the spectrometer. Flow rates higher than 2.0 l/min move the particles through the plasma too rapidly to permit complete dissociation, ionization, and excitation which leads to a reduction in sensitivity and unrepresentative results. High flow rates

also may produce an unstable, flickering plasma with similarly unsatisfactory results. Ames Laboratory personnel have found that the signal intensity is optimized at a gas flow rate of approximately 1.0 l/min. The IDMM team used this figure in its design.

5.2.3 Transport tube characteristics

Ames Laboratory personnel have studied the effects of transport tube length, diameter, material, and path on the efficiency of particle transport at the apparent optimum gas flow rate of 1.0 l/min. Particle precipitation, or drop out, was observed almost exclusively in the first 10 feet of the tube. No significant precipitation occurred beyond 50 feet. While electrostatic precipitation of particles on tube walls might have been expected, apparently little, if any, occurs. Instead, gravitational effects appear to predominate, as the diameter of the precipitated particles nearly all exceeded 10 μm . Since particles of 10 μm or less are desired for analysis, it is recommended that the transport tube be at least 10 feet in length and that a particle trap or easily replaceable initial 10-foot section be incorporated into the design. There appears to be no limitation on the maximum length of the tube.

Transport efficiency of particles of 10 μm or less progressively increased as the tube diameter was increased from $\frac{1}{8}$ inch to $\frac{1}{2}$ inch. No significant improvement was realized beyond this diameter. Therefore, a tube diameter of $\frac{1}{2}$ inch is recommended for the IDMM design.

Tygon® and polyvinace tubes both provided up to 70% better transport than either teflon or polyethylene. Tygon® appears to be the material of choice since it is readily available, is inexpensive, and exhibits desirable stiffness and flexibility properties. A more exhaustive study of additional tubing material is warranted before a final selection is made for a commercial design.

No significant variations in particle transport were observed due to path geometry. Equivalent results were obtained through tubes that were straight or tightly coiled, both vertically and horizontally. Therefore, tube path geometry is not a limiting consideration in the final design.

5.3 Inductively Coupled Plasma–Atomic Emission Spectrometry

Identification and quantitation of soil contaminants is accomplished by spectroscopic analysis of the emissions occurring as dissociated, ionized contaminant particles in an argon plasma relax to lower electron states. The hardware and technology of ICP-AES analysis are well developed. Few design choices remain beyond selecting equipment and components best suited to the specific, mobile environment of the IDMM design. However, a basic understanding of the processes is required. While equipment to accomplish the ICP-AES analysis is often packaged together, the basic elements of ICP and AES, emphasizing the design choices that do exist, are considered separately in the following.

5.3.1 Inductively coupled plasma

A plasma is formed by transferring radio frequency (RF) energy through inductive coupling from a helical coil to the particle-carrying argon delivered through the transport tube. The coil is constructed from copper tubing through which cooling water is pumped. RF energy is supplied to the coil through a coaxial cable from an RF generator delivering approximately 1.1 kW of RF energy at either of two standard frequencies, 27.12 MHz or 40.68 MHz. The 27.12 MHz frequency tends to produce a plasma with a higher spectral background and, hence, lower signal-to-background ratio. Therefore, use of the 40.68 MHz frequency may provide better detection limits for some elements. However, this higher frequency may tend to produce a lower plasma temperature which may introduce soil matrix effects into the analysis. Although either of the RF generator frequencies would function within the IDMM design configuration, experience tends to favor the selection of the 40.68 MHz RF frequency.

Three distinct argon gas flows, arranged in an annular pattern, are used in the ICP torch. The auxiliary or shielding gas, flowing through the intermediate channel of the torch at approximately 0.8 l/min, raises the plasma above the copper coil and away from the quartz torch assembly. The plasma gas, flowing through the outer channel at approximately 16 l/min, forms the argon plasma. The sample gas, flowing at approximately 1.0 l/min and carrying the entrained particles, is introduced through the central channel. Upon leaving the plasma region, the argon gas, flowing at a combined rate of approximately 18 l/min, is vented to the atmosphere through a high-efficiency particulate air (HEPA) filter. Since the argon plasma may reach temperatures of 3,000° to 10,000° C, cooling air must be mixed with the argon and the inlet temperature at the HEPA filter must be monitored. To account for the loss of argon at the ablation cell/sample interface and for additional uses such as backflushing or pressure seal actuation, a total argon expenditure rate of approximately 20 l/min should be planned.

Emissions from the ICP may be conducted to the spectrometer through an optical fiber bundle or through a series of argon-purged tubes and mirrors. Due to its small size and relative flexibility, the fiber bundle can easily be routed between the ICP and the spectrometer, regardless of their relative positions. Although a fiber bundle has been employed with excellent results in the current MDLEST, a fiber bundle may be inappropriate for conducting the emissions of some elements due to the higher absorbance of their far-UV characteristic wavelengths by the bundle. No such absorbance can occur in the purged tube and mirrors system. Therefore, in spite of its increased complexity, the purged tube and mirror system is recommended for the IDMM design to insure maximum utility over the widest possible range of contaminants.

5.3.2 Atomic emission spectrometry

Emissions arriving from the ICP are dispersed into an array of different wavelengths by the spectrometer. Each element is identified by characteristic wavelengths unique to that element. The concentration of the element is determined by comparing the intensity of its characteristic emission to the intensity of the emission from an element of known concentration, such as silicon.

The spectrometer must be able to analyze elemental contaminants of varying concentrations in near real-time with a high degree of sensitivity, precision, and accuracy. The analysis must be accomplished in a self-contained, mobile setting in which fluctuations in temperature, humidity, and power and shock from rough terrain may be encountered. The analysis leading to the selection of a specific spectrometer may be found in Chapter 9, Spectrometer Comparison and Selection.

The IDMM team recommends that the possible use of inductively coupled plasma-mass spectroscopy (ICP-MS) be studied. In ICP-MS, the sample is excited to the plasma state in the same manner as in ICP-AES. Ions of given mass-to-charge ratios are then differentially deflected by a magnetic field and are counted in the mass spectrometer. In this manner, elemental concentrations can be determined with detection limits from 100 to 1000 times superior to those routinely achieved with ICP-AES. Additionally, ICP-MS can differentiate between elemental isotopes, which is not possible with ICP-AES. These capabilities may offset the additional cost and complexity of ICP-MS.

5.4 References

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- IS-5106. 1994. Laser Ablation ICP-Mass Spectrometry Determination of Th230 in Soils at the Gunnison, Colorado UMTRA Site. Ames, Iowa: Ames Laboratory.
- Radziemski, Leon, and David A. Cremers. 1989. *Laser-induced Plasmas and Applications*. New York: M. Dekker.

Chapter 6. Operating Protocols, Dynamic Sampling, and Data Integration⁶

This chapter discusses operating protocols related to three distinct sampling modes and fundamental health and safety protocols. Each of the sampling modes uses slightly different data integration protocols; these are briefly outlined. This chapter also includes a summary of the dynamic sampling strategy that is an essential design component of the IDMM conceptual design; related information can be found in Chapter 2, section 2.4, Dynamic Sampling Strategy.

6.1 Operating Protocols Overview

Specific operating protocols must be followed related to sampling and analysis, data integration, and field health and safety to realize efficient utilization of the system. A significant advantage of the IDMM design is the integration of sample location and analytical data in a near-realtime setting to develop a site characterization model.

The IDMM design uses *in situ* sampling and analysis to give site contaminant distribution information. The sample location is determined with a global positioning system (GPS) simultaneous with the analysis. The GPS analytical and location data are supplied to a geographic information system (GIS) that develops a three-dimensional model of the site. Development of the model is dynamic, based on each new piece of information supplied during the characterization. This is an extremely efficient methodology because of time saved due to the ability to make field decisions that help characterize the site with a minimum of sample duplication.

The following protocols define the field methods for characterization in three different sampling modes: *in situ* sampling, fixed on-site sampling, and downhole sampling. Included with each description is a method for integrating data related to site modeling. Following these sampling mode protocols is the health and safety protocol for the IDMM conceptual design.

6.1.1 GPS overview

In order to efficiently characterize a particular site, the exact location of every sample must be accurately known. Operation of the laboratory in combination with a GPS system permits the immediate integration of x, y, and z coordinates and elemental concentration data.

Various GPS configurations can be utilized depending on the accuracy requirements and the mode of operation of single or multiple GPS receivers. Single receiver GPS systems are not as accurate as multiple receiver systems because multiple receiver readings of known locations

⁶ While the entire IDMM team investigated the conceptual design, credit for writing this chapter goes to Kelly Tilford, Scott Moreland, and Darren Almond.

can be used to improve the accuracy of coordinates at unknown locations, assuming each receiver is "listening" to the same satellites (i. e., they are relatively close together).

The GPS location will be determined simultaneously while the LA-ICP-AES system analyzes a particular sample. In a one-receiver configuration, accuracies of less than ten meters are difficult to achieve in the approximately ten minutes required to analyze a particular sample. When utilizing at least two receivers, a ten-minute sample run can yield accuracies of less than 3 meters when corrections are transmitted from a known-location receiver. In real time kinetic (RTK) configurations, sub-meter accuracies have been achieved, but the RTK process is more labor intensive and prone to failures because each receiver must be in **constant** satellite contact.

Post-processing improves the accuracies of GPS readings. In post-processing, readings taken over the course of a relatively long period are stored at regular intervals. Post-processing this set of data to get average errors in readings can yield accuracies on some high-end equipment in the centimeter range. The major drawback to this approach is the fact that the accurate location data cannot be captured in real-time.

6.2 *In situ* Sampling

In the *in situ* sampling mode, the laboratory moves around the site and the surface sampler is positioned to run the analysis at the sampling location. The following protocol should be followed in the *in situ* sampling mode:

1. prepare the location to accept the surface sampler by removing all rocks or sod and creating a flat sampling surface
2. install the aluminum plate over the prepared surface
3. mate the surface sampler with the aluminum plate
4. obtain GPS location and analyze the sample simultaneously
5. verify sample results and GPS location
6. move surface sampler to next sampling location and repeat

6.2.1 *In situ* sampling data integration protocol

As part of the IDMM design, a GPS receiver would be mounted on the surface sampler used for *in situ* analysis. The capture of the location data would be essentially transparent to the operators. Most GPS receivers have standard RS-232 or RS-422 communication links so the computer used to run each sample could also monitor the GPS system and request sample locations without operator intervention.

In addition to automated location data integration, it would also be possible for an operator to enter sample coordinates through the standard operator interface used to control the rest of the laboratory. This would be a necessary capability of the system, because on some sites it may not be possible to get accurate satellite readings (such as deep valleys, urban areas, or mountainous areas). In some cases the site may already be surveyed or may use a project-based

local coordinate system, in which case the operator should be able to manually enter the known data location.

6.3 Fixed On-Site Sampling

Fixed on-site sampling means that the mobile laboratory is brought to the site and operates in a fixed location, with samples gathered and brought to the lab for analysis. The following protocol should be followed in the fixed location sampling mode:

1. collect sample, assign sample number, flag and number location
2. install sample in sample introduction device
3. run sample analysis
4. determine sample location with GPS independently and correlate with the assigned sample number
5. merge location data with analytical data
6. install next sample and run next analysis

In the fixed on-site sampling mode, the sample location is independent of the mobile laboratory. This allows analysis of either surface or subsurface samples. Samples could be gathered directly by hand on the surface or by a number of subsurface penetrometer methods. This would allow both areal and vertical contaminant analysis, resulting in a 3-dimensional model of contaminant distribution.

6.3.1 Fixed location sampling data integration protocol

The fixed location strategy requires a different approach to identify the location of each sample because the testing equipment never actually resides at the site of each sample. In this scenario location data must be integrated manually through the operator interface, electronically by positioning a GPS receiver at the sample location during the time that the sample is being analyzed, or in batches by merging a file of sample data with a file of location data.

Manual operation through the operator interface would simply require that the sample location (from GPS or other survey techniques) be entered at the completion of each sample run. Electronic location integration would require that the laboratory computer communicate with the remote GPS receiver at the sample site. Batch operation would require a unique sample identifier to be used to log both the sample results and the location data. These data could then be merged after a series of sample runs.

6.4 *In situ* Downhole Sampling

In situ downhole sampling is not presently part of the IDMM design but could be done with the downhole probe under development through the CRADA (cooperative research and development agreement) between TIP and Layne Environmental Services, Inc. The main difference between the proposed IDMM conceptual design and the downhole tool under development at TIP is the placement of the laser head within the sampler rather than conveying the laser beam through

fiber optics to the sampler (as in the TIP design). However, IDMM investigations identified a laser head that may be small enough to be incorporated into the TIP downhole sampler.

The following protocol should be followed in the *in situ* downhole sampling mode:

1. drive casing to desired depth
2. install downhole probe within casing
3. determine downhole sample location (x,y,z) with GPS and enter downhole depth data
4. perform downhole analysis
5. verify sample results and GPS location
6. drive casing to new depth or go to new location

6.4.1 *In situ* downhole sampling data integration protocol

In situ location data demands are essentially identical to the demands of the fixed sampling strategy mentioned earlier. The only exception would be the capture of the z coordinate (depth). This data could either be obtained electronically by monitoring the depth of the sampling penetrometer with sensors, or by simply requiring the operator to manually enter a z offset, or depth, for each sample run.

6.5 Health and Safety Protocols

Site personnel health and safety (H&S) is a critical consideration in the design of any field instrument. In all environmental work, each site is assigned a health and safety officer who is responsible for assuring the safety of all site personnel. Decisions regarding all site work are ultimately the responsibility of this individual. The H&S officer also writes a Health and Safety Plan that determines what activities may be performed at the site and the procedures and personal protective equipment (PPE) requirements for each task. The H&S Plan is written specifically for each site and considers the type of contamination present as well as the likely exposure pathways for site personnel.

To meet H&S considerations, the instruments must be easily operated under a variety of PPE levels and must not inhibit the mobility of the operators in these situations. There are two types of H&S considerations at any site, considerations associated with operation of the equipment and considerations related to exposure of personnel to on-site hazards.

For example, assuring that personnel are not exposed to laser energy during operation would be classified as an equipment operation safety concern. It is also important to design a system that doesn't compromise the integrity of the personal protective equipment and protocols must prevent accidental exposure of the field personnel to site contamination.

The IDMM mobile laboratory is designed to be used in moderate-to-low contamination levels. Two principal design considerations are the health and safety of the operators and harsh equipment decontamination procedures. The design is based on site conditions where the highest

level of PPE and complete decontamination of the system will not be required. These conditions correspond to PPE levels D and C (USEPA 1988). These PPE levels are described below.

6.5.1 PPE Level D

Level D is the minimum PPE level. No respiratory protection is required; limited skin protection is required. Recommended equipment for Level D includes

- disposable coveralls over work clothes
- hard hat
- safety glasses or goggles
- work gloves
- chemical-resistant boots or shoes

6.5.2 PPE Level C

Level C requires limited respiratory protection and skin protection from airborne hazards. Recommended equipment for Level C includes

- chemical-resistant clothing: overalls and long-sleeve jacket; hooded, one- or two-piece chemical splash suit or limited use chemical-resistant one-piece suit
- full-face air purifying respirator
- hard hat
- inner and outer chemical-resistant gloves
- chemical-resistant boots

6.5.3 Equipment operation safety

The component of the IDMM mobile laboratory with the highest hazard potential to the operators is the high-powered laser used for ablation. Two safety measures have been incorporated into the design of the sampling system to provide a safe working environment for the operators.

Before sampling can take place, two conditions must be met to ensure a safe sampling session. First, there are three electric contacts on the bottom of the surface sampler that must come in contact with an imbedded copper ring in the aluminum plate. These contacts will close a circuit and let the controlling computer know that the surface sampler is mated to the aluminum plate. Any break in this circuit will immediately shut down the laser. This will prevent any inadvertent firing of the laser while it is being carried to or from the sampling site and will shut down the laser if the surface sampler tips over during a sampling run.

The second safety measure is a "deadman" switch on the surface sampler which must be set to the firing mode by the operator at the sampling site in order for the sample to be taken. If, for any reason, the operator at the sampling site deems it necessary to immediately discontinue the sampling run, the operator release the "deadman" switch.

6.6 References

USEPA. 1988. *Guidance for Conducting Remedial Investigations and Feasibility Studies Under CERCLA*. U.S. Environmental Protection Agency, Office of Emergency and Remedial Response.

Chapter 7. IDMM Computer and Control System⁷

The IDMM design incorporates comprehensive computer and control systems to coordinate the operation of the mobile laboratory's on-board equipment and instrumentation with the activities of the sampling team external to the lab. A graphical representation of the computer and controls system is given in Figure 7.1 below. The major functions of the computer and control systems are to

- provide a two-way interface to all laboratory and support equipment
- provide a user-friendly graphical user interface
- automate the sampling procedure to the greatest extent possible
- acquire and analyze data
- detect and report errors
- maintain a complete record of critical sampling data
- generate reports

A cost estimate for the equipment required to fulfill these functions concludes this chapter.

Figure 7.1 Computer and control system.

⁷ While the IDMM team researched the computer and control system for the conceptual design, credit for writing this chapter goes to Scott Moreland and Kwi Chuan Ng.

7.1 Equipment Interface

To achieve automation and simplify operator tasks during normal operation, the computer system must maintain two-way communication with, monitor, and control all of the instrumentation and support systems within the laboratory. This interaction and coordination between devices is essential for normal operation as well as error detection and recovery. In cases where the system is unable to immediately recover from an error condition, the operator should be notified and any sampling runs should be safely terminated. In general, the computer controlled devices include

- the laser and laser rastering system
- the inductively coupled plasma-atomic emission spectrometer (ICP-AES)
- the uninterruptible power supply (UPS)
- sensors and controllers to regulate environmental conditions and support systems behavior within the mobile laboratory (support equipment)
- Global Positioning System and other system add-ons

7.2 User Interface

The computer and control system design incorporates a user-friendly graphical user interface (GUI). This GUI presents the mobile laboratory status in a coherent, organized, and easy-to-understand way, including anomalous conditions, available on-line documentation, and help screens. The GUI will also provide the user with a means to control laboratory equipment, initiate and abort sample runs, review system maintenance and activity logs, run system diagnostics, and produce desired reports.

A primary consideration in the implementation of a user interface is the environment in which it will be used. The IDMM conceptual design requires that the sampling and analysis equipment be operated from outside the vehicle. The protective clothing that may be required in hazardous environments prohibits the use of a traditional keyboard. Therefore, the physical interface to the computer will require minimal operator dexterity, such as a joy stick or touch screen interface.

7.3 Automation

To minimize required interactions between the operator and the operations of the laboratory, the computer and control system must have the capacity to handle all details of a sample run automatically. The computer and controls system must be able to flexibly sequence the operations in a sample run and possess contingency plans and countermeasures for anomalous conditions.

7.4 Data Acquisition and Analysis

Data acquisition and storage are integral to the collection of sample data and the monitoring of a sample run. In order to monitor sample runs, data is collected continuously on all critical

instrumentation to monitor for anomalous conditions. Upon completion of a sample run, data collected from the spectrometer is used to quantify sample results. All sample data will be written to a write-once-read-many (WORM) drive to ensure that data can not be modified following a sample run.

These data permit the generation of various reports and plots of contaminant concentration for site administrators, reports of system performance for operators and engineers, and a complete system log for sample verification and chain of custody issues. In addition, the sample data must be readily exportable to geographic information systems and other analysis tools.

7.5 Error Detection and Reporting

The computer system must detect when an error has occurred with any of the mobile lab's instrumentation or support systems. When an error is detected, the operators should be immediately notified of an anomalous condition, and, if necessary, sample runs should cease automatically.

Operators could be kept abreast of system status with red-yellow-green status indicators for each subsystem in the laboratory. Under this scheme, a green status would indicate all systems operational and within specifications, yellow would indicate a warning condition such as a system performance variable that was barely within specifications, and red would indicate a critical error, or operation outside of specifications, that requires system shut-down. In the event of power loss, the computer system must have a disaster recovery procedure that safely shuts down all equipment and instrumentation.

7.6 Critical Data Recording

Information from all critical sensors and equipment shall be incorporated into a common data stream and monitored to insure that all operating parameters are within acceptable levels. These data will be periodically stored on permanent media to form a secure copy of system performance variables. For example, throughout an individual run, periodic data on laser intensity, argon flow rate, instrumentation status, elapsed time, etc., must be preserved as an indication that all systems were operating within specifications during a given sample.

In addition to storing data at predetermined intervals, the computer would continuously store any variables that exceed threshold values throughout the interval that a given variable remains outside of acceptable levels, such as during a yellow status interval. The final results must be stored on the WORM drive and retained for report generation.

7.7 Report Generation

In order to guide on-site personnel through sampling or remediation efforts, immediate access to analysis results is essential. Therefore, the computer and control system should generate various presentable reports while still in the field. These include audit information on the mobile

laboratory's activities, analytical summaries for individual sample locations and for each successful sample run, color contour plots and color three-dimensional plots for the whole site, and complete system logs.

7.8 Cost Estimate

In order to accomplish the tasks described in this chapter, certain baseline computer and control equipment would be required. A preliminary estimate of the cost of this equipment is \$23,150. This total amount breaks out as follows:

Computers	
486DX, 50MHz, EISA-bus, 16 MB RAM	\$4,000
486DX, 33MHz, 4MB RAM	2,100
Extender set, VGA, 0-150'	400
Cables (2)	100
DAS boards (2)	2,000
Operator interface	1,400
WORM drive	2,500
Plotter, 6 pen, A/B	1,300
Printer, color	850
Monitors, 17", flat (2)	7,000
Software—Operating system ^a	<u>1,500</u>
Total	\$23,150

^a Operating system software is assumed to include word processing and other basic utilities. Remaining software, such as plotting software, is available on a share-ware/free-ware basis

Part III

Technical Reports on Components of the IDMM Conceptual Design

Chapter 8. Power Generation and Distribution System⁸

This chapter has five main parts. The first part addresses the sizing of the generator, the second part addresses the fuel type for the generator, the third part addresses the alternating current distribution system used in the unit, the fourth part addresses the uninterruptible power supply, and the final section covers the direct current distribution system.

8.1 Generator Sizing

The sizing of the generator was dependent on the following factors: voltage rating, amperage rating, capacity, weight, and physical size.

These factors were first explored as functional requirements, and when more complete information about the components of the IDMM design was known, decisions for the actual sizing of the generator were made.

8.1.1 Voltage rating

The generator should be capable of operating in the range of 95% to 115% of the nominal operating voltage of 120 VAC and 240 VAC required by the equipment used in the mobile laboratory. The IDMM team wanted the efficiency and stability of a three-phase generator. A delta-connected system is less affected by load imbalances caused by varying quantities of power being drawn from the different phases of the generator. For these reasons, a three-phase, 240 VAC, delta-connected, center-tapped generator was chosen to allow for a three wire (plus ground wire), 120/240 VAC power supply. A line drawing of a delta-connected, center-tapped generator is shown in Figure 8.1.

The center-tap is connected to ground to provide a stable, reliable ground wire connection for the system. 240 VAC power is provided by the BC phase of the generator.

Figure 8.1 Delta-connected, center-tapped generator

⁸ While the IDMM team researched the power requirements and distribution systems for the conceptual design, credit for writing this chapter goes to Doug Shanda.

120 VAC power is provided by the AB and AC phases of the generator through 15 KVA, 2:1 stepdown transformers. The neutral side of each transformer is connected to the grounded center-tap to complete the system ground.

8.1.2 Amperage rating

The amperage rating of the generator should be equal to at least 100% of the non-continuous amp draw plus 125% of the continuous amp draw, where non-continuous amp draw is the sum of the amp ratings of equipment that does not run continuously and the continuous amp draw is the sum of the amp ratings of the equipment that does run continuously. This is in accordance with the National Electric Code-1990 , Article 220-3(a), which is the section outlining branch circuit rating calculations (National Fire Protection Association 1990).

The required amperage output of the generator was determined to be 236.9 A. The amp ratings of the electrical loads are shown in Table 8.1. The IDMM team added 10% to the final value to allow for any future expansion of the load. This resulted in a final required amperage output of 260.6 A. The calculations follow as section 8.7.

8.1.3 Capacity

The capacity of the generator should be a conservative estimate of the power required by the equipment. This should include the power consumption that has been adjusted for load demand, voltage fluctuations, and future expansion.

The power capacity of the generator was determined to be 30 kW. To obtain this value, the demand factor had to be found. The demand factor is a multiplying factor that indicates how large the power capacity has to be, given the total power required by all equipment in the laboratory. The demand factor was obtained from Equation 1

$$\text{Demand Factor} = \text{Maximum Demand} \div \text{Connected Load} \quad (1).$$

where maximum demand was the largest power load demand over any given period of time and the connected load was the sum of all the power requirements of all equipment connected to the system. As a probable worst case, we assumed that all equipment would run at the same time except for the air conditioning unit and the heater and heating devices. Using the values of 28.318 kW for maximum demand and 32.314 kW for connected load, we calculated the demand factor to be 0.876. The required base load demand is the base amount of power required by the equipment in the unit and was determined from Equation 2

$$\text{Load Demand} = \text{Demand Factor} \times \text{Total Load Power} \quad (2).$$

Using the total load power in kilowatts from Table 8.1, the required base load demand was found to be 28.318 kW.

	120/240 VAC Equipment Ratings		
	Voltage (V)	Current (A)	Power (kW)
Spectrometer	200-240	30.0	7.200
ICP	190-260	20.0	4.800
Laser	220	20.0	4.400
AMN for ICP	220	0.5	0.110
Rastering system	120	2.5	0.300
Battery charger	120	25.0	3.000
Water recirculator	120	6.0	0.720
Chiller	120	12.9	1.548
Air conditioning	120	30.1 operating 38.0 starting	3.612 operating 4.560 starting
Heating devices	120	20.0	2.400
Heater	120	13.3	1.596
Lighting (exterior)	120	12.5	1.500
Printer and plotter	120	0.8	0.096
Computers (2)	120	5.0	0.600
Monitors (2)	120	3.6	0.432
Total (operating)	---	202.2	32.314

Table 8.1 AC equipment ratings.

We also took into account a possible voltage drop at the generator output due to a device starting current. The only starting current that could cause a significant voltage fluctuation was that of the air conditioning (A/C) unit. The starting current of the suggested A/C unit as measured by the manufacturer was 38 amps. The starting power demand of the A/C unit was determined to be 4.560 kW. This value minus the full load power demand of the A/C unit was added to the required capacity, which resulted in a load demand of 29.266 kW. Also, to help eliminate voltage fluctuations and equalize the load on each phase of the generator, one phase of the generator was dedicated to the A/C unit, the heater, and the heating devices.

We then added a small safety factor to the adjusted load demand value to raise the capacity to a standard generator size of 30 kW. The calculations follow in section 8.7.

8.1.4 Weight

The generator must weigh as little as possible while still being capable of performing its intended function.

The weight of the generator will depend mainly on the required voltage, amperage, and capacity ratings. The lightest generator that can be found which meets those requirements yet be capable of withstanding the rigors of a mobile installation is preferred.

8.1.5 Physical size

The physical size of the generator should not exceed the length x width x height dimensions of 7' x 3' x 4'. This will allow the generator to be readily placed on the vehicle platform.

The physical size of the generator will also depend mainly on the required voltage, amperage, and capacity ratings. The smallest generator that will meet those requirements in a mobile setting is preferred.

8.2 Fuel

The generator must be capable of operating in a mobile environment with its own fuel supply.

Liquid propane (LP) was selected to fuel the generator because LP powered generators are slightly more efficient, require less maintenance, start easier, and burn cleaner than diesel generators. On the other hand, diesel generators may last longer and weigh about 25% less, but they have more maintenance problems and are harder to start, especially in cold weather. An LP powered generator may also be operated indoors, which would be desirable if shore power (power supplied through a cable connecting the unit distribution system to the local power system) could not be obtained.

The availability of LP fuel was also investigated. According to the National Propane Gas Association (1993), the production of the LP fuel and the number of LP distribution centers

around the country are projected to increase in the next seven years. Even now, sufficient LP distribution centers are located throughout the country to ensure ready access to LP fuel.

The mounting and ventilation of the generator is planned in accordance with Article 551-30 of the National Electric Code-1990 (National Fire Protection Association 1990).

Other possibilities were considered for power generation. A two generator system was considered, one generator for the A/C and the heater, and one generator for the balance of the equipment in the unit, providing one power supply for the large inductive ("noisy") loads and one "clean" power supply for sensitive equipment. Also, this design would have allowed one generator to provide limited emergency power in the event the second became inoperable. We opted not to use this design because of the added weight of two generators, the extra space that two generators would take, and our ability to provide good, "clean" power to sensitive equipment even with the A/C load connected to the same generator. The weight and size of each smaller generator is nearly comparable to that of the larger generator. Also, the cost of two small generators is almost the same as one large generator. Although the redundancy of the generators could be a benefit in the field, we felt that with proper maintenance, a breakdown is not very probable.

8.3 Alternating Current Distribution System

The internal alternating current distribution system was designed in accordance with the specifications given in Article 550 and 551-47 through 551-57 of the National Electric Code-1990 (National Fire Protection Association 1990), which outlines distribution systems in mobile homes. The IDMM team felt this was the closest applicable article since the unit is primarily powered by 120/240 VAC as opposed to 12 VDC, in which case the unit would be more like a recreational vehicle.

A line conditioner was investigated for placement in the two phases of the generator which supply the sensitive equipment in the unit, such as the computers and spectrometer. The line conditioner was not used for the following reasons: (1) the weight was approximately 800 pounds, (2) the size was approximately 5' x 2' x 2', (3) the cost was approximately \$20,000. Instead of using a line conditioner, the generator capacity was increased to help avoid voltage fluctuations at the generator output.

A shore power source in addition to the generator was designed into the distribution system. A single, four wire cable that can connect to a standard 120/240 system is linked to the distribution system of the mobile laboratory to supply power to each of the three circuits that the generator supplies. The cable and generator are connected to the distribution system through a fused disconnect box. The fuses provide additional overcurrent protection for the system. The disconnect box is a break-before-make switch and allows only one of the supplies to be connected to the distribution system at a time. This eliminates the possibility of connecting the two supplies together out of synchronization. It also prevents the different phases of the generator from being connected together through the cable connection.

8.4 Uninterruptible Power Supply

An uninterruptible power supply (UPS) is necessary to maintain power to the computer system and the ICP exhaust fan until the ICP can be properly shut down in the event that the normal power supply, either the generator or the shore power, is lost.

A small UPS with an internal battery and inverter was selected. The unit is capable of delivering 10 A of current at 120 VAC for at least 30 minutes, which is enough time for the systems to be shut down. The unit weighs approximately 50 pounds and measures 24" x 6" x 8".

8.5 Direct Current Supply and Distribution System

The direct current supply and distribution system is necessary to provide power to the interior lighting, provide power to the relays and some of the instrumentation, start the generator, and provide power to other miscellaneous equipment.

	12 VDC Equipment Ratings	
	Current (A)	Power (W)
Refrigerator	4.8	57.6
Lighting (indoor)	8.0	150.0
Instrumentation and relays	15.0	170.0
Water pump	5.0	60.0
Leveling jacks	15.0	170.0
Burglar alarm and fire alarm	15.0	170.0
Miscellaneous	5.0	60.0
Total	67.8	837.6

Table 8.2 DC equipment ratings.

The equipment powered by the 12 VDC distribution system is shown in Table 8.2. The total DC amperage required by the unit is 67.8 amps.

For this system, two 12 VDC batteries were specified, mainly because two batteries are required to start the generator. The system will normally be energized through the batteries by an AC-powered battery charger. The battery charger is approximately the size of one battery and weighs about 40 pounds. The batteries will provide power to the DC lighting system and other critical DC equipment for at least 8 hours if the normal DC power supply (the AC-powered battery charger) is lost.

The installation of the batteries and the DC distribution system is planned in accordance with Articles 550, 551–47 through 551–57, and 480 of the National Electric Code–1990 (National Fire Protection Association 1990).

8.6 Calculations

To calculate the capacity and amperage requirements for the generator the power and current requirements for non-continuously operating equipment and for continuously operating equipment must first be identified. Non-continuously operating equipment includes that which would never all be operated at the same time; i.e., the air conditioning unit or the heater and other heating devices. All other equipment was conservatively designated as continuously operating since, even though very unlikely, it could all be operated at the same time.

8.6.1 Capacity calculations

To calculate the required generator capacity the demand factor for the unit was first determined using Equation 1

$$\text{Demand Factor} = \text{Maximum Demand} \div \text{Connected Load} \quad (1).$$

The maximum demand is the largest power load that might be required at any given time. To obtain this figure the power requirement of the continuously operating equipment (24.706 kW) was added to the largest power requirement of the non-continuously operating equipment (3.612 kW from the air conditioning.) (Note that the heater plus heating devices total of 3.996 kW was not used since the air conditioning required 4.560 kW at starting.) The maximum demand totaled 28.318 kW. The connected load is the sum of all the power requirements of all the equipment in the unit, which was equal to 32.314 kW. The demand factor was calculated to be 0.876.

$$\begin{aligned} \text{Demand Factor} &= 28.318 \div 32.314 \\ &= 0.876 \end{aligned}$$

The base load demand was then determined from Equation 2

$$\text{Base Load Demand} = \text{Demand Factor} \times \text{Total Load Power} \quad (2).$$

The total load power accounts for the power factor correction necessitated by reactive loads. Since very little of the load in the unit is reactive, the total load power was set equal to the connected load, 32.314 kW. The base load demand was found to be 28.318 kW.

$$\begin{aligned} \text{Base Load Demand} &= 0.876 \times 32.314 \\ &= 28.318 \text{ kW} \end{aligned}$$

The base load demand was then adjusted to minimize the voltage fluctuations that could be caused by a large inductive load starting, such as the A/C compressor. The A/C starting power requirement was found to be 4.560 kW. The A/C steady state power requirement of 3.612

kW was then subtracted from this value to give the additional power required for the A/C starting, 0.948 kW.

$$4.560 - 3.612 = 0.948 \text{ kW}$$

This value was then added to the original base load demand, yielding an adjusted base load demand of 29.266 kW.

$$28.318 + 0.948 = 29.266 \text{ kW}$$

Allowing a small safety factor of approximately 2.5% yielded a final required generator capacity of 30 kW, a standard generator size.

$$1.025 \times 29.266 \approx 30 \text{ kW}$$

8.6.2 Amperage calculations

First, the amp ratings of the non-continuously operating equipment were totaled (63.4 A) and multiplied by 1.00 (100%), as required by the NEC. Then, the amp ratings of the continuously operating equipment were totaled (138.8 A) and multiplied by 1.25 (125%). The total amp draw was then calculated to be 236.9 A by Equation 3

$$\begin{aligned} \text{Total Amp Draw} &= (1.00 \times \text{Non-continuous}) + (1.25 \times \text{Continuous}) & (3). \\ &= (1.00 \times 63.4) + (1.25 \times 138.8) \\ &= 236.9 \text{ A} \end{aligned}$$

Ten percent was added to this value for a safety factor and future expansion yielding a final required generator amperage of 260.6 A.

$$\begin{aligned} \text{Required Amperage} &= 1.10 \times \text{Total Amp Draw} \\ &= 1.10 \times 236.9 \\ &= 260.6 \text{ A.} \end{aligned}$$

8.7 References

National Fire Protection Association. 1990. *National Electrical Code—1990*. Quincy, MA: NFPA.

National Propane Gas Association. 1993. *Outlook for the Gas Liquids Industry: 1985–2000*.

Chapter 9. Spectrometer Comparison and Selection⁹

This chapter has two parts. The first part gives a brief overview of spectrometry in the context of the IDMM design. This overview section first discusses the signals measured by both types of spectrometers when performing the elemental analysis, followed by a comparison of their performance, followed by a discussion of the functional requirement and design parameters for each type of spectrometer. The second part of the chapter describes the process used by the IDMM team in making a hypothetical selection of a spectrometer for the IDMM mobile laboratory.

9.1 Spectrometry Overview

The IDMM design uses a spectrometer for elemental analysis of the ablated sample. Two types of spectrometers—atomic emission spectrometers (AES) and mass spectrometers (MS)—were investigated by the IDMM team as possible candidates for inclusion in the IDMM conceptual design. The IDMM conceptual design is based on sample analysis performed by laser ablation for obtaining a sample which is transmitted to an inductively coupled plasma torch. From this point, either atomic emission spectrometry or mass spectrometry may be used to analyze the sample. Note that the IDMM team selected AES as the basic spectrometer for the IDMM conceptual design. However, our system is designed on a modular basis and has the flexibility to incorporate MS with only slight modifications.

In ICP-AES analysis, the sample to be analyzed is excited and associated into individual atoms and ions by the ICP torch. When the excited atoms and ions relax, they emit radiance characteristic of the elements present. The AES then resolves the emitted radiance into its constituent wavelengths and isolates each one of interest. According to Thompson and Barnes, when the spectral radiance passes through an exit slit of the spectrometer, the intensity (i.e., the total spectral radiance) which consists of photons originating from analyte atoms plus photons from the remaining plasma, is measured by the instrument. Thus, to obtain the net response from the analyte atoms alone, the background response (i.e., the spectral radiance that would have been produced if no analyte atoms were present) must be estimated and subtracted from the total (Thompson and Barnes 1992). Since these intensities are proportional to elemental concentration in the sample, one is able to obtain the elemental concentration of interest in the sample.

In ICP-MS, the sample to be analyzed is excited to a plasma in the same manner as in ICP-AES. "The plasma flows around the tip of a water-cooled metal cone called the sampler. This cone has a circular orifice of 0.5-1.0 mm diameter drilled into its tip" (Houk 1986, 98A). According to Houk, the plasma flows through the orifice and a vacuum chamber. The pressure in the vacuum chamber is low enough for plasma to be transmitted to the mass analyzer. Ions of selected mass to charge ratio (m/z value) "leave the mass analyzer and are deflected into an electron multiplier for detection" (Houk 1986, 100A). The intensity of the detected signal is

⁹ While the entire IDMM team researched spectrometers, credit for writing this chapter goes to Kwi Chuan Ng, Sarina Tantri, and Matt Reid.

proportional to the number of ions arriving. Thus, measurement of elemental concentration of interest is possible.

9.2 Comparisons of ICP-AES and ICP-MS

Both ICP-AES and ICP-MS serve the same purpose of performing the analytical elemental analysis in the IDMM conceptual design. Their basic differences on performance are related to detection limits, isotopic discrimination, interference, analytical concentration range, maintenance, control over interference, and ruggedness.

9.2.1 Detection limits

ICP-MS offers very low detection limits. "Current detection limits for the direct analysis of solution samples are in the range of 1 to 100 pg/ml for most elements. In most cases, these detection limits are 100-1000 times superior to those that can be routinely achieved by ICP-AES" (Horlick and Shao 1992, 552).

9.2.2 Isotopic measurement

According to Horlick and Shao (1992), qualitative identification of an element can be achieved by MS due to the simplicity and uniqueness of the mass spectra. Thus, ICP-MS has the ability to measure elemental isotope ratios. In ICP-AES, the emitted spectral lines are very complicated and difficult to resolve. The complicated isotopic splitting of optical transitions is difficult and therefore isotopic analysis is almost impossible in ICP-AES.

9.2.3 Interference

Interference is a problem which occurs when the spectrometer is unable to distinguish the signal of the specific analyte from the signals of other ions. According to Thompson and Barnes, ICP-MS exhibits larger interference effects than ICP-AES. The problems of mass-overlapping (i.e., problems which results from the inability of MS to distinguish the ions which have the same mass, e.g. $^{40}\text{Ca}(\text{Ar}^+)$, $^{56}\text{Fe}(\text{ArO}^+)$, and others), oxide and hydroxide formation which cause serious spectral interference (as almost all analyte and matrix elements form monoxide and hydroxide ions to some extent in ICP-MS system), and selective volatilization which arise in ICP-MS do not occur in ICP-AES (1992, 277).

9.2.4 Analytical concentration range

AES can determine the elemental concentration in a wider range than MS. Therefore, dilution might be needed in MS analysis for a high concentration analyte.

9.2.5 Maintenance

ICP-AES requires less maintenance as only light is passed through the instrument. "Thus, highly radioactive analytes can be studied by ICP-AES without contamination of the spectrometer" (Edelson 1992, 357). On the other hand, ICP-MS counts the ions emitted by plasma species. Thus, more maintenance is required by ICP-MS.

9.2.6 Control over interference

"In ICP-MS, spectral overlap problems arise primarily from the generation of molecular species from sample, plasma, and matrix constituents, while in ICP-AES spectral overlap problems are a result of the spectral complexity of certain constituents. We cannot alter the atomic spectral complexity of a plasma constituent (e.g., we cannot change the spectrum of Fe), and high resolution in ICP-AES is the best solution to spectral overlap problems. But, by changing plasma conditions and plasma chemistry, we can alter the nature of plasma molecular constituents (i.e., mixed gas plasmas), hence control and eliminate certain spectral interferents in ICP-MS" (Horlick and Shao 1992, 571).

9.2.7 Ruggedness

According to Houk (1993), unlike ICP-AES, which requires accurate alignment of optics, ICP-MS is less susceptible to temperature, shocks, and vibration.

9.3 Functional requirements and design parameters of ICP-AES and ICP-MS

Both ICP-AES and ICP-MS give rapid multi-element analysis quantitatively and qualitatively. Even though there are differences in both instruments in the aspects of performance, for the purpose of IDMM design, the basic functional requirement for either kind of spectrometer is the same: the instrument should analyze soil samples to determine radioactive or other elemental contaminants (such as uranium, thorium, lead, and chromium) of varying degrees of concentration.

To obtain quantitative and qualitative measurement, the instrument must analyze with high sensitivity and accuracy. Therefore the spectrometer must be capable of the following

- analyzing samples introduced by ablation
- determining multiple element ratios
- obtaining detection limit for elements smaller than one order of magnitude of the remediation levels
- measuring fast transient signals by a rapid scan through the entire spectrum range

To get accurate measurements, it is necessary to minimize the occurrence of spectral interference, which result from the inability of a spectrometer to resolve a spectral line emitted by a specific analyte from light emitted by other atoms or ions. In an ICP-AES system, spectral interference is produced because of the imperfections of the instrument, such as finite resolving power, aberrations, and misalignment of the optical components. As for the ICP-MS, spectral interference arises primarily from the generation of molecular species from sample, plasma, and matrix constituents. To minimize these instrumental effects, a high resolution system is desired for the measurements. A high resolution system will be able to resolve the width of spectral lines emitted by atoms and ions produced in an atmospheric-pressure plasma. The line widths are

typically in the range of 0.2 to 0.6 nanometers for ICP-AES. As for ICP-MS, the resolution is desired to be around 0.6 AMU (atomic mass unit).

For ICP-MS, doubly charged ions and molecular oxide ions are observed in the spectra and can produce spectral interference problems. In laser ablation studies, the ionization energy is high enough to cause an element to release another electron which finally leads to the doubly charged ions. Then, the mass-to-charge ratio of this doubly charged ion will interfere with other elements with the same mass-to-charge ratio. It is desirable to have low level of doubly charged ions of elements, especially barium (Ba), since it has the highest level of doubly charged ions among other elements. The observed doubly charged ions level for Ba is 2.7%. On the other hand, oxide ions are formed because of the interaction of ionized elements generated from ICP with oxygen that is contained in water vapor. The oxide ions will interfere with other elements that have the same mass-to-charge ratio with this oxide form. Thus, it is desirable to have a low percentage of oxide levels. Barium is also the element which has the highest level of oxide, observed to be around 0.2%.

Memory effect is also a primary concern in the performance of ICP-MS. Memory effect is the percentage of residual signal of the sample signal when a new sample is introduced to the mass analyzer. So, it is desirable to have relatively small percentage of memory effect within 1–2 minutes of running.

Since the whole system will be in a mobile configuration, the instrument must withstand environmental effects (such as temperature, humidity, and power fluctuation), the effects of shock due to rough terrain, and be of minimal size and weight.

In order to withstand the shock due to rough terrain, the instrument must be shock mounted either by the manufacturer, vendor, or installer. The instrument must be as insensitive as possible to temperature and humidity fluctuations.

To meet the design requirements for fast analysis, the instrument must analyze samples in near real-time operation and report results in a minimum time. Thus, the instrument must have software that has the capability of rapid time acquisition, multi-tasking, and producing results in near-realtime.

Because of the self-contained mobile configuration, the instruments must be power efficient. Therefore, it is important that the spectrometer consume as little power as possible. Also, the instrument must be relatively small, compact, and weigh no more than 2200 lb.

Finally, the spectrometer must have a high degree of reliability. It must be durable, have low maintenance requirements, and be able to function in the field for numerous days without maintenance or repair that would require moving the vehicle off-site.

9.4 IDMM Spectrometer Selection Process

A sub-group of the IDMM team was given the task of surveying AES spectrometers on the market and selecting models which were best suited to the IDMM system's needs. It is important to remember that our determination and our results are only valid for the system that we are proposing and are not meant to be an overall judgement of spectrometers. We limited our survey to vendors located in the United States for ease of contact and service. From eight spectrometer manufacturers who produce simultaneous ICP-AES systems, we identified the following eleven models as possible candidates for our design:

<u>Company</u>	<u>Models</u>
Baird Corporation	Baird ICP 2000
Fisons Instruments	Accuris
	ARL 3560
	Maxim
Instruments SA, Inc.	JY46P
Leeman Labs, Inc.	PS3000
Leco Corporation	Leco ICP-3000
Perkin-Elmer Corporation	Optima 3000
Spectro Analytical Instruments	Spectroflame Modula
Thermo Jarrell Ash Corporation	IRIS
	61E

In the process of selecting spectrometers, we arbitrarily assigned the above models with generic names such as Model 1, Model 2, Model 3, and so on; the model number designations were assigned in no particular order.

9.4.1 Evaluation characteristics

We established a uniform set of characteristics to judge the models, and used a matrix of these characteristics to determine the best model for our system. Our selection matrix incorporated a multiplicative weight between one and ten for each characteristic, as well as a number between one and ten as to how each model performs that characteristic. The two numbers are then cross-referenced and multiplied together; each product is then summed to produce a total score for each model, with the highest score representing the most favorable spectrometer. The total score is then matched with the cost of the system to determine its cost effectiveness.

Cost was not included in the matrix because we felt that it was so important as to receive a separate treatment. Other key decision factors which were used in the final decision were vendor reputation and spectrometer software. These were not incorporated into the matrix because they were difficult to quantify. They were left to break ties between models after the matrix was done.

After selecting the characteristics we granted each one a weighting factor from one to ten. This was done by establishing a relative weight between each characteristic and coming to a

consensus about assigning each weight. The characteristics that we selected and their corresponding weights are shown below.

9.4.1.1 Resolution (10) This is the resolution in nanometers in the first order for the optics. The unit with the best resolution was given a ten and the worst was given a zero. The remaining scores were interpolated to give a number between zero and ten.

9.4.1.2 Detection Limits (8.5) We compared data for detection limits using the following five elements: Aluminum, Chromium, Iron, Lead and Sodium. The detection limits for these elements were summed and the model with the best (lowest) detection limits was given a ten, while the model with the worst detection limits was given a zero. The remaining models were interpolated to give a value between zero and ten.

9.4.1.3 Volume (5) This refers to the overall dimensions of each system. We calculated the volume of space that each unit occupied and rated the one with the smallest overall volume a ten, and the largest a zero, and interpolated the volume of the remaining models between zero and ten.

9.4.1.4 Shocks (4.75) This refers to whether the unit came equipped with special optics lock-downs or special rugged hardware. Units with shock mounting received a ten, while units without received a five.

9.4.1.5 Power (3) This refers to the total power consumption of the spectrometer and ICP. The unit with the lowest power consumption was given a ten, while the unit with the greatest power consumption was given a zero, and the remaining models were interpolated between zero and ten.

9.4.1.6 Weight (2.5) This refers to the overall weight of each model. The lightest unit received a ten, while the heaviest received a zero and the remaining models were interpolated to values between zero and ten.

9.4.1.7 Thermostatic (1.75) This refers to the temperature control of the spectrometer. Units that were thermostatic received a ten, while others received a five.

9.4.1.8 Argon (1.5) This designates whether the system incorporates an argon purge for the optics or another system such as vacuum or nitrogen purge. Since our system uses argon gas to carry the ablated samples from the plasma torch, argon purge is more favorable. So, we decided systems specifically designed for argon purge received a ten, while systems without argon purge were given a five,

9.4.2 A note on weights

In general, higher weights were given to things that could not be modified by our team, like resolution. Other characteristics such as shock mounting and temperature control were given

lower weighting because we felt we could engineer around some of the negative aspects of these characteristics.

9.4.3 Matrix analysis

After determining the weights, our group used a spreadsheet to calculate the total scores for each model of AES Spectrometer as shown in Figure 9.1.

After scoring the spectrometers, we did an informal sensitivity analysis of the results to determine if small changes in weights could drastically effect the scores. We modified some or all of the weighting factors and recalculating to see how the scores were affected. We did not find any significant changes in the results of the study when this was done.

With the objective of selecting one spectrometer, we decided to have four models in our first selection. As can be seen from Figure 9.1, the first selection can be achieved by setting the break point to be 250. Therefore, Models 3, 9, 10, and 11 were selected.

Next we turned to cost to compare the remaining four spectrometers. Figure 9.2 shows a plot of score versus cost for all of the spectrometers in the survey. The models which have high score with low cost are favorable. Therefore, Models 3, 9, and 11 remained for consideration. In order to decide between the remaining three spectrometers we compared reputations of the manufacturers by looking at the following three factors:

- number of years in business selling AES spectrometers,
- number of models sold in the last year, and
- interviews with users of various systems.

9.4.4 Conclusion

Through our analysis of manufacturer reputation, it was determined that the company of Model 11 was the largest of the three remaining companies and had the largest number of units in the field.

We also looked at the score per unit cost of the remaining three systems. Model 11 scored the highest, indicating that it was the best spectrometer for the money. For these reasons, we decided that Model 11 would be the ideal spectrometer to incorporate into our LA-ICP-AES system. We also recognized that the score was close and that any of the top four spectrometers would probably serve the needs of a mobile LA-ICP-AES system.

Figure 9.2 Score/cost ratio.

9.5 References

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Chapter 10. Rastering Requirements¹⁰

Laser ablation is the sample introduction method used in the IDMM analysis technology. In order to accurately characterize a site, a representative sample of each sampling location is required. To obtain a representative ablated sample, the laser is rastered over the soil surface by a rastering system. This chapter presents functional requirements for the rastering system design based on the following factors: the sample area, the rastering pattern, the rastering velocity and acceleration, and the rastering system size and weight.

10.1 Sample Area

Initial research at Ames Laboratory (performed by Dr. Art D'Silva's Spectrochemistry Group) showed that a sample covering about one square inch of the surface reasonably represents characteristics of soil in its vicinity. While the specific grid or pattern of sampling locations is site-dependent, the area ablated at each sample location remains constant. The ablation cell and the rastering system are both designed to meet the one square inch sample area requirement. A significantly larger area would require a larger ablation cell and a larger rastering system. Therefore, the rastering area is kept close to the necessary one square inch minimum.

10.2 Rastering Pattern

An important requirement of the rastering pattern is to avoid overlap of ablation craters, (i.e., ablation of a previously ablated region). Upon ablation, the chemical and physical properties of the soil may change and, therefore, particles collected from a previously ablated area may produce unrepresentative data. Another requirement is that as much as possible of the one square inch area should be uniformly ablated during sampling within a reasonable period of time, i.e., 1 to 2 minutes.

Currently, the rastering in the MDLEST is performed by a precision x-y positioning table which is programmed to form a spiral pattern on the sampling surface. A spiral allows the rastering table to remain in a smooth curvilinear motion instead of a rectilinear, stop-and-go motion. In rectilinear motion, the momentum of the table and attached components may be greater than the table actuators are capable of overcoming rapidly enough to prevent crater overlapping. Furthermore, the large accelerations required for such rapid starting and stopping associated with a rectilinear rastering pattern will subject the table and attached components (e.g., the compact laser and optics) to jarring and vibration. On the other hand, the first and second spatial derivatives (velocity and acceleration) of a spiral rastering pattern are nearly constant, making the a spiral pattern the ideal rastering pattern for the IDMM design.

A minimum spiral rastering diameter of 1.13" is required to cover the specified one square inch of ablated sample area. Therefore, the x-y positioning table must be capable of moving at least 1.13" in both the x and y directions. The IDMM team found several tables with x

¹⁰ While the entire IDMM team investigated the conceptual design, credit for writing this chapter goes to Zia Haque and Ralph E (Pat) Patterson III.

and y ranges of motion of 2". Such tables not only meet the minimum motion requirements, but they also allow for future expansion without being excessively large.

10.3 Rastering Precision

The rastering system must be able to position the laser spots with sufficient precision to prevent overlapping of successive laser spots. Providing a small buffer distance between each spot reduces this requirement. However, an excessively large buffer increases the maximum velocity required of the system and reduces the effective area available for ablation, possibly shortening the sampling time below the desired one minute minimum for a large spot diameter. A 10 μm buffer appears to be an acceptable compromise. Thus the rastering system must be able to position the laser spots with a precision of $\pm 5 \mu\text{m}$.

10.4 Rastering Velocity and Acceleration

The rastering system must be able to move at a velocity sufficient to prevent the overlap of laser ablation spots at the fastest probable laser repetition rate and largest probable laser spot diameter. For the laser power density of 10^{10} W/cm^2 and the laser specified in Chapter 14, these maximum conditions are 30 Hz and 610 μm (including a 10 μm buffer specified above). Therefore, the maximum probable rastering velocity is 18.3 mm/s (610 $\mu\text{m} \times 30 \text{ Hz}$). Including a safety factor of 1.7 mm/s the maximum rastering velocity specification is 20 mm/s.

Even if dynamic focusing is employed (see section 11.2.2 of Chapter 11, Laser Focusing) the maximum z-axis focusing velocity will be much slower than the maximum rastering (x-y axes) velocity. The maximum grade of the sample surface, even for a very poorly prepared sample location, should be significantly less than 10%. For this worst case grade and a maximum laser spot diameter and separation of 610 μm , a maximum z-axis velocity of 1.84 mm/s is required. With a small safety factor, a maximum z-axis velocity of 2 mm/s is specified.

The rastering (x-y axes) acceleration required for a spiral rastering pattern is quite modest, even for the maximum laser spot diameter and separation, since the second spatial derivative (acceleration) of the spiral is small after constant rastering velocity is achieved and since several overlapping spots can be tolerated at the beginning of a rastering cycle. However, if dynamic focusing (z axis) is employed, the system must be capable of accurately tracking the changes in sample surface elevation. For the worst case conditions described above, a maximum z-axis acceleration of $4,392 \text{ mm/s}^2$ is required to track the surface without error. Because this may be an unacceptably large acceleration, a reduction in the rastering system's ability to track very rapid elevation changes may be required.

10.5 Rastering System Size and Weight

The size and weight of the rastering system should be minimized as much as possible since it must be contained in the portable surface sampler. The dimensions of the system, including allowances for maximum travel, should not exceed 12" x 12" x 12". The weight of the system should not exceed 12 lb.

Chapter 11. Laser Focusing¹¹

In Chapter 5, Technical Process Overview, the requirement is established to maintain a minimum power density of 10^{10} W/cm² at a wavelength of 1064 nanometers to achieve uniform, non-selective ablation. In Chapter 14, Laser Requirements and Selection, the specifications for an acceptable laser are identified. Chapter 14 further shows that, for the specified laser operating at a typical pulse repetition rate of 20 pulses per second and pulse length of 15 nanoseconds, the laser beam must be focused to a diameter of 400 micrometers. Three different methods to attain this focus are presented in this chapter.

11.1 Focusing Requirements

Focusing the laser to a 400 micrometer diameter is readily accomplished with a standard double-convex or plano-convex lens. The focused diameter is adjusted by moving the lens with respect to the sample surface with a linear positioner. To minimize the size of the surface sampler and to interface with the ablation cell properly, the focal length of the lens must be short; e.g., approximately 4 inches.

For these laser and optics parameters, the lens must be located 3.748 inches from the sample surface to achieve the required 400 micrometer diameter focus. Errors in positioning the lens cause a degradation of the desired power density as shown below. As seen in Table 11.1, the power density of the laser drops rapidly with vertical positioning error. Maintaining a positioning error of 0.01 inch or less will ensure less than 10% degradation from the desired power density.

Error (inch)	Focus Diameter (micrometer)	Power Density (W/cm ²)	Degradation (%)
0.01	415.9	0.925×10^{10}	7.5
0.02	431.8	0.858×10^{10}	14.2
0.05	479.4	0.696×10^{10}	30.4
0.10	558.8	0.512×10^{10}	48.8

Table 11.1 Power density degradation.

11.2 Focusing Methods

Three different methods for laser focusing are discussed in this section. These three methods are 1) detection of laser intensity via reflection, the method currently in use by the MDLEST; 2)

¹¹ While the entire IDMM team investigated laser focusing, credit for primary research and writing this chapter goes to Zia Haque.

focusing by photodiode array monitoring; and 3) sound travel measurement. Methods 2 and 3 have not yet been tested by the Ames Lab Spectrochemistry group and are merely ideas to be explored further. Therefore, design details for methods 2 and 3 are not presented.

11.2.1 Detection of laser intensity via direct reflection

A photodiode detects the intensity of the laser reflection from the sample surface which is assumed proportional to the incident laser power density. This method is currently in use by the MDLEST and has provided satisfactory results. The configuration shown in Figure 11.1 provides for a dual purpose. The laser output power density is measured using photo diode #1 placed in the direct partial reflection path, while the laser intensity on the sampling surface is measured using photodiode #2. The output from #1 is used to monitor the efficiency of the laser and its delivery system and to ensure that adequate power is being delivered from the laser. The output from #1 is also input to the focusing circuitry to obtain a ratio between the reflection intensity and the laser input intensity. Forming this ratio helps nullify the effect of laser power instability during the focusing process.

A plot of the form shown in Figure 11.1 can be obtained from the ratio as the laser delivery system is moved vertically starting from its upper limit. The signal from photodiode #2 is obtained by effectively re-imaging the laser spot from the sampling surface, back through the focusing lens off the partial reflector, and on to the photodiode window. An aperture placed in

Figure 11.1 Laser focusing via direct reflection.

the reflection path lets through a beam of light of the desired focus diameter and prevents all energy outside of the aperture from reaching the photodiode. In effect, when the laser is out of focus on the soil surface, the image of the reflection formed on the aperture is large and hence only a fraction of the energy is allowed through. The intensity or energy level detected by the

photodiode remains constant for as long as the laser spot size remains smaller than the aperture. However, the detected intensity decreases as a squared function of the spot diameter (which is indicated on the plot in Figure 11.1 by the parabolic slope on either side of the focused position), once the spot size begins to increase beyond the aperture. Therefore, the aperture enables the detection of the vertical position for an acceptable range of power density and amplifies the non-focused effect making it easier to monitor. The focusing circuit design for Method 1 is shown in Figure 11.2.

The laser pulse is short, with a length of no more than 7-8 nanoseconds, making it difficult to sample and measure. In the photodiode charged carriers are created in proportion to the incident light intensity. The output pulse is significantly lengthened due to the 10

Figure 11.2 The focusing circuit in block form.

nanosecond risetime of the diode. However, the total charge created is proportional to the total incident light energy and, since the pulse length is constant, is proportional to the degree of focus. The voltage of this pulse can be measured at times fixed with respect to the laser "firings" and can be used to establish the focused position. A combination of sample and hold and analog to digital conversion is used to perform the sampling.

It is important that each pulse is sampled at precisely the same time. The microprocessor possesses an inherent jitter due its limited clock rate which causes a variation in the recurrent

sampling times. If the extent of the jitter can be determined, the circuit can be designed to overcome the variation. The 2-stage integrator further lengthens each photodiode output pulse such that given the resolution of the A/D converter, the variation in the sampling cycle does not effect the final output. The schmidt trigger along with a delay in the CPU times the sampling of the pulse.

The sampled analog pulses from the two photodiodes are then converted to digital form and transmitted to the lab computer. The algorithm in the lab computer ratios the two outputs to obtain the plot shown in Figure 11.1. The algorithm then detects the peak of the plot to determine the best vertical position.

11.2.2 Laser focusing using off-axis reflection

It may desirable to dynamically adjust the focus of the laser as it rasters over a rough or warped surface. One approach to achieve this dynamic focusing is to use a lens to focus the laser image reflected off the sampling surface. If a convex lens is placed at a fixed, known distance and angle from the focal point of the laser focusing lens, photodiodes can be used to dynamically maintain the focused position using standard feedback control techniques. The advantage of this technique is that by appropriately placing photodiodes in an array, one can easily determine the relative position (higher or lower) of the laser delivery system. Furthermore, by observing predetermined positions of the array, as shown in Figure 11.3 , any desired spot size can be obtained.

A senior design team from the Electrical Engineering and Computer Engineering Department at Iowa State University is currently developing and testing this technique. Their initial research has shown positive results and the successful implementation of this approach, shown in Figure 11.3, seems possible. Both the photo-detection and direct reflection methods as

Figure 11.3 Configuration for laser focusing using photo detection.

described above can be implemented using an additional low-powered laser of a different wave length than that of the ablating laser; e.g. Helium-Neon.

11.2.3 Sound travel measurement

Figure 11.4 shows a diagram of a laser focusing system using sound travel measurements. It is conceivable that the laser focusing lens system can be adjusted to trace the variations in soil levels if the time delay between the rising edge of the laser pulse and the reception of a sound

Figure 11.4 Laser focusing using sound travel measurements.

signal from the ablation spot can be determined. A sound sensor or microphone can be placed at a fixed known distance from the focal point of the focusing lens and therefore a known Δt (time lapse) can be used to determine the appropriate position as the laser rasters vertically. Also, by observing Δt and matching it to a predetermined value, any spot size can be obtained.

Chapter 12. LA-ICP-AES Problems and Solutions¹²

This chapter discusses problems associated with Laser Ablation-Inductively Coupled Plasma-Atomic Emission Spectrometry (LA-ICP-AES), provides a brief overview of selected approaches to these problems, and outlines a realtime calibration method as an alternative solution to the problems.

12.1 Problems Associated with LA-ICP-AES

Two fundamental problems associated with the LA-ICP-AES analysis of soil are variations in laser ablation efficiency, and differences in soil matrix between samples.

As opposed to traditional methods of sample introduction, such as solution nebulization, laser ablation occurs in a less controllable environment. The lack of control causes frequent changes in ablation efficiency and therefore changes in the mass ablated and transported to the ICP. The variations may occur between samples or even during a single sampling cycle. The total mass of any given sample introduced to the plasma is not known with any degree of precision.

Variations in the mass of aerosol entering the ICP occur for the following reasons:

- variations in the laser output power or pulse instability
- light scattering from ablated particles in the ablation cell
- variations in the focus on the soil surface
- light scattering due to dust particles at the laser-fiber coupling point (if an optical fiber is used for laser delivery)
- variations in material transport between the ablation cell and the ICP

The lack of precision caused by the variations in the process necessitates a calibration procedure to complement LA-ICP-AES. A common method, also employed by the MDLEST, uses a soil-matrix element of known concentration for calibration. Due to its abundance in all soils, silicon is the element of choice. The following is an example of the calculations involved in the calibration process and should illustrate the method using silicon.

M_t = total mass of sample introduced to the plasma - unknown (g)

m_a = mass (g) of the analyte derived from its spectral intensity

c_a = concentration of analyte in soil - desired value (ppm/ppb)

m_s = mass (g) of silicon derived from its spectral intensity

c_s = concentration of silicon - assumed to be known based on a predetermined value, obtained using standard (wet) chemical analysis (%)

$\therefore M_t = [m_s(\text{g}) / c_s(\%)] \times 100\% \text{ (g)}$

and $c_a = [m_a(\text{g}) / M_t(\text{g})] \times 10^6 \text{ (ppm)}$

¹² While the entire IDMM team researched some of the problems associated with LA-ICP-AES, credit for writing this chapter goes to Zia Haque.

Note that for the above calculations the concentration of silicon is assumed to be known. A complete standard (wet) chemical analysis initially determines the concentration of silicon, which is then assumed to remain constant from sample to sample for a given site. This assumption oversimplifies reality and may, therefore, decrease the accuracy of the analytical data. The concentration of silicon may vary dramatically between samples even a few inches apart. The soil matrix problem, caused by variations in soil composition between samples, is the second of the two fundamental problems associated with LA-ICP-AES.

12.2 Selected Approaches

Several solutions to normalize the effect of soil matrix instability in laser ablation have been demonstrated by various research groups. Acoustic wave normalization uses the amplitude of acoustic waves generated during ablation as an internal standard (Chen and Yeung 1988, in Richner et al. 1990). This approach requires ablation to take place under well controlled conditions and may not be useful in field applications.

A method proposed by Richner et al. (1990) requires the characterization of the crater formed by the ablation process. The characterization of craters is experimentally complex and thus inappropriate for on-site sampling. Another method to determine the mass of a sample measures attenuation of a light beam by the ablated particles as they pass through a cell placed in the path to the ICP. The results from this approach are matrix dependent and have the same effect as using an emission spectral line, such as silicon, for calibration.

12.3 Realtime Calibration Solution

The goal is to solve the problems of variations in the analytical process by developing a matrix independent technique which allows realtime calibration for field applications of LA-ICP-AES. A technique currently under development by the Spectrochemistry group at Ames Laboratory is expected to account for ablation variations and overcome matrix differences by using aerosol mass monitoring and solution standard additions. The solute in the solution is the element under analysis.

The instrumentation set-up is shown in a block diagram in Figure 12.1. A piezobalance is used to measure the mass of aerosol entering the ICP, which enables variations in laser ablation efficiency to be taken into account. A fraction, a fixed percentage in the range of 5–15%, of the sample aerosol is diverted from its path to the ICP and introduced into the mass-monitor. If the percentage of aerosol drawn is known, the total mass introduced into the torch can be determined. The design of the split junction between the ICP and the mass-monitor paths is non-trivial and critical to the success of this approach.

Figure 12.1 Instrumentation set-up for realtime calibration of LA-ICP-AES.

Solution standard addition is used to generate a standard addition curve for the element under analysis which corrects for soil-matrix effects in the data. An ultrasonic nebulizer is used to inject solutions of varying concentrations into the aerosol path between the mass balance and the ICP while ablation continues. The first addition is an acid blank, giving the output S0 in Figure 12.2 and subsequent solution additions are of increasing element concentration based on the initial data from the spectrometer. As shown in the figure, several additions of increasing concentrations X1, X2, X3, and X4 are made to generate the spectral intensity (spectrometer output) points S1, S2, S3, and S4. A linear regression is then performed on the data points and the x-axis intercept of the straight line gives the concentration of the standard element in the nebulized liquid. The intercept, labeled 'I' in the figure, is proportional to the initial spectral output S0 but calibrated for the matrix related variations in the atomic emission.

Figure 12.2 Calibration curve.

The piezobalance and the ICP and AES combined are initially calibrated using a single standard (known) soil sample of matrix similar to that of the unknown samples. It is important that the matrix of the standard is similar because the mass monitoring system may function differently for different soil types (Baldwin, D'Silva, and Zamzow, forthcoming). The following calculations are performed to obtain a constant 'K' which is then used to calibrate the data from unknown samples.

$$K = \frac{\text{Conc}_{\text{known}}}{\left[\frac{\text{Mass}_{\text{standard}}}{\text{Int}_{\text{standard}}} \right]}$$

$\text{Conc}_{\text{known}} \equiv$ Predetermined concentration of the matrix element, for example silicon, in the standard being used for the calibration.
 $\text{Mass}_{\text{standard}} \equiv$ Mass of the standard sample as measured by the piezobalance.
 $\text{Int}_{\text{standard}} \equiv$ X-intercept from the linear regression of the solution additions using the standard soil sample.

The ratio K can be used for calibrating the unknown for as long as the system and its environment are unchanged. Some of the many factors that can effect the value of K are

temperature variation, wearing of tubing, accumulation of particles on the piezo crystal of the mass monitor, nebulizer efficiency, etc. If considerable changes occur, the system will need to be re-calibrated to obtain the new ratio K.

Once K is known, the calibrated concentration of analyte in the unknown sample can be obtained by the following calculation,

$$\text{Conc}_{\text{unknown}} = \frac{\text{Int}_{\text{unknown}}}{\text{Mass}_{\text{unknown}}} \times K$$

$\text{Conc}_{\text{unknown}}$	$\equiv$	Concentration of analyte in the unknown sample.
$\text{Int}_{\text{unknown}}$	$\equiv$	X-intercept from the regression of the solution additions for the unknown sample.
$\text{Mass}_{\text{unknown}}$	$\equiv$	Mass of the unknown sample as measured by the piezobalance.

In conclusion, mass monitoring allows normalization of laser ablation variations by including in the analysis the true mass of ablated particles introduced into the ICP. The standard addition process on the other hand, calibrates for soil matrix effects by using a solution of known concentration. The two processes combined allow realtime calibration of LA-ICP-AES and improve the robustness of the analysis. If these processes are appropriately automated and controlled, they can be incorporated into mobile labs for on-site sampling.

12.4 References

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Chapter 13. Argon Distribution System¹³

The IDMM conceptual design uses argon gas for several purposes. A controlled flow of argon is used to create and maintain the inductively coupled plasma (ICP) and to entrain the laser ablated sample and transport the particles to the ICP for analysis. Additionally, argon is used to purge the spectrometer optics and may be used to back flush (clean) the aerosol transport tubing and for other miscellaneous requirements.

This chapter first discusses the argon flow rate requirements. The second section discusses argon supply. The next section presents the rationale for and a diagram of the argon distribution system of the IDMM conceptual design. A diagram of a possible gas flow monitoring and control system concludes the chapter.

13.1 Argon Flow Requirements

Argon flow requirements during sampling can be summarized as follows:

- Inductively Coupled Plasma
 - Shielding gas flow rate 0.8 L/min
 - Plasma gas flow rate 16 L/min
 - The mass sample flow rate ~ 1 L/min
- Spectrometer Optics Purge
 - Flow rate 25 L/min (maximum)
- Back Flush
 - Flow rate Based on aerosol transport tubing size
- Other Purposes, such as seal formation, etc.
 - Flow rate Based on ablation cell design, etc.

13.2 Argon Supply

Argon is carried and stored in the mobile laboratory in liquid form in a dewar. There are no known specific gas temperature requirements; as long as argon is in its gaseous state, its temperature is irrelevant. Between the dewar and the ICP or the spectrometer, the liquid argon is changed to gaseous state by heating it to ambient temperature. The most efficient method of accomplishing this is by passing the liquid gas through a heat exchanger which may simply be a copper tubing coil. As argon flows through the long tube it absorbs heat from the surrounding and eventually approaches ambient temperature and, thus, its naturally occurring gaseous state.

¹³ While the entire IDMM team investigated various aspects of LA-ICP-AES, credit for writing this chapter goes to Zia Haque.

13.3 Argon Distribution

Once in its useable gaseous form, argon can be distributed to the ICP, the ablation cell, and the spectrometer. The gas source to the ICP is further distributed within the ICP compartment to form the plasma gas flow, the shielding gas flow, and the mass sample flow to the ablation cell. Figure 13.1 shows, in block form, the configuration for a gas handling system. The line labeled

Figure 13.1 Argon supply and distribution system.

'Other Purposes' in Figure 13.1 may be used to provide gas pressure for seal-rings and other similar applications. The back flush may be used to flush out particles present in the sample transport tube upon completion of each sampling cycle.

Regulators, solenoid valves, pressure transducers, and pressure relief valves are used to control and monitor the gas flow. Regulators are used for maintaining a constant flow rate; solenoid valves allow computer control of 2-way valves for on/off operations; transducers provide information on pressure in individual gas lines to the central controller; and relief valves are used to keep the pressure in the argon line from exceeding the maximum allowable level. The block diagram in Figure 13.2 shows one possible configuration of a typical section of the flow-control system.

13.2 Gas flow monitoring and control system.

Chapter 14. Laser Requirements and Selection¹⁴

Performing fixed on-site and *in situ* laser ablation in a mobile laboratory configuration places a variety of operational constraints on the laser. The laser energy discharged at the sample site must meet the specifications discussed in Technical Process Overview (Chapter 5). In addition, the laser must satisfy several design objectives that will allow it to be operated on site in a mobile laboratory configuration. In order to determine if these requirements could be met by a laser presently on the market, research was performed to determine current laser capabilities.

This chapter identifies the laser ablation requirements and technical specifications that the IDMM team used in evaluating the availability of lasers for use in the IDMM conceptual design.

14.1 Laser Ablation Requirements

In order to fulfill the laser ablation requirements defined in the Chapter 5, the Technical Process Overview and the design objectives presented in Chapter 2, the IDMM conceptual design, the laser must satisfy the following requirements:

- power density of 10^{10} W/cm² or greater can be produced on a spot size of at least 100 micrometers in diameter
- operating wavelength must be in the infrared region, e.g., 1064 nm
- frequency doubler or tripler can be added without major design alterations
- Q-Switched pulses can be specified
- at least 20 Q-switched cycles per second at specified minimum power density can be achieved
- remote operation in surface sampler must be feasible
- operation at distances of 20–100 ft. from the trailer can be achieved
- laser head must weigh less than 10 lbs. to allow rastering
- operation in temperatures from 5–120°F must be possible
- jarring and general motion of the laser in the surface sampler or in the mobile laboratory must be withstood
- vibrations resulting from travel must not damage the laser or laser components
- maintenance can be performed by operators who have had little specialized training

Using these requirements as a guide for inquiry, IDMM team members contacted eight different companies that commercially produce compact lasers. These companies provided information on lasers which they believed would accomplish the specified requirements.

The information returned from laser vendors was studied by IDMM team members to determine if any of the lasers could meet the requirements needed for effective field application. The types of lasers investigated varied from solid state diode and Nd:YAG lasers to excimer

¹⁴ While the IDMM team researched the lasers that might be used in the IDMM conceptual design, credit for writing this chapter goes to Craig Zeutzius.

lasers. Low repetition rate-high output energy lasers and high repetition rate-low output energy lasers were also examined.

The IDMM team concluded that tightly focusing low output energy lasers on a variable height soil sample would be too difficult, and that the excimer lasers were not rugged enough for field use. The team also believed that the toxic gases used in excimer lasers could present undesirable safety concerns. Attention was then focused on three different solid state Nd:YAG lasers that meet the requirements.

14.2 Laser Technical Specifications

After weighing the effects each laser's individual characteristics would have on the mobile laboratory design and cost, a compact solid state Nd:YAG laser was selected to incorporate into the IDMM conceptual design. The specifications are listed below.

Wavelength	1064 nm
Repetition rate	Variable: 1Hz–199 Hz
Energy per pulse	Variable: 3.75J at 1Hz–18.8mJ at 199Hz
Average power output	3.75 W
Average power consumption	800 W
Divergence ^a	< 4 mrad
Pulse length	<20 ns
Beam diameter	0.25 in.
Beam quality	Uniform, Multimode
Voltage requirements	120 VAC $\pm$ 10%
Recommended operating temperature	5–140°F
Maximum operating humidity	99%
Laser head size	6" X 2.5" X 2.2"
Laser head weight	< 5 lb
PFN ^b and heat exchanger size	16" X 6.5" X 7"
PFN and heat exchanger weight	Approximately 30 lbs.
Charge supply size	20.5" X 7" X 22" (rack mount)
Charge supply weight	Approximately 50 lbs
Cost	$\approx$ \$30,000

^aLower beam divergence can be obtained but wasn't believed to be necessary

^bPFN=Pulse Forming Network

Several laser options would be needed to fulfill these technical specifications. These options include Q-switched pulsing and an RS232 computer interface. A power density of 10^{10} W/cm² results from a repetition rate of 20Hz and pulse length of 15 nanoseconds focused to a diameter of 400 micrometers.

14.3 Laser Selection

The first objective of the laser requirements and selection group of the IDMM team was to determine if a laser currently on the market could satisfy the system requirements. We determined that at least three of the lasers researched meet the requirements. The second objective of this group was to identify technical specifications of a laser that best fulfilled our needs and to use these specifications for a detailed design. Because the technology was currently available to satisfy our stated requirements, it was possible to learn the technical specifications of a laser that most appropriately met the requirements of the IDMM conceptual design.

The laser technical specifications listed above are used throughout this report as an example of how we meet the perceived requirements for the field application of laser ablation technology. As research more accurately identifies the factors affecting laser ablation of soil, and as laser technology improves, it may be possible to refine the laser ablation process utilized for soil analysis. The capabilities of the laser and the flexibility of the mobile laboratory will allow improvements in laser ablation of soil to be easily incorporated.

Chapter 15. Volatile Organic Compound Analysis¹⁵

15.1 Introduction

Volatile organic compounds (VOCs), such as trichloroethylene and toluene, are common among pollutants detected at hazardous waste sites. Analysis of soil VOCs is an integral part of the assessment and remediation of hazardous waste sites. Therefore, accurate and precise measurement of VOC concentrations in the region of interest is essential. However, there are currently no standardized procedures for the sampling and analysis of VOCs (Siegrist and Jenssen 1990).

Soil VOC concentrations are difficult to measure and reproduce. One major factor affecting the detection of VOCs is the level of volatility exhibited by the chemical compound. Common classes of more volatile compounds include lighter halogenated hydrocarbons, like methylene chloride, whereas semi-volatile compounds consist of heavier halogenated hydrocarbons, such as polyhalogenated aromatics. Volatile organics tend to decompose when destabilized or removed from the stable soil environment. Semi-volatile compounds are more stable than the volatile organics and thus are easier to detect.

This chapter will briefly discuss the common laboratory methods and conventional portable methods used to determine the presence and concentration of soil VOCs. Finally, two innovative techniques that allow chemical measurements to be obtained without actually removing a contaminated sample will be described.

15.2 Fixed Laboratory Analysis

Fixed laboratory analysis techniques include gas chromatography (GC), flame ionization detectors (FID), photoionization detectors (PID), mass spectrometry (MS), and laser mass spectrometry (LMS).

15.2.1 Gas chromatography

A gas chromatograph (GC) is commonly used when performing VOC analysis. Generally, a gas chromatograph system consists of a mechanism of sample injection, a separation column, a detector (such as FID or PID), and a means of quantifying the results. The standard method used for volatile chemical analysis is the purge-and-trap method because it provides lower detection limits than many other methods (Sutton 1992; Lewis, Deason, and Gerlach 1990). The most commonly used detection mechanisms are flame ionization, photoionization, and mass spectrometry. Once the constituents leave the column, they are carried to the detector. The GC detector can vary according to the method used and whether or not subsequent analysis is desired. The detector records the analysis results and sends a signal to the quantifying unit. The

¹⁵ Credit for researching and writing this chapter goes to Lisa Schultz Blanchet.

quantifying unit translates the detector's signal into a chromatogram, and this is used to identify the constituent. Chromatograms can be produced using a simple chart recorder or a sophisticated computerized integrator (Lewis, Deason, and Gerlach 1990; USEPA 1990).

One major drawback to using gas chromatography is the overlap and interference of chromatogram peaks as recorded by the GC quantifying unit. This problem can be remedied by using a mass spectrometer detector (MS). Nearly all of the priority pollutant volatile compounds can be detected using GC/MS (Sutton 1992).

15.2.2 Flame ionization detector

A flame ionization detector (FID) utilizes a hydrogen flame to ionize molecules of VOC constituents in vapor samples. The FID does not ionize ambient gases such as CO and CO₂ that may be used as carrier gases for the GC column (USEPA 1990). This detector is useful for analyzing aliphatic hydrocarbons, ketones, alcohols, and other compounds that burn easily (Sutton 1992). Analytes passing through an FID are destroyed, thus this form of detection should only be used when no further sample analysis is desired. Obtaining reliable readings requires high sample flow rates when using an FID. This is a serious limitation when high flow rates are not possible, which may occur when an injection method other than purge-and-trap is used in the GC column. Another limitation is that insufficient amounts of oxygen present in the soil gas sample can extinguish the hydrogen flame. The typical response time for most FID instruments is approximately 2 seconds or less (USEPA 1990).

15.2.3 Photoionization detector

A photoionization detector (PID) utilizes a lamp that emits ultraviolet (UV) light to ionize the VOC molecules, while leaving compounds found in ambient air unaltered. This detector is useful in analyzing aromatics and other conjugated bond compounds (Sutton 1992). The highest energy lamp (11.7 eV) exhibits the widest detection range of volatile compounds; however, the lamp used for detection depends on the ionization potential of the desired analyte. Since a PID is nondestructive, it is often used in conjunction with another detector for better accuracy and precision. The response time for most PID instruments ranges from approximately 2 to 5 seconds (USEPA 1990).

15.2.4 Mass spectrometry

A mass spectrometer (MS) utilizes electron bombardment to cause the volatile compounds in a vapor sample to fragment into a group of ions. The resulting ions are then used to identify and quantify the original chemical compounds. Mass spectrometry is occasionally used alone to detect soil VOCs. However, prior knowledge of the compounds present in the sample, as provided by a gas chromatograph, is required due to similarity among the molecular weights of fragments. For this reason, a GC/MS combination provides the most accurate and complete results (Sutton 1992; Lewis, Deason, and Gerlach 1990; USEPA 1990).

15.2.5 Laser mass spectrometry

Laser mass spectrometry (LMS) utilizes a Q-switched laser to ionize soil samples and then send the ionized constituents to a time-of-flight mass analyzer. The advantage of using a laser as a source for mass spectrometry is that it can volatilize/ionize solid samples directly (Wilk, et al. 1988). Three major requirements that affect the reproducibility and reliability of LMS are: 1) the laser beam focus must be constant, 2) the laser power density must also be constant, and 3) sample preparation techniques must be used (Wilk, et al. 1988; Kovalenko, et al. 1992). The benefits of using LMS is selective desorption that will not destroy the sample surface. Laser-induced desorption has also been shown to minimize decomposition of organic compounds (Kovalenko, et al. 1992). The major drawbacks to using LMS are the strict operation requirements, the lack of consistently reliable results, and the likelihood that volatile compounds may be destabilized and thus reduce the accuracy of analysis.

15.3 Portable Analysis

Immunoassay, soil gas, portable gas chromatography, and combined gas chromatography/mass spectrometry are the conventional portable methods of analyzing soils for VOCs.

15.3.1 Immunoassay

Immunoassay procedures consist of utilizing chemical reagents to indicate the presence or relative concentration of organic compounds. Immunoassay methods are conducted on an aqueous basis and require extensive sample preparation. Because results from immunoassay analysis are relatively inaccurate, these methods are usually used for site screening or "plume-hunting" (USEPA 1991). The reduced level of accuracy, however, is balanced by the low sample cost, minimal operator training, and rapid turnaround time for sample analysis.

15.3.2 Soil gas analysis

Soil gas analysis consists of collecting and analyzing headspace vapors for the presence of organic contaminants in subsurface soil samples. Soil gas methods are often used in preliminary site characterization studies and provide immediate data at a lower cost than other conventional subsurface sampling and chemical analysis techniques (Heins, et al. 1992). Soil gas surveying is useful for detecting a wide range of VOCs at ppm levels under a variety of geologic and hydrologic environments. Headspace vapors are typically analyzed using a GC equipped with a PID or similar detector. Evaluation of gas chromatographs, however, shows a tendency to misidentify some chemical compounds (Sutton 1992; USEPA 1990; USEPA 1991). Additionally, the potential for negative bias (i.e., measured concentration lower than actual value) is significant and difficult to control. Negative bias is primarily caused from volatilization losses when the headspace sample is collected (Siegrist and Jenssen 1990). Because of the potential errors in compound identification and concentration, soil gas methods are primarily used for site screening.

15.3.3 Portable gas chromatography

Portable gas chromatographs consist of a separation column and a detection system (usually a PID or FID). The GC is able to isolate and analyze a wide variety of organic constituents in either liquid or vapor phase. Most portable GC units use a carrier gas to introduce the sample into column. This direct injection method may reduce detection limits if an FID detector is used (USEPA 1990). Portable GCs have the same tendency to misidentify compounds as stationary GC units, but the portable units also have limited temperature and carrier gas control as compared to laboratory gas chromatographs. These additional control limitations cause the portable GC to be less accurate than the fixed laboratory GC.

15.3.4 Portable gas chromatography/Mass spectrometry

As previously stated, the response of the gas chromatograph varies according to the detection method used. The detection method providing highly accurate chromatogram results is the mass spectrometer (Sutton 1992; Lewis, Deason, and Gerlach 1990). Major advances have recently been made in use of MS in the field. The ability of the GC/MS system to delineate organic contaminants found in soil and water samples has made this method of analysis popular. Combining the two methods in tandem decreases the peak interference often exhibited by the GC, while also decreasing the mass overlap errors that occasionally occur when using MS. In addition to reliable and accurate results, detection limits have been reported in the low ppm range for realtime analysis (USEPA 1991).

15.4 Innovative Analysis

The development of field portable analytical instrumentation has increased over the past few years. In addition to mobile analysis, it is becoming increasingly desirable to obtain chemical measurements without actually removing a soil sample. Two possible methods of *in situ* analysis are thermal desorption and laser mass spectrometry.

15.4.1 Thermal desorption

The basic concept behind thermal desorption consists of using a heated, stainless steel sample probe to desorb chemical contaminants from a soil sample. The probe, attached to a portable GC/MS, is lowered into the ground and heated to a pre-selected temperature, usually ranging from 240 to 300°C (Robbat, Liu, and Abraham 1992). As the temperature of the probe increases, chemical contaminants desorb from the soil particles. The freed compounds are then carried directly by ambient air for analysis by a GC equipped with an MS detector. Realtime results are obtained in concentrations as low as 0.5 ppm (Robbat, Liu, and Abraham 1992). Thermal desorption is compound specific in that the temperature of the heating probe must be set in order to desorb desired chemical constituents. Therefore, thermal desorption may not be appropriate when the identity of the chemical contaminants are unknown. Another drawback to thermal desorption is that inaccurate results may occur due to slow or incomplete desorption of organic molecules (Pavlostathis and Mathavan 1992).

15.4.2 Laser mass spectrometry

Another method of *in situ* analysis is laser mass spectrometry (LMS). Laser-induced desorption has been shown to minimize decomposition of organic molecules on soil surfaces (USEPA 1990; Kovalenko, et al. 1992). The LMS method consists of using a low-powered, pulsed infrared laser to desorb constituent molecules from a soil sample. The desorbed molecules are then ionized with a pulsed ultraviolet laser and the resulting ions are analyzed in a mass spectrometer. The realtime results are in the low ppm range, similar to thermal desorption. The variability of soil surfaces causes the laser beam to operate in a defocused mode, and thus minimizes chemical decomposition (USEPA 1990). Operating in this fashion, mass spectra can be obtained without damaging the *in situ* soil sample. Like thermal desorption, it may be difficult to measure compounds that are highly volatile. Currently, there are few methods for *in situ* analysis that are able to identify a wide variety of highly volatile chemical compounds.

One primary benefit to using LMS is that it may potentially be combined with laser ablation techniques. This combination would consist of positioning a laser ablation cell on the soil sample and then desorbing organic particles using a low-power, defocused laser beam. The desorbed compounds would then be carried to the MS by a carrier gas (argon or ambient air). The same soil sample could subsequently be ablated using a high-powered laser beam, and the ablated material sent to an LA-ICP-AES system that would analyze the sample for radionuclides or heavy metals. The addition of a portable GC to this system would further enhance the accuracy of the analysis results for both LMS and LA-ICP-AES.

15.5 Conclusion

The current trend of organic compound analysis is moving towards innovative, on-site techniques. On-site chemical analysis can often provide realtime results as the basis for realtime decision-making at a lower cost than fixed laboratory methods. Realtime results enable immediate response to environmental hazards, whereas laboratory methods usually require waiting periods ranging from days to months. The Mobile Demonstration Laboratory for Environmental Screening Technologies (MDLEST), currently designed to detect radioactive chemicals, is capable of implementing an organic analysis unit. The addition of an organic chemical analysis unit would lead the MDLEST into the forefront of completely mobile site screening technology.

15.6 References

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Acronyms and Initialisms

These acronyms and initialisms are used in this report.

A	Ampere
AA	Atomic absorption
AC	Alternating current
A/C	Air conditioner
AES	Atomic emission spectrometer
AMU	Atomic mass unit
C	Celsius
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act
CRADA	Cooperative research and development agreement
CLP	Contract laboratory program
DC	Direct current
DOE	Department of Energy
DP	Design parameter
DPM	Defense Priority Model
ETD	Environmental Technology Development Program
ERWM (EM)	Environmental Restoration and Waste Management
F	Fahrenheit
FR	Functional requirement
GIS	Geographic information system
GPS	Global positioning system
GUI	Graphical user (or operator) interface
HEPA	High efficiency particulate air
IDMM	Integrated Design for Marketing and Manufacturing
ICP	Inductively coupled plasma
IRP	Installation Restoration Program
kW	Kilowatt
J	Joule
l	Liter
l/m	Liter per minute
LA	Laser ablation
LP	Liquid propane
LA-ICP-AES	Laser ablation-inductively coupled plasma-atomic emission spectrometer
LA-ICP-MS	Laser ablation-inductively coupled plasma-mass spectrometer
μm	Micrometer
MDLEST	Mobile Demonstration Laboratory for Environmental Screening Technologies
mJ	Millijoule
mrاد	Milliradian
MS	Mass spectrometer

mm	Millimeter
Nd-YAG	Neodymium yttrium aluminum garnet
nm	Nanometer
ns	Nanosecond
ppb	Parts per billion
ppm	Parts per million
ppt	Parts per trillion
RTK	Real time kinetic
RF	Radio frequency
s	Second
SARA	Superfund Amendments and Reauthorization Act
TIP	Technology Integration Program
USEPA	United States Environmental Protection Agency
VOCs	Volatile organic compounds
XRF	X-ray fluorescence

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