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Portable Sensor for Hazardous Waste

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LIST OF ACRONYMS AND ABBREVIATIONS

A/D	Analogue to Digital
AAS	Atomic Absorption Spectroscopy
ACGIH	American College of Government and Industrial Hygienists
AES	Atomic Emission Spectroscopy
ANET	Active Nitrogen Energy Transfer
BNC	Baby N Connector
CAA	Clean Air Act
CCD	Charge Coupled Device
CEM	Continuous Emissions Monitor
CEO	Chief Executive Officer
CFO	Chief Financial Officer
D/A	Digital to Analogue
D-B	Dielectric Barrier
D&D	Decontamination and Decommissioning
DCP	Direct Current Plasma
DOE	Department of Energy
DOS	Disk Operating System
DVM	Digital Volt Meter
EEPROM	Electrically Erasable Programmable Read Only Memory
EM	Environmental Management
EMI	Electromagnetic Interference
EPA	Environmental Protection Agency
FDA	Food and Drug Administration
FDF	Fluor Daniel Fernald
FERMCO	Fernald Environmental Restoration Management Company
GC	Gas Chromatography
GETE	Global Environmental Technology Enterprise
GUI	Graphical User Interface
HAPs	Hazardous Air Polutants
HIR	Herman Infrared
HR	Human Resources
HV	High Voltage
HVAC	Heating, Ventilation and Air Conditioning
I/O	Input/Output
ICCD	Intensified Charge Coupled Device
ICP	Inductively Coupled Plasma
IRAD	Internal Research and Development
LASS	Laser Assisted Spark Spectroscopy
LIBS	Laser Induced Breakdown Spectroscopy
LSDP	Large Scale Demonstration Project
MDL	Minimum Detection Limit
MS	Mass Spectrometry
MWFA	Mixed Waste Focus Area

LIST OF ACRONYMS AND ABBREVIATIONS

NIOSH	National Institute of Occupational Safety and Health
NIST	National Institute of Standards and Technology
OES	Optical Emission Spectroscopy
OMA	Optical Multichannel Analyzer
OSHA	Occupational Safety and Health Administration
PC	Personal Computer
PMT	Photomultiplier Tube
POC	Point of Contact
ppb	part per billion
ppbw	part per billion by weight
ppm	part per million
ppmw	part per million by weight
PSI	Physical Sciences Inc.
QA/QC	Quality Assurance and Quality Control
R&D	Research and Development
RAM	Random Access Memory
RCRA	Resource Conservation and Recovery Act
SBIR	Small Business Innovative Research
SIBS	Spark Induced Breakdown Spectroscopy
SVGA	Super Video Graphics Adapter
TLV	Threshold Limit Value
TWA	Time Weighted Average
UV	Ultratiolet
Vis	Visible
WETC	Western Environmental Technology Center
XRF	X-ray Fluorescence

ABSTRACT

This report summarizes accomplishments for the second phase of a 5-year program designed to develop a portable monitor for sensitive hazardous waste detection. The ultimate goal of the program is to develop our concept to the prototype instrument level and to have thoroughly tested it in the field. Our monitor will be a compact, portable instrument that will allow real-time, *in situ,* monitoring of hazardous wastes. This instrument should prove useful in a variety of commercial and DOE applications. These include process control; off gas monitoring; ambient air quality during decontamination and decommissioning (D&D) operations, at firing ranges, at metals fabricators and finishers, or at smelters; hazardous waste site mapping; and verification of cleaning technologies. In addition, our instrument is sufficiently compact that it is amenable to robotic mounting for monitoring and remote sensing applications.

Our approach is to excite atomic fluorescence by the technique of Spark-Induced Breakdown Spectroscopy (SIBS). This system vaporizes particulate samples in a high energy, electrically generated spark. With suitable gating between the spark, and the observation of the fluorescence, background emissions can be suppressed with respect to the atomic fluorescence of the analyte species. Each element in the excitation region has a unique spectroscopic signature which allows it to be distinguished from emissions from other species in the discharge region. The overall intensity of the emission from each element provides a quantitative measurement of the amount of the element in the sample.

Our principal goals for this second phase of the program were to demonstrate sensitive detection of additional species, both RCRA metals (Sb, Be, Cd, Cr, Pb, As, Hg) and radionuclides (U, Th, Tc); to identify potential applications and develop instrument component processes, including, sample collection and excitation, measurement and test procedures, and calibration procedures; and to design a prototype instrument. Successful completion of these tasks results in our being able to fabricate and field test a prototype of our instrument during the program's third phase.

Early in the program we surveyed various DOE sites regarding their needs, and eventually visited one of the sites to discuss such issues in more detail. The results of this activity indicated that most applications which could benefit by using our technology required handling particulate samples. This information helped guide us toward adopting the SIBS technique, rather than our originally proposed excitation technique, active nitrogen energy transfer (ANET). The SIBS-based system proved much simpler to engineer while retaining excellent sensitivity. This report details how we have incorporated this technology into our prototype instrument design.

The third, and final, phase of the program involves fabricating a prototype monitor based on the design considerations described herein, and then proving our design by participating in field tests associated with one or more of the large-scale demonstration projects (LSDPs) DOE has ongoing. In addition we will continue the commercialization activities we have already begun so that our technology can be transferred to the commercial sector at the conclusion of the third and final phase of the program.

EXECUTIVE SUMMARY

This report summarizes accomplishments for the second phase of a 5-year program designed to develop a portable monitor for sensitive hazardous waste detection. The ultimate goal of the program is to develop our concept to the prototype instrument level, including prototype field testing. Our monitor will be a compact, portable instrument that will allow real-time, *in situ,* monitoring of hazardous wastes. This instrument should prove useful in a variety of commercial and DOE applications (please see Figure 1). These include process control; off gas monitoring; ambient air quality during decontamination and decommissioning (D&D) operations, at firing ranges, at metals fabricators and finishers, or at smelters; hazardous waste site mapping; and verification of cleaning technologies. In addition, our instrument is sufficiently compact that it is amenable to robotic mounting for monitoring and remote sensing applications.

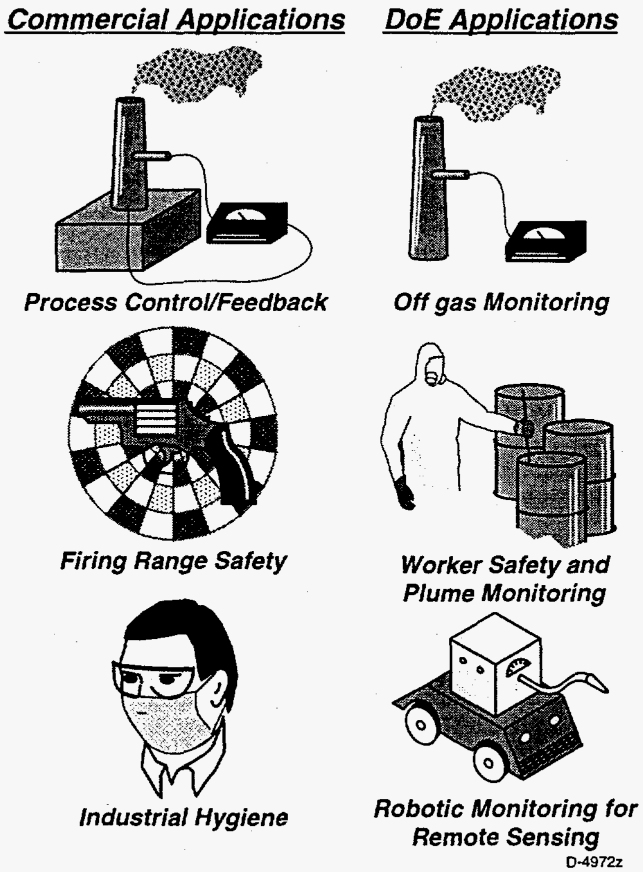

Figure 1. Potential applications for hazardous waste monitor.

Our approach is to excite atomic fluorescence by a high voltage spark. Each element excited by the spark plasma has a unique spectroscopic signature which allows it to be distinguished from emissions from other species. The overall intensity of the emission from each element provides a quantitative measure of the amount of the element in the sample. This excitation technique is compact and requires only modest amounts of electrical power. Thus our technology is ideal for producing a compact, portable instrument. In addition our technology is considerably less expensive than other plasma excitation techniques such as laser-induced breakdown spectroscopy (LIBS) or inductively coupled plasma spectroscopy (ICP).

During the first phase of the program[1] we demonstrated that a variety of hazardous species could be detected sensitively by a novel adaptation of the active nitrogen energy transfer (ANET) technique. Species investigated included heavy metals, Hg, Cr, and Se, both chlorinated and non-chlorinated organics, and uranyl compounds. For most of these species we demonstrated sensitivity limits for their detection at parts per billion (ppb) levels.

Our principal goals for this second phase of the program were three fold:

1. Demonstrate sensitive detection of additional species
    - RCRA metals: Sb, Be, Cd, Cr, Pb, As, Hg
    - radionuclides: U, Th, Tc
2. Identify potential applications and develop instrument component processes
    - sample collection and excitation
    - measurement and test procedures
    - calibration procedures
3. Design a prototype instrument
    - engineering considerations
    - produce engineering-design drawings with component specifications

Our successful completion of these tasks means we will be able to fabricate and field test a prototype of our instrument during the program's third phase.

Early in the second-phase program we used ANET to demonstrate sensitive detection of Pb, Sb, and As. While we were doing this work, we put out a survey to the various DOE sites regarding their needs, and eventually visited one of the sites to discuss such issues with site personnel in more detail. The results of these surveys and the site visit indicated to us that most applications which could benefit by using our technology required handling particulate samples. As a result, we developed the spark-induced breakdown spectroscopy (SIBS) system, and used it to investigate the remainder of the elements we had been tasked to detect.

The SIBS system vaporizes particulate samples in a high energy, electrically generated spark. With suitable gating between the spark, and the observation of the fluorescence, background emissions can be suppressed with respect to the atomic fluorescence of the analyte species.

The major problem to overcome in terms of instrument design was developing procedures for sample handling and analysis. In particular, when dealing with samples on particulates, the particulates must first be vaporized, and the vapor must then be excited. Our SIBS technology proved ideal in that it is able both to vaporize and to excite simultaneously. In addition, its sensitivity is comparable to or better than that of competing technologies, but it holds considerable cost advantages over them. We therefore developed this technology during this phase of the program and incorporated it into our prototype instrument design.

The final element of this phase of the program was to design a prototype hazardous waste monitor. This design includes not only identifying each of the components to be incorporated into the instrument and determining how they will be integrated into a compact package, but also specifying component technical requirements and their vendors. Now, at the end of this current phase, we have a detailed set of drawings and specifications for the construction of a first-generation, or alpha-, prototype instrument. This instrument will be built and field tested as part of the third and final phase of the program.

We are already actively commercializing this technology with assistance from the Global Environment Technology Enterprise (GETE). We have established our proprietary position and have written a business plan under DOE's "Dawnbreaker" program. In addition, we have committed internal funding to developing and testing a lead monitor for firing ranges, and we are establishing a test program for Phase C which will include one or more field tests under the large scale demonstration program.

The third, and final, phase of the program involves fabrication and field testing of the alpha-prototype instrument designed during the program's second phase. We will test and refine the instrument in the laboratory first, then conclude the program with an extensive series of field tests.

1. INTRODUCTION

Hazardous materials, particularly heavy metals and certain organic molecules, particularly chlorinated ones, have become a ubiquitous environmental problem. Our country is spotted with a number of sites in which hazardous waste has been deposited. In some instances hazardous materials were unthinkingly dumped in ponds and land fills. In other instances the materials were sealed in containers before being buried or land filled. In many instances, these containers have begun leaking and releasing their waste to the environment. Another on-going source of hazardous waste is the emissions from various combustion activities such as coal-fired power plants, incinerators for municipal and hazardous wastes, and crematoria. A third site of hazardous waste is in buildings and on properties where these various hazardous materials have been used in numerous activities. For example, mercury was once an important component in a lithium isotope separation process that was used at radioactive materials processing centers. Oak Ridge National Laboratory, for example has nearly nine metric tons of mercury on site. Some of this is safely stored, some remains spread throughout the buildings in which it was used, and some has found its way into local waterways.

In many instances the actual locations and distribution of the hazardous materials are well known, but in others all that is known for sure is that hazardous materials are buried somewhere on a site that may extend over hundreds of acres. Mapping out these sites then becomes a problem. Once the identity and exact location of hazardous materials are known, appropriate remediation efforts can begin. It then becomes important to be able to easily quantify the success of these operations so that one can know if more work is needed or if efforts have been effective in reducing hazardous species to levels currently considered safe.

While extractive sampling is somewhat slow and cumbersome, it can often suffice for site mapping applications. Where real-time monitoring can be particularly useful is in applications such as remediation process monitoring and control and industrial hygiene at remediation sites. For example, DOE has many acres of cement floors that are impregnated with hazardous species such as uranium and thorium. The primary approach for cleaning up these floors is a process knows as scabbling wherein the top layer of the floor is pulverized and swept up, the contamination being taken up with the pulverized cement. The residue from that process is then disposed of in a sealed landfill or perhaps vitrified. Clearly, both the efficiency of the scabbling process as well as the minimization of the volume of secure landfill will be related to how little of the floor must be scabbled to remove the contaminants to levels below which they no longer pose an environmental threat. Being able to monitor the dust kicked up in the scabbling process in real time for the presence of the contaminants would prove invaluable in enhancing the efficiency of the process. Currently what is often done is to agree with regulators that an inch of material will no doubt remove contaminants adequately. In many instances, however, the actual amounts of floor that need to be scabbled are more on the scale of millimeters. Thus, on real-time monitoring of the process has the potential to reduce both the scabbling time and the volume of waste requiring disposal by more than an order of magnitude.

In virtually all dismantlement processes involving contaminated buildings, some levels of dust will be released to the immediate environment. This will be so even if the basic process is designed to contain, as much as possible, dust escape. Real-time monitoring could benefit these activities by being able to monitor levels of contaminants in the dust. The monitor could then set off an alarm should air-borne contaminant levels rise to levels posing a risk to worker safety. Alternatively, the monitors might be able to indicate that dust containment measures during the dismantlement process could be relaxed without compromising worker safety. In this case, there could be considerable savings in the process because the dust containment procedures would no longer have to be immensely over engineered to ensure worker safety.

Although real-time monitoring can have a multitude of benefits, we will mention only one more, that of continuous emissions monitoring of off gases from hazardous-waste incineration and vitrification processes. The wastes to be incinerated or vitrified are highly concentrated repositories of RCRA metals and some radionuclides such as U and Th. Although the Environmental Protection Agency has yet to promulgate regulations regarding the concentrations of these species they will permit in stack-gas flues, such regulations are almost certain to appear in the near future. In the absence of such regulations, DOE in particular, will have a very difficult time convincing stakeholders to accept, in the absence of actual verification, that effluent levels from these processes are safe.

Current analytical technology generally requires samples to be taken from a site in suitable containers and taken to analytical laboratories where they are processed. This approach is expensive and time consuming. Often several weeks will pass before analytical results are reported back to the waste site. Clearly what is needed is a portable, field-operable instrument that can detect various hazardous species in real time. Instrumentation that is sufficiently compact to be transported to and operated in the field tends to lack adequate sensitivity to detect many hazardous species at the low levels required to achieve environmental compliance.

The most common analytical techniques that have been applied to heavy metal contaminant analysis are atomic absorption spectrometry (AAS) and atomic (or optical) emission spectrometry (AES or OES). Samples are usually atomized and excited, where necessary, in a flame or plasma, generally a direct current plasma (DCP) or an inductively coupled plasma (ICP). Although these techniques are generally quite sensitive, often capable of part-per-billion (ppb) detection levels, being able to achieve such good detectability invariably requires special sample handling and preparation. Some other drawbacks of these techniques are the following:

- They are not readily adaptable to real-time monitoring. Samples must be extracted and shipped to another lab for analysis

- They require extensive operator training

- They are not readily field operable or portable although systems can be placed in a truck for on-site operation

- They tend to be expensive to purchase, operate, and maintain.

As we describe below, our approach obviates these problems and offers several distinct advantages including absence of special sample preparation, field operability, and lower cost.

The next section follows with a statement of the overall project objective, and is, in turn, followed by a detailed description of our activities during this phase of the program. This includes a discussion of experimental apparatus and techniques, including calibration procedures, results of experimental measurements, results of several exercises we undertook to better understand the particular needs of the DOE community, and a description of our thinking regarding the various component parts necessary to make a viable, field-operable, real-time instrument, and finally a description of our design ideas for the prototype we propose to build and field test in the third and final phase of this program.

2. PROJECT OBJECTIVE

The overall objective for this 5-year program is to develop a portable monitor for hazardous waste that can be used in D&D activities at the various DOE sites that were involved in nuclear materials processing. And, in addition, to commercialize our technology and make it available to the private sector. The program is planned in three phases with decision points at the end of each phase to decide whether or not the subsequent phase should be pursued. In the initial phase of the program we demonstrated the applicability of ANET excitation of fluorescence to the detection of hazardous species. Our novel approach used D-B discharge technology to generate the active nitrogen at atmospheric pressure.

During the current phase of the program we developed a second excitation technique which we think is applicable to a wider range of DOE problems, Spark-Induced Breakdown Spectroscopy (SIBS). We also developed this technology to the process level and undertook an engineering design of a portable hazardous waste monitor. Finally, we demonstrated our ability to detect additional species of interest to DOE that we did not have time to investigate during the program's first phase.

During the program's final phase, we will fabricate a prototype instrument, prove our design in the field by participating in one or more of DOE's large-scale demonstration projects (LSDPs), and transition our technology to the commercial sector.

3. RESULTS AND DISCUSSION

The work in the first phase of this program[1] successfully demonstrated that ANET technology holds great promise for development into a sensitive, multi-element hazardous species monitor. Appendix A summarizes the principal results of this work. Our plans for the second phase of the program were to develop a breadboard prototype system and characterize the ANET process under more realistic conditions. As our work during this phase of the program evolved, we realized a somewhat different technology would probably be more readily applied to tackle DOE's problems. The focus of this section will, therefore, be on this alternative technology, SIBS, and our discussion of problems related to instrument design will also focus on design of an instrument using the SIBS technology. Our efforts in developing the ANET technology are detailed in Appendix B.

The Phase B program had three primary components:

- Technology extension
- Process development
- Design engineering.

For the technology extension component we wanted to demonstrate the applicability of our technology to detecting a number of hazardous species not investigated in Phase A. The activities on this task involved not only identifying unique finger prints for each of the species to be investigated, but also determineing quantitative limits for their detection. The species investigated include the heavy metals, Sb, As, Be, Cd, Cr, Pb, and Hg, and the radionuclides, Th and U. We had also hoped to demonstrate detection of Tc, but could not find a suitable site for doing the work. We did demonstrate sensitive detection of a Tc surrogate, Mn.

The purpose of the process development task was to establish the procedures for sample handling and analysis, and to develop systems and software needed to automate these processes. System components and processes to be examined include sample collection and introduction, excitation source stability, fluorescence detection and analysis, and measurement, calibration, and test procedures. An additional, and quite important, part of this set of tasks was to survey DOE needs. We did this through a questionnaire sent out to a number of DOE sites early on in the program, and also through a visit to the Fernald site, where we had detailed discussions with the personnel there. The results of this activity guided us in developing technology we think can be most readily applied to current DOE needs.

The design engineering task had two elements. The first of these was to identify and specify each of the components to be incorporated into the prototype instrument we shall fabricate as a part of the final phase of the program. Where possible, we planned to identify commercial suppliers of the necessary components. We also have good in-house capabilities for construction of components peculiar to our instrument.

The second element of the design engineering task was to design a prototype hazardous waste monitor. This design balanced a number of considerations including power management and portability. After making these considerations, we generated set of drawings and specifications for the construction of a first-generation, or alpha-, prototype instrument.

The following subsections detail our activities on each of the three program components outlined above.

3.1 Technology Extension Tasks

Activities on this task follow procedures developed during the first phase of the program. That is, we generated quantitative samples of the species to be detected, determined their atomic fluorescence finger prints, and constructed calibration curves to establish minimum detection levels and also to show that the atomic fluorescence intensities scaled linearly with concentration of the analyte. The list of species investigated included the heavy metals, Sb, Be, Cd, Cr, Pb, As, and Hg, and the radionuclides, U and Th. We had also hoped to apply our technique to the detection of Tc, but we were unsuccessful in coordinating with DOE a suitable site that could handle that material. We did investigate the Tc surrogate, Mn. This element is chemically and electronically similar to Tc and the detection limits for the two elements should, therefore, be similar.

Initially we investigated detectability of these metals using ANET detection with volatile compounds of the elements. We realize, of course, that the majority of metallic compounds we would be likely to analyze would not have appreciable vapor pressure. They exist primarily as solids, either aerosol particulates or as absorbed species on larger scale solid materials. Our initial indications from Phase A were that the ANET system *could* detect species bound to aerosols. Once we had the aerosol generator, which we describe in the next section, working properly, we used it to investigate ANET detection of species on aerosols more thoroughly. What we discovered was that, by and large, the ANET technique is *not* adequate for detecting most species bound up as aerosols. We therefore focused our remaining efforts on developing an alternative technique, Spark-Induced Breakdown Spectroscopy (SIBS), which *does* provide sensitive detection of species associated with particulate samples.

The techniques used in the ANET studies are virtually the same as those described in detail in our first-phase topical report. Since we have determined that using SIBS provides a scheme that had a wider range of applicability to D&D problems, we will focus on the SIBS techniques and measurements in the body of this report. The results from the ANET work are only summarized below. Complete details on ANET measurements are given in Appendix B.

3.1.1 Experimental Details of SIBS Measurements

Our apparatus for making the SIBS measurements has three major sections, an aerosol generator, a spark excitation system, and a detection system. The aerosol generator has two components: a droplet generator and a drying column. The droplet generator is a variant on the design first demonstrated by Berglund and Liu[2] and is shown in Figure 2. The operating principle involves the imposition of a periodic instability on a thin stream of fluid flowing from a pinhole orifice. The instability is induced by coupling a single frequency vibration into the fluid

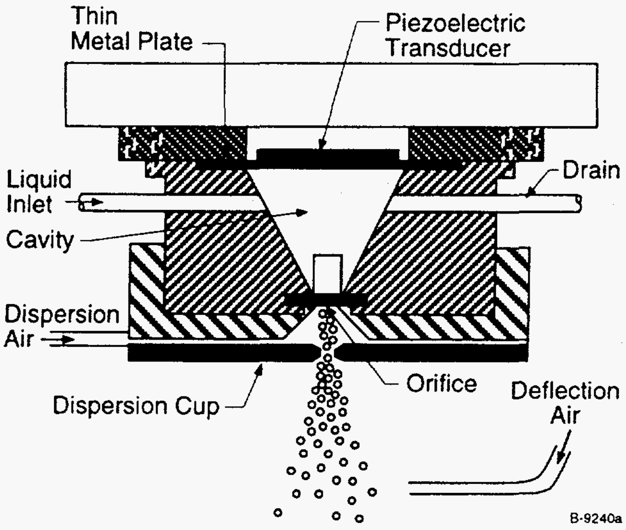

Figure 2. The monodisperse droplet generator.

using a piezoelectric transducer driven by a square wave function generator. Under certain conditions of fluid flow rate and instability frequency, monodisperse aerosols are generated.

The size of the droplet is a function of the instability frequency and fluid flow rate through the orifice:

$$D_p = \left(\frac{6Q}{\pi f}\right)^{\frac{1}{3}} , \tag{1}$$

where Q is the fluid flow and f is the frequency. For previous studies done with this generator, a frequency of 100 kHz and a flow rate of 0.34 ml min^{-1} was used to produce droplets 48 µm in diameter. The fluid flow itself is a function of orifice size. Typically we use orifices that are 20 µm in diameter.

This droplet generator is situated at the top of a Plexiglas tube in a downward directed orientation toward the drying column (Figure 3). Loss of particles on the drying column walls is minimized by using a porous, stainless steel inner tube through which air is drawn at a fixed rate. The air is heated to 100°C to facilitate removal of water from the droplets and is drawn out the bottom of the column by a filtered pumping system. The dry aerosol (typically 2 to 10 µm diam) is trapped on a filter placed at the bottom of a Plexiglas extension under the drying column that houses the spark chamber. This filter prevents particles from exiting the generator and contaminating the laboratory environment.

The spark chamber resides at the bottom of the drying column and houses the electrodes. Rhenium electrodes are used because of their resistance to oxidation and arc corrosion, and also due to their high melting point (3180°C). In some cases we used iridium electrodes which have somewhat similar characteristics. The electrodes are mounted directly to stainless steel blocks which are in turn mounted on ceramic standoffs inserted into the sealed aerosol source. The chamber has arms with windows at the ends to pass the emission generated upon sparking.

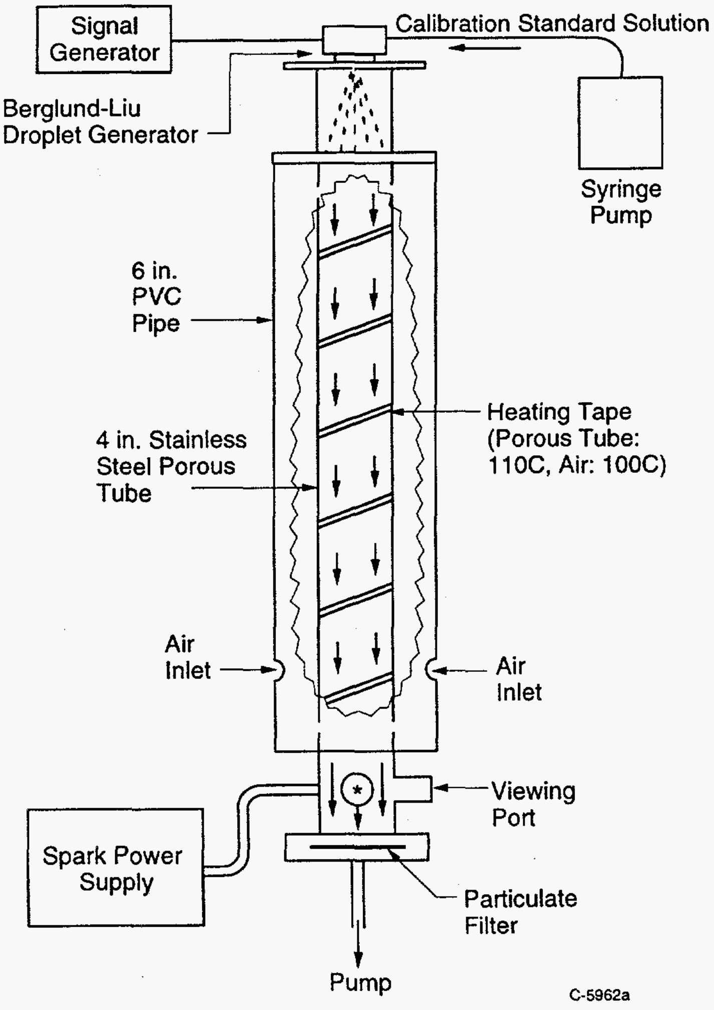

Figure 3. The dry aerosol source, including spark chamber and drying tube.

The detection system (monochromator and OMA) relies upon a timing system which allows the analysis of the atomic emission after a delay to eliminate interference from the prompt spark-plasma emission.

Our spark-generating power supply produces volume-filling 5 J sparks at varying repetition rates from single shot to >20 Hz. It has safety interlocks that will not permit the device to power up without a complete connection to the spark chamber. The electronics are entirely enclosed, for obvious safety reasons. The entire assembly occupies a box that is 14.5 x 17.5 x 17 in., (37 x 44 x 43 cm) and weighs about 25 lb (11.5 kg). Figure 4 shows a schematic of the system.

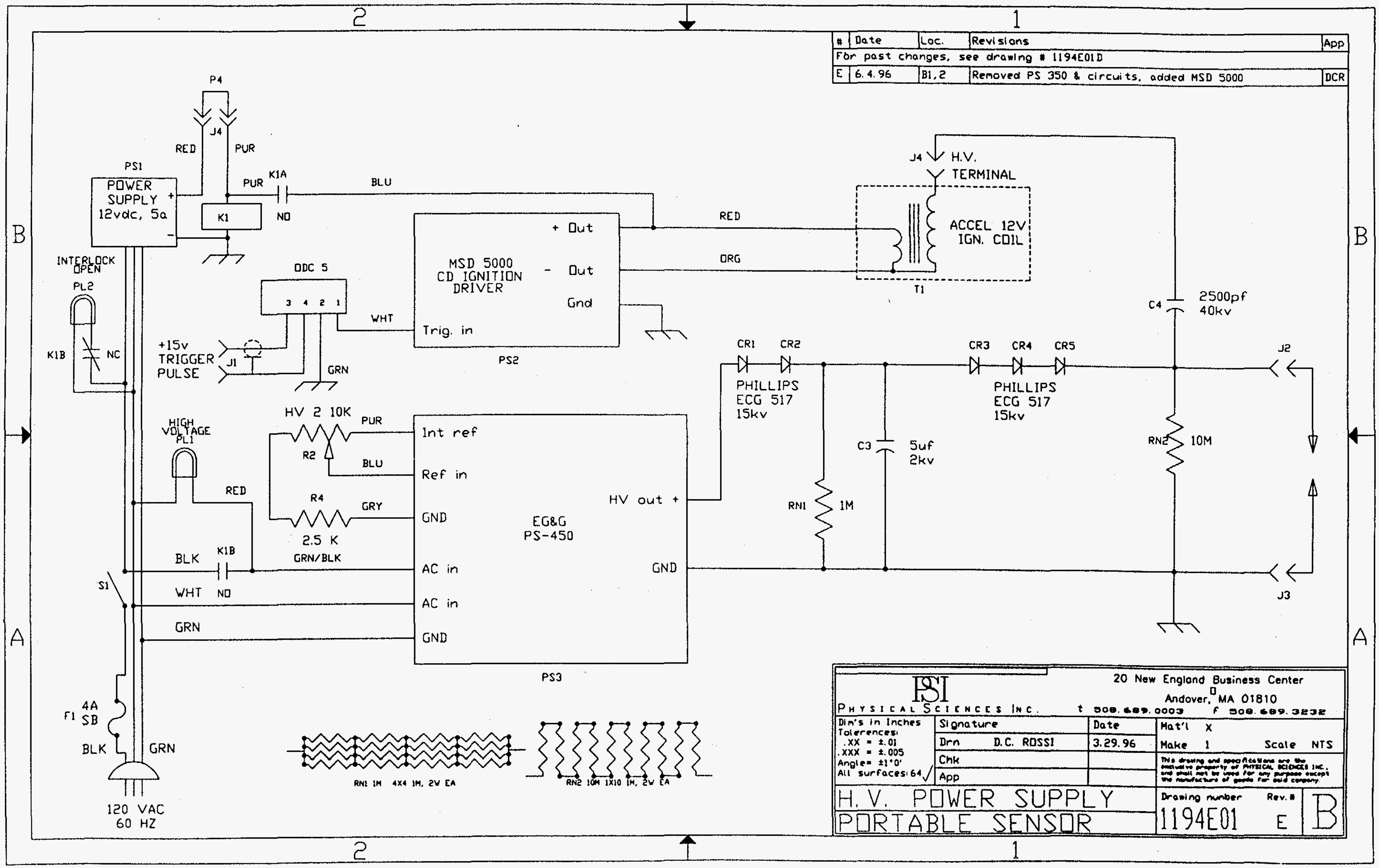

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Figure 4. Schematic of pulsed high voltage power supply for SIBS system.

In order to calculate the concentration of aerosol in the air, one needs to measure the efficiency with which the aerosol traverses the drying tube:

$$C_{ppmw(air)} = \frac{M(gm/min) \cdot E}{F(cm^3/min) \cdot \rho(gm/cm^3)} \; 1 \times 10^6 \qquad (2)$$

Here, M is the mass introduction rate, E is the passage efficiency (particle loss in the generator), F is the air flow and ρ is the air density. Under normal operating conditions in the generator, a 1% by weight solution of lead nitrate corresponds to about 50 ppmw (Pb in air). The only component of this equation that is related to the initial concentration of lead is the mass introduction rate. Therefore, to calibrate for other densities, different solution concentrations need to be introduced (please see below).

When the dry aerosol is exposed to the spark, it is atomized and excited simultaneously. To avoid errors associated with inhomogeneity in sampling, having a volume-filling spark that samples many particles at once is desirable. Our aerosol source produces sufficient particle densities to ensure the processing of many particles during a spark event:

$$\rho(cm^{-3}) = \frac{R(s^{-1}) \cdot E}{F(cm^3 s^{-1})} \;, \qquad (3)$$

where R is the particle generation rate (100 kHz), E is the passage efficiency, and F is the gas flow rate through the system. In a typical experiment, the particle density was about 170 cm^{-3}. A 5 J spark transcribes a cylinder that is 7 mm in length and 4 mm in diameter. The corresponding volume is 0.09 cm^3. Consequently, about 16 aerosol particles were sampled in each pulse. Naturally, sampling many particles not only results in reduced sample inhomogeneity errors, but also in larger signal levels.

3.1.2 Calibration of Aerosol Delivery System

We calibrated the dry aerosol generator gravimetrically. We describe the process for a lead nitrate, $Pb(NO_3)_2$, aerosol. We compare the mass rate at which lead nitrate passes through the particle generator with the mass recovered on a filter at the bottom of the drying tube to determine the efficiency at which lead particles pass through the apparatus.

A high flow filter with a nominal pore size of 1 micron was dried in an oven at 160°C for about half an hour to remove any water absorbed from the atmosphere. The filter was then weighed and introduced into the aerosol generator without the spark chamber, and one of several solutions of lead nitrate was fed through the droplet generator. The solutions are prepared from NIST-traceable ICP standards. After enough mass had accumulated on the filter to be easily differentiated from the pre-weight, the filter was removed, heated again to 160°C for half an hour (since the column beneath the droplet generator was heated to 110°C, there was probably not any water remaining, but this step assured that each filter was in the same dry state, before and after). Following the final drying step, the filter was weighed again. The mass difference was then compared with the known amount of lead nitrate introduced into the generator. This ratio is the mass recovery efficiency. Our mass recoveries are uniformly high (0.85 to 0.95), indicating that particle losses within the generator/drying tube are minimal.

Table 1 displays the results of the mass recoveries and the calculations of dry particle diameter and lead concentration. These mass recoveries reproduce the results of prior experimentation at PSI very well.

Table 1. Results of Aerosol Mass Recovery Tests

Solution Concentration (% wt)	Mass Recovery Efficiency	Dry Particle Diameter (microns)	Lead Concentration (ppmw in air)
0.091	0.95	4.6	8.6
0.41	0.90	7.6	36.2
0.41	0.88	7.6	35.8
0.93	0.85	10	78.4

3.1.3 SIBS Spectra of Aerosols

We will describe the operation of our SIBS system using the detection of $Pb(NO_3)_2$ aerosols for our primary example. Procedures for detecting the other species is similar. Results for all species detected are summarized in the following subsection.

We used the apparatus shown schematically in Figure 5 for the SIBS calibration experiments. It consists of the aerosol generator discussed above, high energy spark source, and detection electronics. The spark is initiated inside the drying tube following the aerosol injector. A lens collects light at right angles to the axis defined by the two discharge electrodes, and focuses it on the entrance slit of a monochromator system with an OMA detector. In a number of experiments, rather than using the lens system, we use an optical fiber bundle to collect the light and transport it directly to the monochromator entrance slit.

In order to obtain accurate and sensitive results, the timing between the initiation of the spark and the detection of the plasma is crucial. The spark generation unit is driven by a delay generator that allows the sparks to occur at set intervals. Because of the possibility of the occasional misfire or delayed sparking event, the detection system is triggered by a photodiode. Triggering from the photodiode assures that each observation takes place after an actual excitation event. When the radiation from the spark is observed by the photodiode, a second

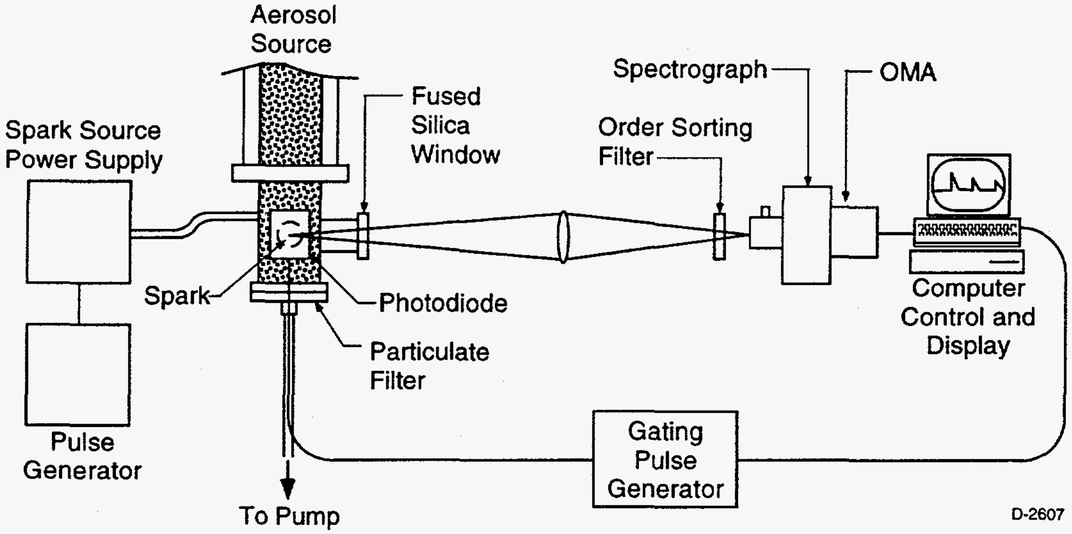

Figure 5. Schematic of system for detecting contaminants on particles or aerosols using the SIBS technique.

delay generator is activated. This generator delays the turn-on time of the OMA, so that the OMA will not be saturated by the very bright initial plasma of the spark itself. This initial bright emission is dominated by a spectral continuum arising from free electrons (bremsstrahlung radiation) present in the spark-created plasma. As the plasma ages, it cools, and line emission from highly excited atomic and molecular species appear. Initially, these excited species are primarily ions. With further plasma cooling, ions and electrons recombine and emission from neutral species of lower energy becomes more prominent. In the final stages of cooling, which can extend past 200 μs for 5 J pulses, only emission from species of lowest internal energy persists. Generally, these are the emissions of interest, i.e., those peculiar to the analytes being introduced.

By carefully choosing an appropriate delay between the spark ignition and the observation period (gate), we can optimize detection conditions for a given element. The spectrum simplifies with longer delays after spark ignition since the emission from the higher energy species disappears. Consequently, even though total intensity is reduced, it is generally useful to observe the signal at long delays after spark ignition.

Figures 6 and 7 show the spectra of lead nitrate aerosols near 405.8 nm under conditions of no delay, and with a 75 μs delay (both with a 20 μs gate), respectively. The spark produces an intense, prompt plasma, so the spectrum taken with no delay is very complex, showing many wide, unidentifiable features. Applying a delay, however, greatly simplifies the spectrum and atomic lead emissions are readily apparent. This is because the prompt emitters radiate quickly leaving only persistent metastables which can excite the atomic states. Data similar to that in Figure 7, taken for a number of different aerosol concentrations, allows us to construct a calibration curve (Figure 8). Similiar calibrations have demonstrated a minimum detection limit (MDL) for lead of 10 ppbw, well below the NIOSH TWA limit for lead dust (80 ppbw or 0.10 mg m^{-3}).

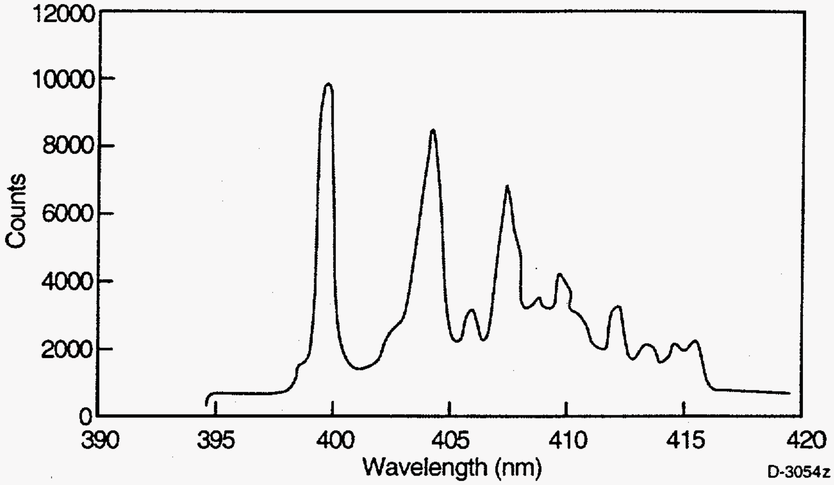

Figure 6. SIBS spectrum of Pb aerosol with no delay between spark and detection.

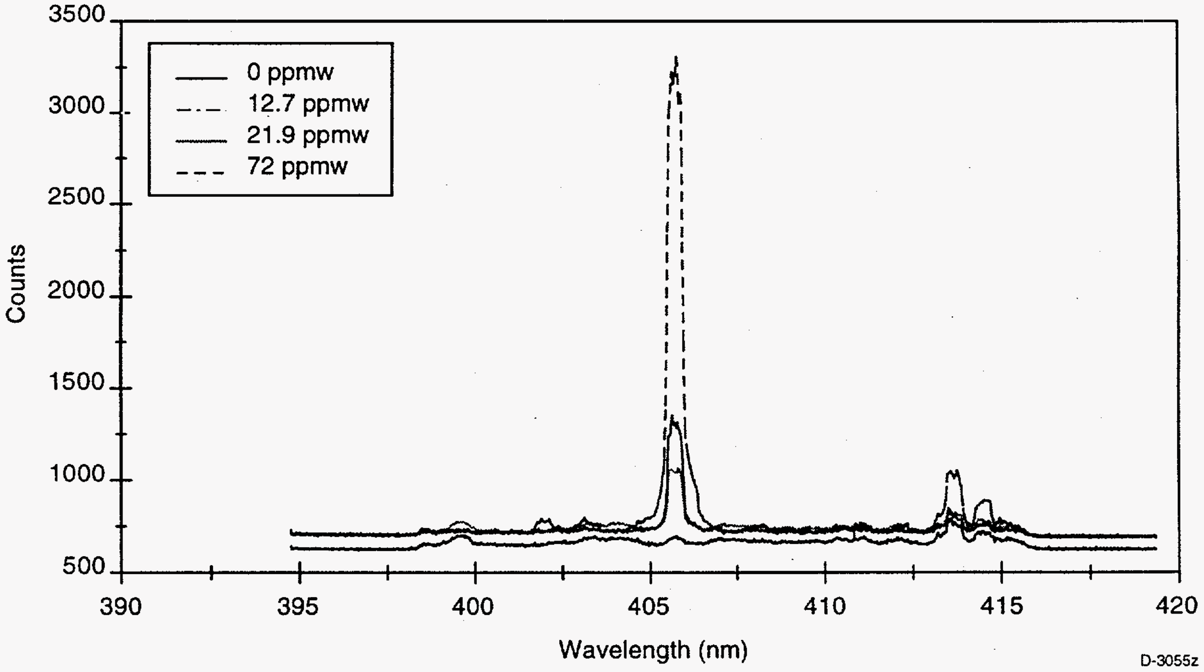

Figure 7. SIBS spectra around 406 nm at different Pb-aerosol concentrations with detection delayed 75 μs after the excitation spark.

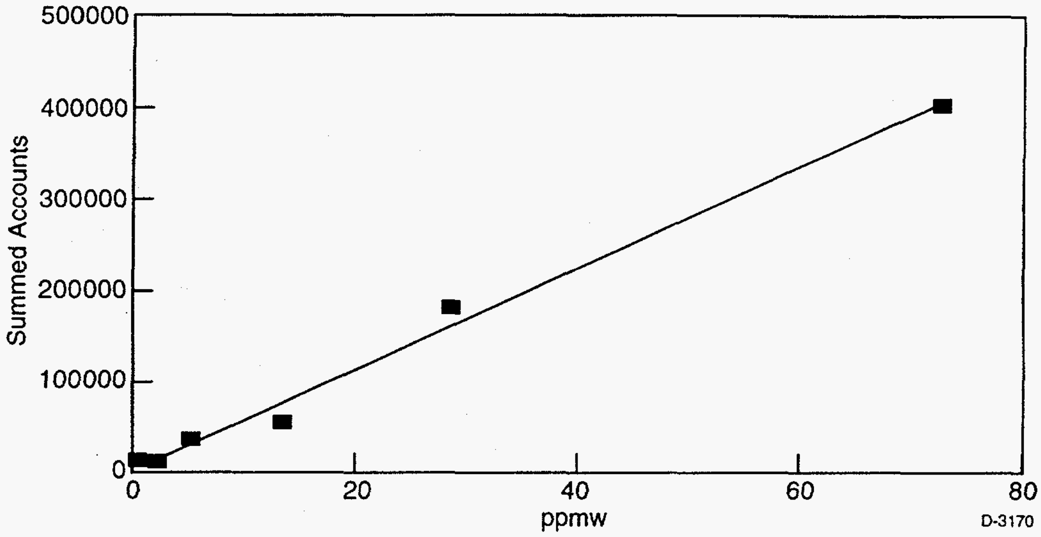

Figure 8. Calibration curve for the detection of Pb aerosols by SIBS.

3.1.4 Results of Technology Extension Tasks

Figures 9 through16 show representative SIBS spectra and accompanying calibration curves for the elements Cd, U, Th, and Mn (a Tc surrogate), respectively. Figures 17 and 18 show the SIBS spectra for Hg and Cr detection. For these atoms we did not construct a full calibration curve, but can readily estimate a minimum detection limit for these species based on the intensity of the lines in the spectra, and the typical noise levels observed in all our other measurements. Table 2 summarizes the results for all species investigated for the diagnostic extension tasks. Because we were intent on surveying a number of different species, we did not spend much time trying to optimize detection of individual species. We are confident that with a little refinement in our detection and analysis techniques that the MDLs given in Table 2 can be reduced significantly. As it stands, our MDLs are already significantly below the proposed regulatory limits for most species.

3.2 Analytical Testing Survey, Fernald Site Visit and Applications Identification

In order to help us focus our efforts on developing technology best related to immediate DOE needs, we prepared and disseminated an analytical testing survey to a number of DOE sites. Later on, we visited one of these sites (Fernald) for more detailed discussions with personnel directly involved with DOE D&D activities. The results of these two activities dictated the nature of the instrument we have designed and which is to be built and field tested in the third phase of the program. We summarize the results of these two activities in this section. Complete details of the analytical testing survey can be found in Appendix C.

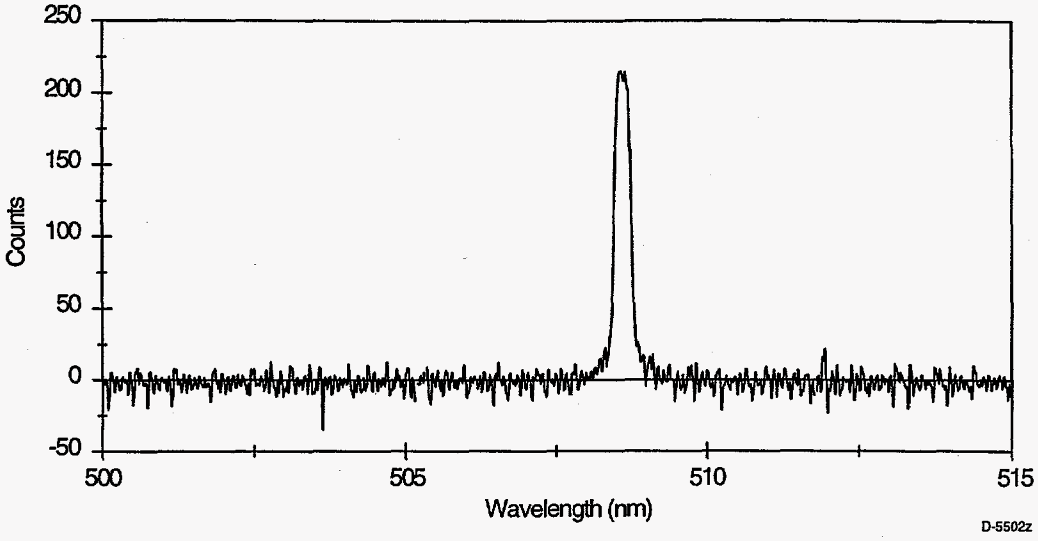

Figure 9. SIBS spectra around 509 nm for Cd aerosol.

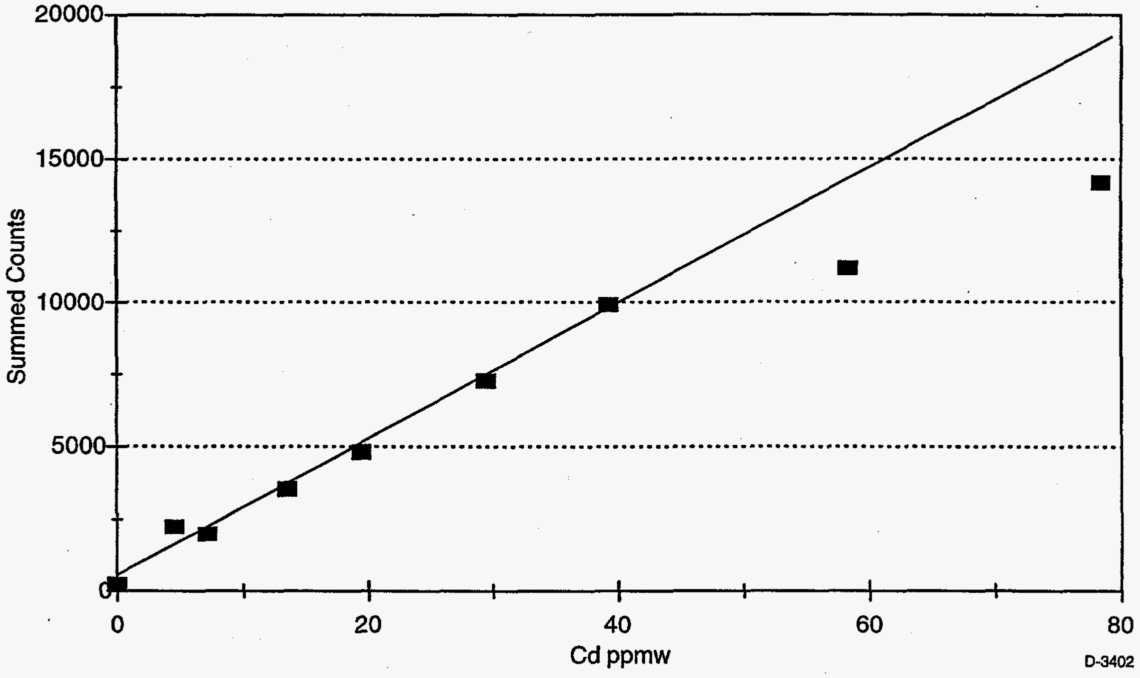

Figure 10. Calibration curve for the detection of Cd-containing aerosols by SIBS.

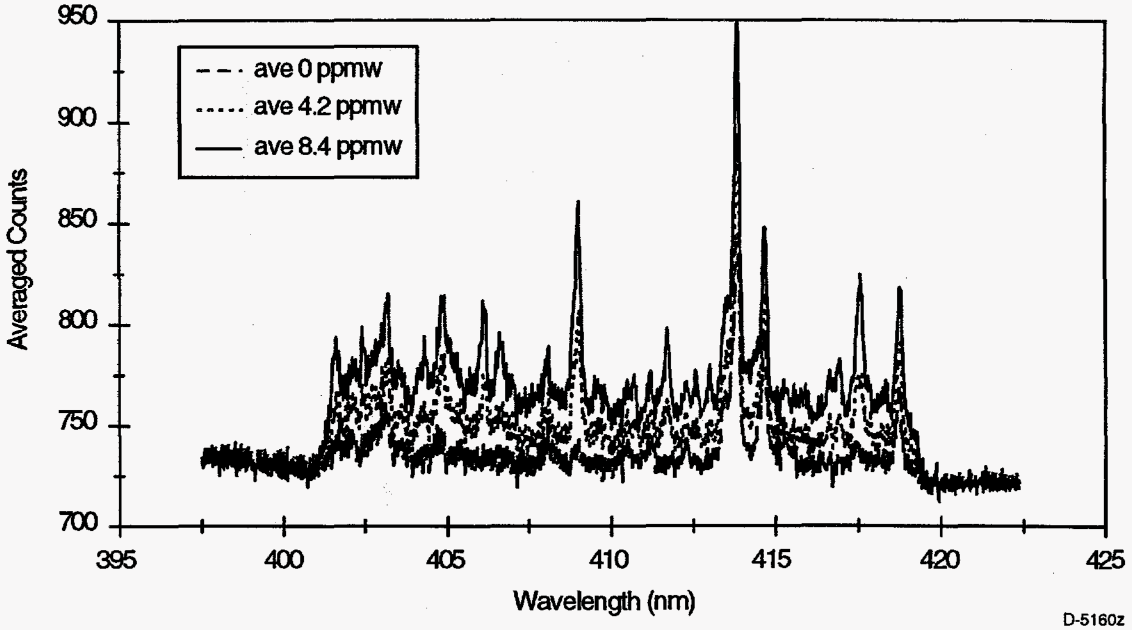

Figure 11. SIBS spectra around 410 nm for several different U-aerosol concentrations.

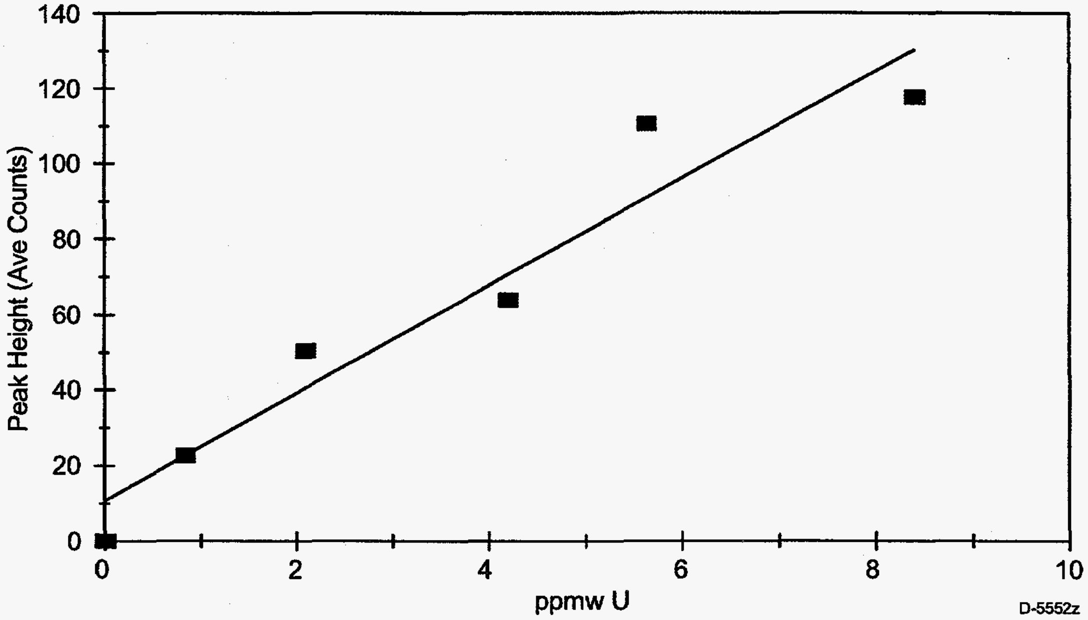

Figure 12. Calibration curve for the detection of U-containing aerosols by SIBS.

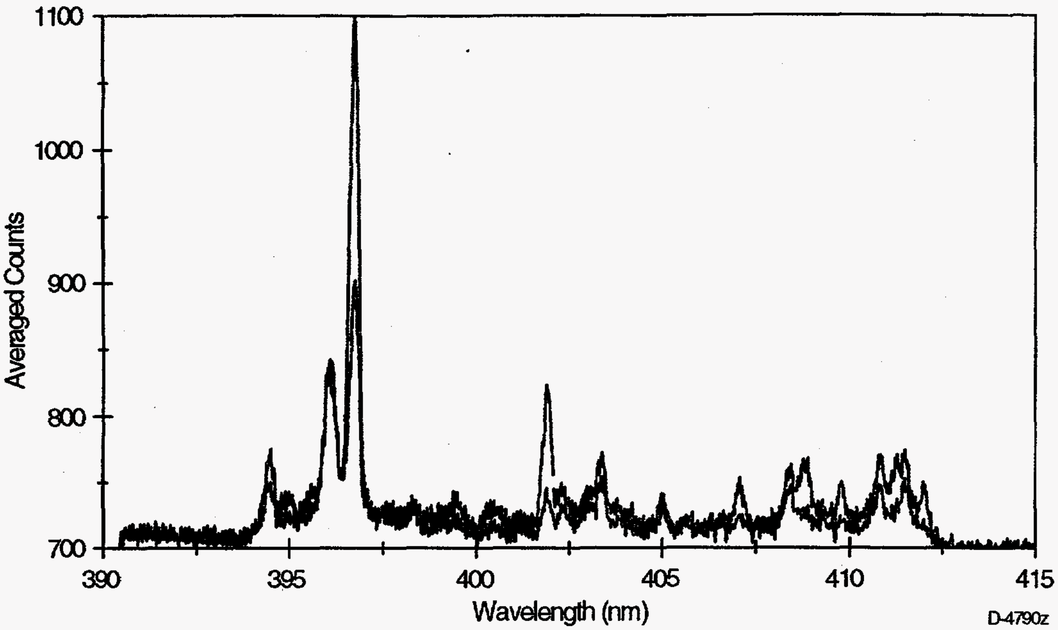

Figure 13. SIBS spectra around 400 nm in the absence of any aerosol, and in the presence of Th-containing aerosol.

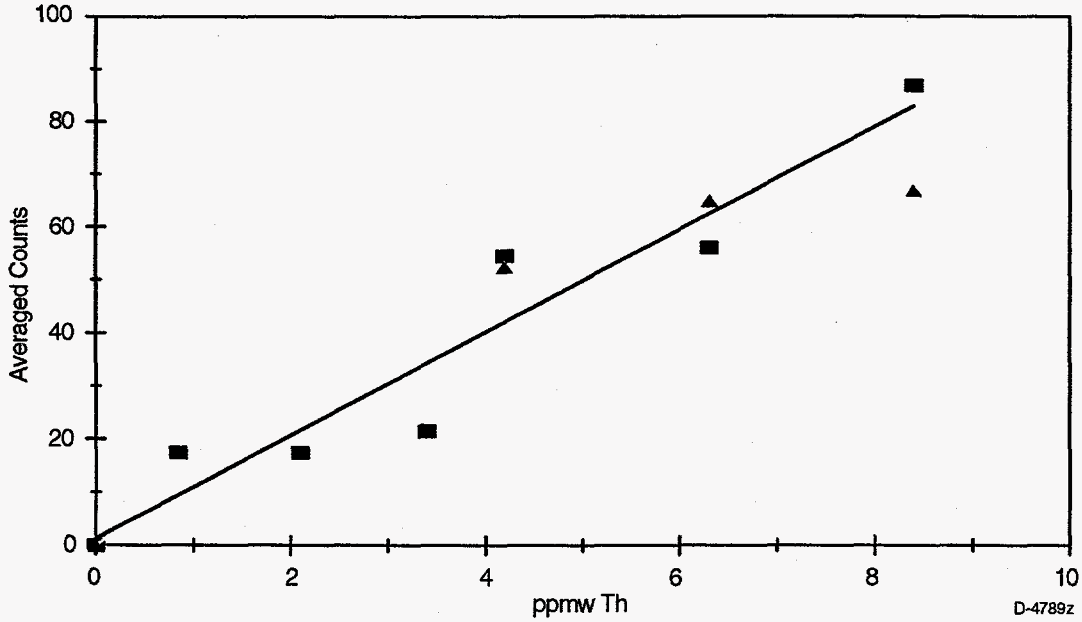

Figure 14. Calibration curve for the detection of Th-containing aerosols by SIBS.

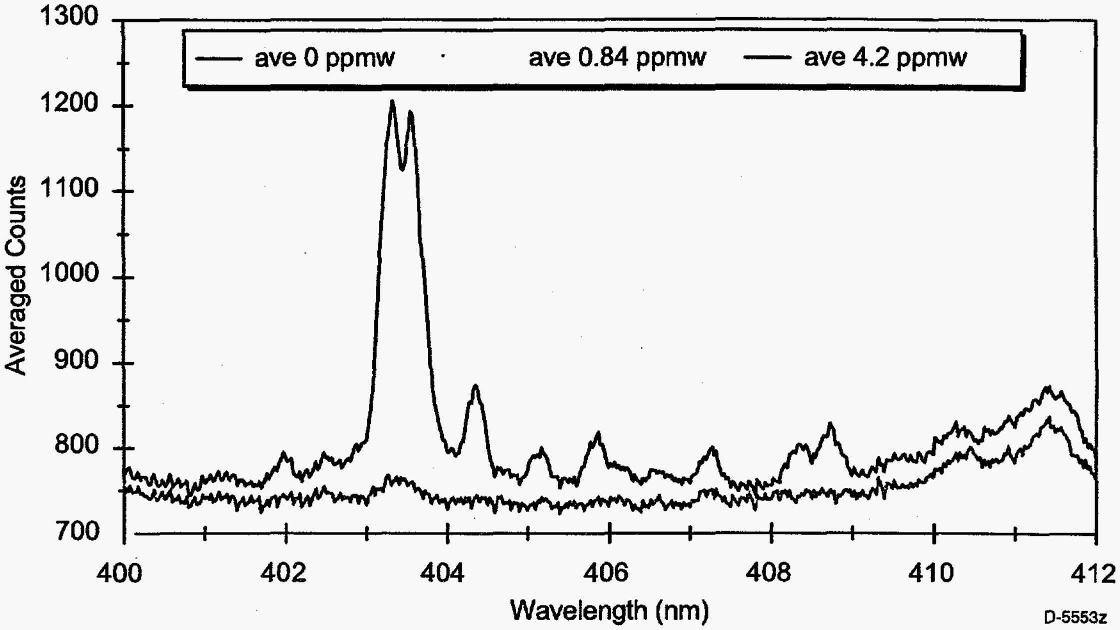

Figure 15. SIBS spectra around 405 nm for several different Mn-aerosol concentrations. Mn, being chemically and electronically similar to Tc acts as a surrogate for the latter species.

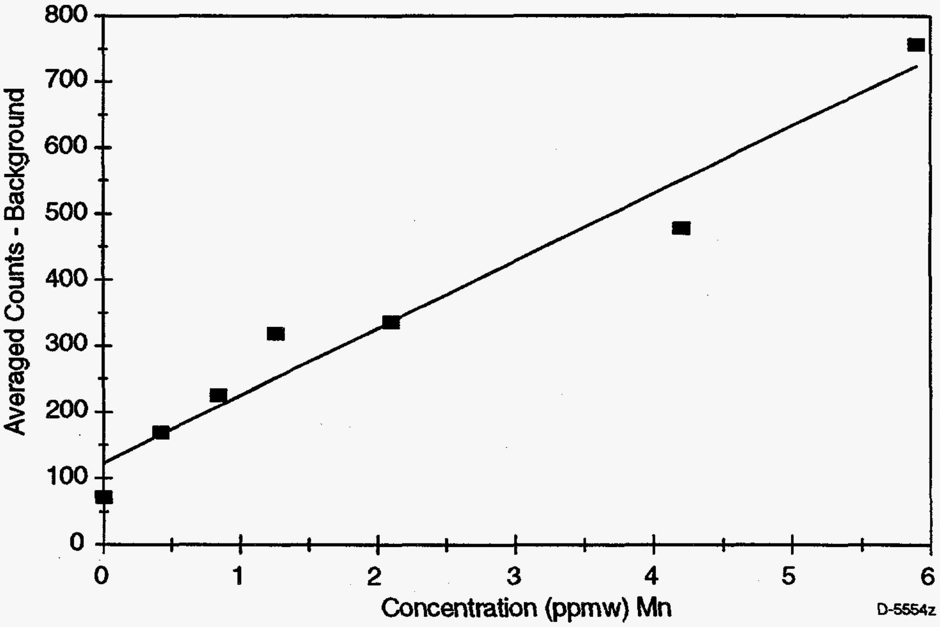

Figure 16. Calibration curve for the detection of Mn-containing aerosols by SIBS.

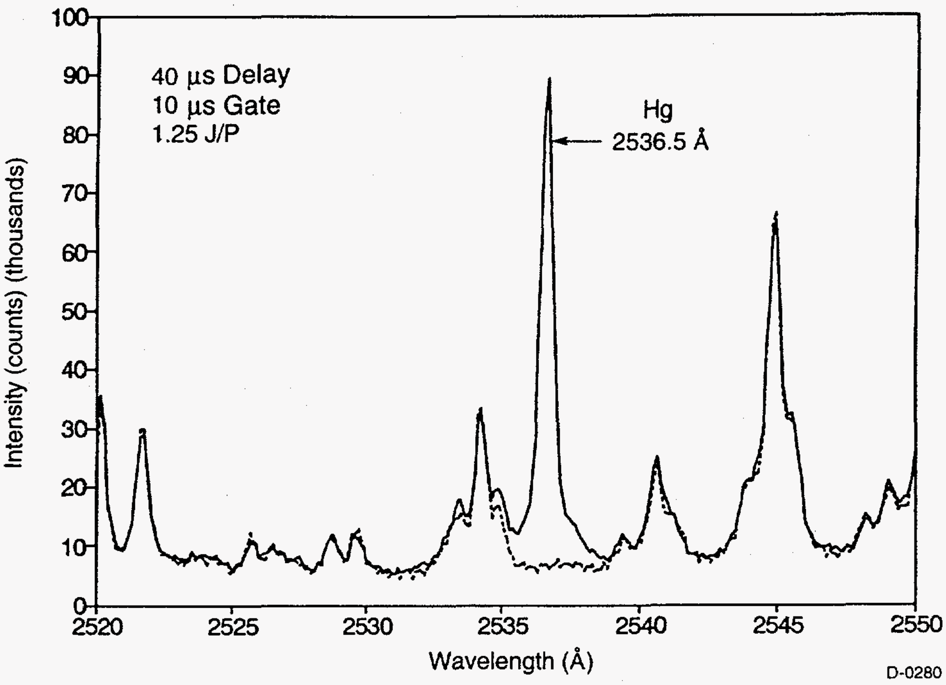

Figure 17. SIBS spectra around 254 nm for Hg-containing aerosol.

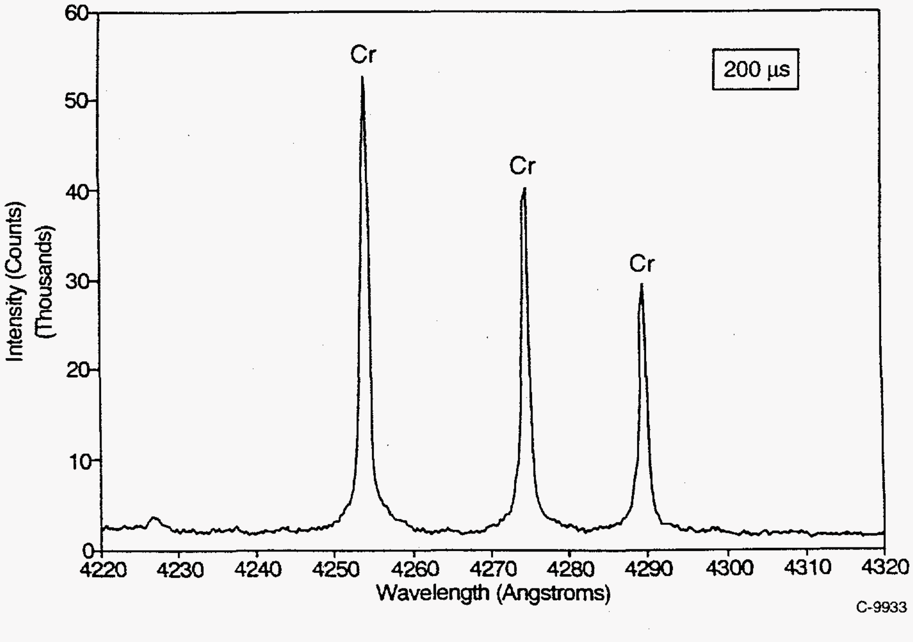

Figure 18. SIBS spectra around 427 nm for Cr-containing aerosol.

Table 2. Results from Technology Extension Tasks

Detection Method	Element	Detection Sensitivity (ppbw)	Regulatory Limit[2] (ppbw)
	Pb	<10	80
	Sb	<200	400
	As	<200	400
	Cr	<25,000	400
	Hg	≤10	40
SIBS (metal-laden aerosols)	Pb	10	40
	Hg	<25	40
	Cd	<100	80
	Cr	<10	400
	U	<300	480
	Th	<1000	120
	Mn (Tc)	<40	(2.5)

1. ANET sensitivities are for detection of a sample in air. Reducing the oxygen content of the sample dramatically improves detection limits. Some reduction in the D-B lamp pressure is also beneficial.

2. Regulatory limits refer to ACGIH time weighted average (TWA) levels except for the radionuclides. The radionuclide limits are based on maximum quarterly intakes by inhalation of insoluble compounds.

3.2.1 Site Survey Results

In order to match our design to the needs of the clients, a survey was performed to determine their chief concerns. This survey was developed to address primarily the issues of the types of applications for which the client required analytical testing, the analytes of interest and the concentration ranges that were expected for each analyte. We also inquired about the matrix in which the sample was found, what methodology they were currently using to analyze the sample and whether the testing was done in-house or sent to an outside laboratory. Related questions included what issues they would like to see addressed in the development of new technology. The results of these surveys were in some ways predictable, but in others quite surprising.

With respect to their uses of the current technology, the majority of the respondents are performing site and risk assessment; a few are doing actual D&D. Others are using current analytical technology to do environmental restoration, waste management and emissions and effluent monitoring. Clients were analyzing for a wide range of species, from organics to metals and radioactives. The majority of the respondents send their work to outside laboratories. An almost universal complaint is turn-around time, with samples often taking 6 weeks to be analyzed. Many respondents were also dissatisfied with the cost of these analyses. Additionally, it should be mentioned that most of the respondents have analytical budgets exceeding $500K per year.

The results of the new technology development portion of the survey reflect directly on the above results. The respondents wished to see instrumentation developed that was highly accurate, sensitive and reliable (i.e., it must meet regulatory requirements). Additionally, it must perform on-site and in real time. New technology would be expected to show a direct savings with testing (lower cost per analysis) and also show savings by enabling faster and more efficient D&D operations. While savings during operation are crucial, outright costs of the new technology were not ranked high in importance. Somewhat surprisingly, multi-species and speciation capabilities were also not ranked highly. Lastly, the survey shows that the mechanism for introducing the technology and regulatory approval are very important issues to address.

If we exclude organics, a multi-species monitor will be competing with ICP, AAS, AES and radiochemistry. We will need to be able to meet or better their performance while being able to analyze on-site and in real time. This clearly raises many questions with regard to the issues of sampling, speciation and preferred suite of contaminants. These questions are be best addressed during site visits. Other key issues that must be addressed are engineering and business issues as diverse as decontamination procedures and field portability versus lab use and how many units would be required for each site.

The results of this survey are summarized in Appendix C.

3.2.2 Summary of Fernald Visit

Two people from PSI went to visit Fernald in southern Ohio, some 18 miles northwest of Cincinnati on 21 November 1996. The Fernald facility was initially set up as part of the Manhattan project and its aftermath. Their charter was to refine pitchblende into uranium metal. They would then ship the uranium elsewhere for further processing, i.e., refining, isotope separation, fuel pellet preparation, etc. A number of years ago, they stopped operating, and now the focus of people on the site is to clean it up and return it to public sector use.

The site has been operated by Fernald Environmental Restoration Management Company (FEMCO). Recently they changed their name to Fluor Daniel Fernald (FDF).

The purpose of the visit was to get a better understanding of the actual problems PSI personnel would be dealing with were we to become involved in DOE D&D activities. We proposed a fairly detailed agenda for the meeting (please see Appendix D). Many of our more detailed questions, however, could not be addressed in the time available. We left a list of our detailed concerns with the people we met and they promised to respond to us within a couple of weeks.

The primary lesson we learned at the meeting was that D&D activities are extremely site specific, and any instrumentation developed to aid the D&D program necessarily needs to be designed with very specific applications in mind. Another important lesson was that requirements for instrumentation to determine cleanliness levels of wastes may not be all that important or useful at some sites. In some instances it appears that the most economically viable clean-up procedure involves burying any waste that could conceivably be contaminated in sealed bunkers. The current costs of disposing waste in this manner is often less than the cost of testing the waste to see if contamination levels warrant such disposal. Such decisions, naturally, do vary depending on the quantity and nature of the contamination involved. It becomes particularly important, then for DOE to continue funding the development of new characterization techniques. Ultimately, long-term disposal merely defers characterization and cleanup to future generations.

3.2.3 Identification of Near-Term Applications

Based upon the results of the site surveys, the information learned during our visit to Fernald, information obtained from various DOE world-wide-web pages, and the recent redirection by DOE of their technology development programs away from development and toward rapid deployment, we have identified the following applications as ones our technology can address most readily in the near term:

- Ambient air quality during decontamination and dismantlement processes
- Monitoring/controlling decontamination procedures
  - Pb-based paint removal
  - cement-floor scabbling.
- Off-gas continuous emissions monitoring
  - vitrification plants
  - hazardous waste incineration
- Process control for vitrification or incineration.

Our technology can also address other needs, such as monitoring contamination on surfaces or in sludges and waters, but some additional developmental work will be necessary. Basically, our technology is ready now to address the applications listed above. All items on our near-term applications list have in common that the contamination to be measured is air-borne.

While most decontamination and dismantlement processes are designed to minimize the escape of contaminated dust, no containment process is completely fool proof. In addition, it may be possible in some situations to relax containment procedures considerably without adversely affecting worker safety. Our system could be placed on location, where the clean up processes are being undertaken, to ensure that ambient air quality remains below levels that pose a hazard to workers. As we understand it, current procedure involves considerable over application of safety measures just to be safe. This over application can be both expensive and inefficient. Employing one of our stand-alone systems on site, could result in considerable speed up of remediation operations without compromising worker safety.

A number of decontamination processes involve activities in which coatings are removed from surfaces, or thin layers of the surfaces themselves are removed. In particular, DOE sites are reputed to contain thousands of acres of concrete that is contaminated by various materials such as uranium and thorium. Our monitor could be used in concert with the decontamination processes to signal when the coatings were completely removed, or when a contaminated floor had been scabbled to sufficient depth that remaining contaminant levels were no longer a hazardous. Such monitoring would both speed up the scabbling process and reduce significantly the volume of waste generated that would require safe disposal.

Finally, the compact nature of our sampling head, and the relatively inert nature of the materials used in its fabrication, allow off-gas monitoring to be done *in situ*. That is, the samples need not be removed from the flue through a probe first. One can verify contamination levels, in real time, because our monitor provides readings every few minutes at the most, that RCRA metals and species such as U and Th are below proposed regulatory limits in the effluent from incineration or vitrification processes. Furthermore, because our detection is real time, species concentration measurements can be used for process control purposes. That is feed rates of hazardous materials, or additives used in off-gas cleanup processes can be varied in real time to make the processes work at their most efficient levels.

3.3 Process Development Tasks

An instrument using SIBS to monitor hazardous wastes in real-time will have four essential components:

1. A spark system for atomizing the aerosols and exciting contaminant fluorescence

2. A detection system for separating contaminant fluorescence from other features excited by the spark

3. A data processing system for controlling the various instrument components, for collecting the data, for converting the raw data into hazardous waste concentrations in the sample, and for reporting and archiving hazardous waste analysis results

4. A calibration system to ensure the accuracy of the hazardous waste measurements.

In our developmental work, we considered each of these issues in some detail before beginning our instrument design.

We will begin by describing the basic principles of the instrument operation. Figure 19 shows a block schematic of the instrument where the component subsystems are identified. Samples are typically drawn through the spark chamber by a small pump. In the spark chamber, the aerosols are vaporized contaminant fluorescence is excited. Light from the spark region is collected by optical fibers and transported to the detection module which can consist of either a pair of matched photometers for single element detection, or an optical multichannel analyzer (OMA) for multielement detection. The detected signals are read and processed by a computer system, and results are displayed and stored. The computer system also provides timing signals to drive the spark source and gate the detection system, and where needed, can also provide feedback signals for active control of remediation processes.

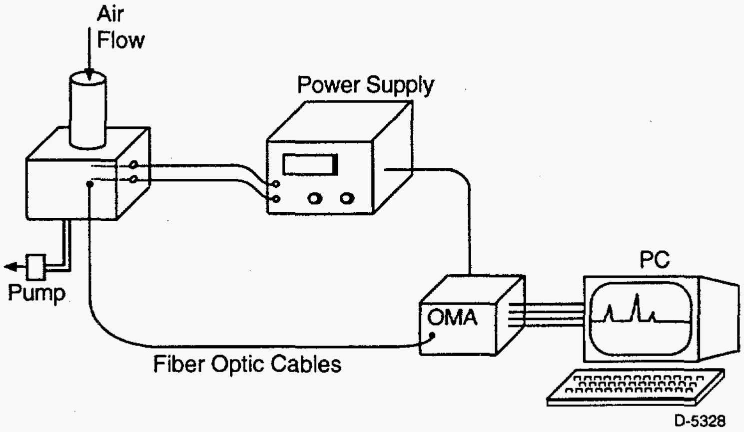

Figure 19. Block diagram of SIBS-based hazardous waste monitor.

A calibration system will be included with the instrument. This system will be able to generate known quantities of contaminant, and will be so configured that the detection head can be bolted directly to it.

Our initial system performance and design goals are as follows:

- Ability to detect heavy metals and radionuclides in gas phase and on particulates
- Sensitivity range for all species below OSHA limits
- Automated calibration for all contaminant species
- Analysis and display of results in less than 1 min
- Size, <65 x 65 x 125 cm (approximately 15 ft^3)
- Weight <115 kg
- Power <3.5 kW.

We will now describe each of these component systems in detail

3.3.1 Spark Source

Our monitor uses atomic fluorescence emission spectroscopy for its primary diagnostic input. This sensitive detection method requires a means to excite the analyte metal atoms. During Phase B we have tested two methods of excitation: active nitrogen energy transfer (ANET) and spark induced breakdown spectroscopy (SIBS). As noted above, most applications we envision being able to address in the near term pointed us toward SIBS excitation because of its greater overall flexibility compared to ANET. Thus, our design is based upon the requirements for SIBS.

The spark source for SIBS must provide a short duration spark (≈2 μs) of moderate energy (1 to 5 J). During Phase B we designed and built a power supply that provided up to 5 J in a 2 μs pulse at 1 Hz. This power supply was adequate for our verification tests. In order to provide enhanced sensitivity and efficient real-time signal averaging capabilities, however, we think an operating rate of at least 10 Hz is desirable. We could design and build such a device, but these requirements are readily met by commercial pulsed power supplies that are commonly used in flashlamp pumped lasers. For example, solid state Nd:YAG lasers or alexandrite lasers that produce tens of joules of electrical energy per pulse and operate at 10 to 20 Hz are readily available and not overly expensive. Consequently, we may well use a commercial, portable power supply. A unit manufactured by Kaiser Systems Inc. has the characteristics we desire (please see Table 3).

If we do decide to build our own supply, it will have a circuit like that shown above in Figure 4, and will use the components listed in Table 4.

Table 3. Characteristics of Pulsed High-Voltage Power Supply for SIBS System

Voltage	≤ 30 kV
Current	100 mA
Energy out	1500 J/s
Approximate cost	$3,000

Table 4. Component Specification for High-Voltage Power Supply Shown in Figure 4

Part	Manufacturer	Part No.
1. Strobe power supply	EG&G	PS-450
2. 12 Vdc power supply	Sola	SLS-12-051
3. Blocking capacitor	Sprague	40DK25
4. Capacitive discharge ignition system	MSD	Blaster 2
5. Diodes — 15 kV	NTE	517
6. Connectors	Superior	PP50 GR
7. Connectors	Superior	RS50 GR
8. High-voltage cable (18 ga., 40 kV)	Rowe	R800-4018-9
9. Interlock Relay	Potter and Brumfield	
10. Energy storage capacitors (0.64 μF @ 3kV)	Cornell Dubliner	92 6049
11. Power switch (fused)	Heinemann/Eaton	PS1
12. Switch bezel	Heinemann/Eaton	PS1-BZ
13. Switch lamp	Heinemann/Eaton	009-18250
14. Retainer clips	Heinemann/Eaton	
15. Potentiometer	Bourns	3540S-1-1-3
16. Resistors (6 MΩ , 2W, 750 V)	Allen-Bradley	RC 42
17. Rack-mount chassis	Bud	CH-14404
18. Chassis cover	Bud	CH-14432
19. Power input filter	Corcom	6VM4
20. Trigger relay	Crydom	ODC-15

The output of the power supply will be sent to energy storage capacitors and then connected to the discharge electrodes using a high voltage coax cable. We have chosen Re as the electrode material based upon the Phase B results and its characteristics. For example, it has a high melting point and is resistant to ablation. In addition, Re is very resistant to oxidation, a crucial characteristic for monitoring in air. The properties of Re are provided in Table 5.

Table 5. Physical Characteristics of Rhenium

Melting point (°C)	3180
Boiling point (°C)	5650
Density (g cm^{-3})	21.0 (25°C)
Electrical resistivity (µΩ -cm)	19.3 (20°C)

The electrodes will be held in holders that allow adjustment of the gap. Our Phase B results have indicated that electrode spacing about 3 mm provides discharges that result in optimum atomic emissions.

The electrode assembly will be a part of the active sensor head that is used to sample the material to be tested. The sensor head will be modular to allow for various applications. For example, for air sampling of materials that may be produced during remediation activities, the sensor head can be made of plexiglas. For other potential applications such as off-gas monitoring where the temperatures may be several hundred degrees a more refractory material such as alumina will be used. Regardless of the application, the main purpose of the sensor head is to provide a uniform sampling volume that is excited by the discharge and viewed by the optical collection system. In addition, where necessary, the sensor head will be equipped with a small air evacuation pump to provide a small flow (liter s^{-1}) of the air to be sampled.

In order to make the sensor head as portable as possible, we will make extensive use of fiber optic cables to collect the atomic emission optical radiation that is produced by the spark. In our Phase B experiments we found that bare fibers (600 micron core) located 5 cm from the discharge volume provided adequate collection. Our alpha prototype however will be equipped with the option of using a collection lens to increase the collection efficiency. This will further increase sensitivity of the instrument. The design of the sensor head is detailed in Figure 20 that illustrates the relative arrangement of the electrodes, and fiber optic collection cables.

We plan to use at least two fiber optic cables. One cable will terminate at the input of an optical multichannel analyzer that will be used to examine the atomic emission. The second fiber optic cable will be used to provide a trigger source for the OMA. The delay time between the plasma initiation and the beginning of the OMA observation window is a critical parameter. The selectivity and sensitivity of the SIBS monitor, therefore, is maximized by proper selection of this delay time. The second optical fiber will terminate on a Si photodiode/transimpedence amplifier that will be used to establish the clock for the OMA data acquisition of each pulse.

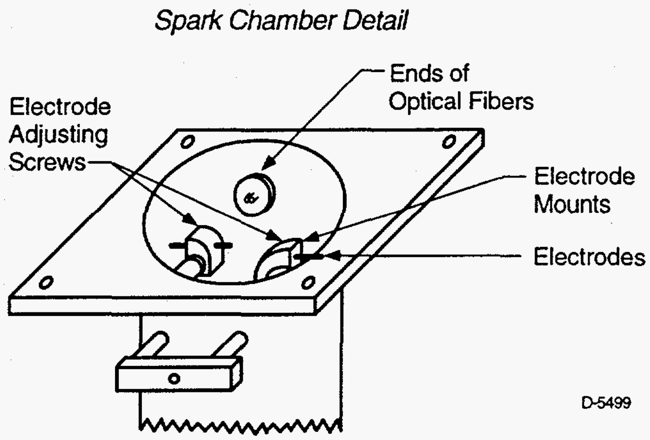

Figure 20. Detail of spark chamber, showing relative positions of electrodes and optical fibers.

The transimpedence amplifier output will provide a trigger pulse to the OMA gate delay. Thus if there is any pulse-to-pulse temporal variation in the formation of the plasma, the OMA will be able to examine a window at a known fixed time after the formation of each plasma pulse. This will significantly reduce systematic variations in the observed metal atom emission signals.

3.3.2 Optical Detection System

Our Phase B work indicated two possible optical detection systems that we will use for our Phase C alpha prototype unit:

- A narrow bandpass filter photometer for analysis of materials containing only one or a few metals,
- An OMA for multiple metals analysis of samples.

The following two subsections describe our approaches for employing these detection schemes in our instrument.

3.3.2.1 Design of Filter Radiometer

The Phase B results, along with additional data obtained under PSI IRAD funding, have shown that SIBS spectra for some metal atoms are quite simple. For example, spectra for Pb, Cd, Cr, and Hg were shown above in Figures 7, 9, 11, and 19, respectively. Using these spectra we developed detection strategies for some metals that require only two narrow band interference filters and a pair of miniature photomultiplier tubes (PMTs). Under our IRAD program we designed and constructed a Pb monitor using the strategy illustrated in Figure 21. It shows the Pb SIBS emission spectrum from Pb containing aerosols superimposed on the transmission spectra of two narrow-band interference filters. As illustrated, one filter passes emission from the lead line as well as from near by background emissions while the other observes only the background emission. The difference between the signals monitored at the two different

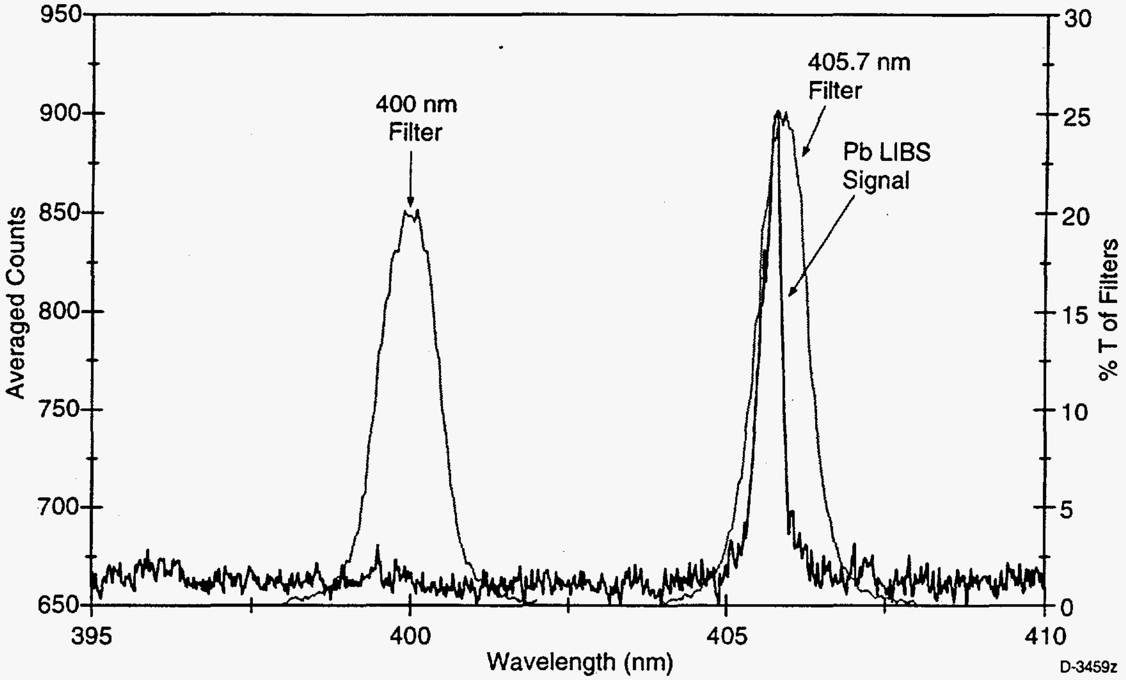

Figure 21. SIBS emission spectrum from Pb containing aerosols superimposed on the transmission spectra of two narrow-band interference filters.

wavelengths is due only to Pb emission. This approach provides a very sensitive means of detection Pb emission in our system. Similar strategies are appropriate for detecting some of the other RCRA metals, most notably, Cd and Cr.

The filtered-photometer approach should also be appropriate for samples containing two or three metals, e.g., Cr, Pb, and Cd. Appropriately chosen and matched pairs of interference filters and PMTs would be used to detect each of these metals in real time. For some applications where it is known that only a few metals will be required, this radiometric design approach will be used. For example, Figures 22 and 23 show background-corrected spectra in regions suitable for Pb and Cd detection respectively. These spectra were taken with the OMA system when a mixed aerosol containing both species was in the spark chamber. These figures illustrate, therefore, that our technology can detect these two important metals simultaneously, and that having one of them present does not interfere significantly with our ability to detect the other. Table 6 lists the component parts used in our radiometer system.

3.3.2.2 Optical Multi-channel Analyzer for Multi-element Analysis

For many applications involving multiple metals or metals with more congested spectra, such as U and Th, we will use an OMA to detect the atomic fluorescence. We plan to use the InstaSpec® optical multichannel analyzer made by Oriel Instruments. This device is very sensitive and is equipped with significant operational and data analysis software. One of the key features of this software is that it allows the user to display spectra in real time or display intensity of chosen spectral peaks in real time. This feature, by itself, provides relative metal-atom concentrations in real-time. Table 7 lists the component parts used in the OMA system.

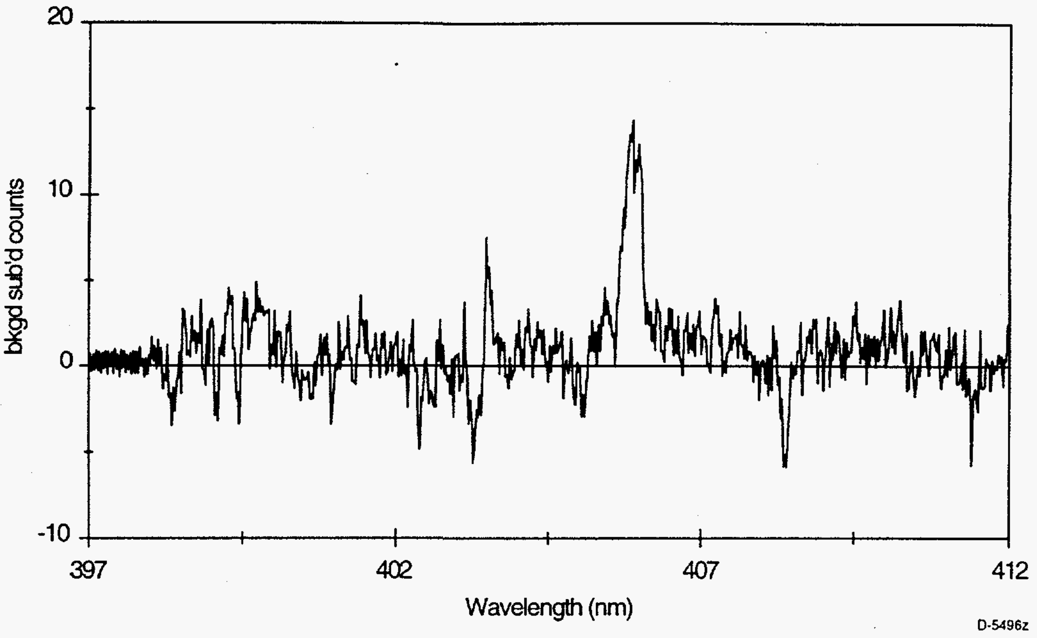

Figure 22. SIBS spectrum of Pb emission around 405 nm from the spark-induced breakdown of an aerosol containing both Pb and Cd.

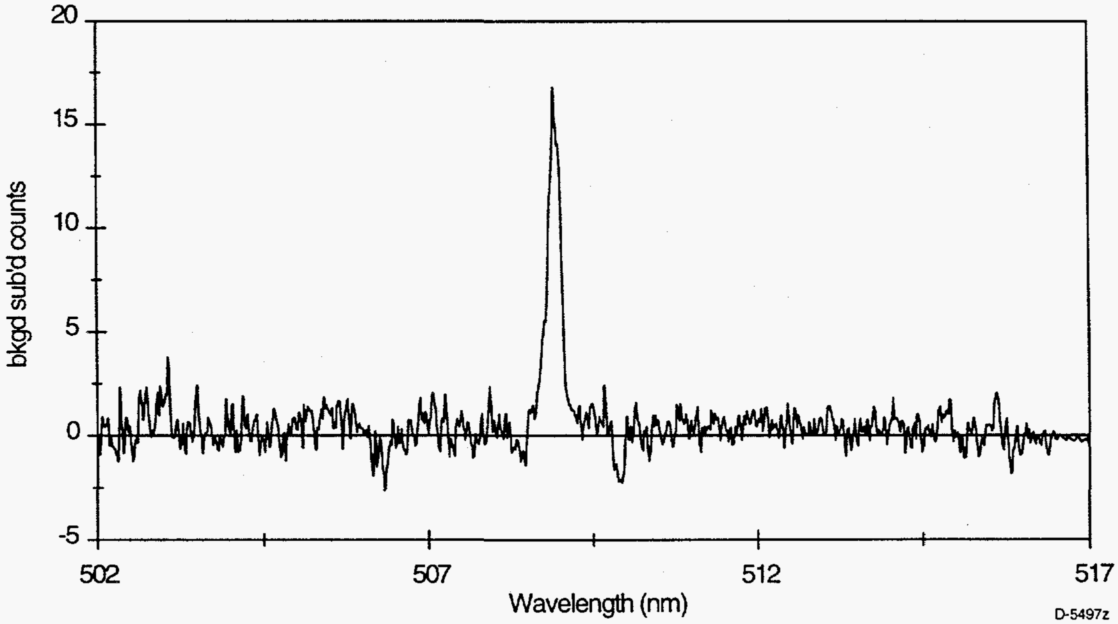

Figure 23. SIBS spectrum of Cd emission around 510 nm from the spark-induced breakdown of an aerosol containing both Pb and Cd.

Table 6. Components List for Radiometer and Data Acquisition Systems

Pentium 100 MHz, 16 MB RAM, 850 hard drive, 1.44 floppy, keyboard, 14 in. SVGA monitor, 1 MB video card, DOS, Windows 3.1

Thorlabs adjustable lens holder SM1V10

Thorlabs lens tube SM1L20

Thorlabs SM1 to fiber coupler adaptor S1TM11

Andover Corporation 400 nm interference filter (fwhm 1 nm)

Andover Corporation 405 nm interference filter (fwhm 1 nm)

(2) Thorlabs cablized fiber, one end SMD, one end cleaved FT-600-UAT

National Instruments data acquisition card HTMI016E-1: PN/777142-01

National Instruments breakout box SCB-68; PN/776844-01

National Instruments cable SH6868; PN 182419-01

Rose Instrument enclosure 07.40.0530-00

Hamamatsu miniature photomultiplier tube assemblies: HC120-06
(185-950 nm, 40 k amp, 500 kHz bandwidth)

Melles Griot lenses (1) 01LQF028 and (2) 01LQF136

(2) Thorlabs fiber collimation packages F270SMA

(2) Digikey 10 turn, 10 k, 2W pot 73UA103-ND

(2) Digikey 20 turn dial and lock 3412KL-ND

(2) Red Lion miniature DVM display (200 mV full scale)

(2) Digikey +-15 Vdc/0.4 A power supplies PW9946-ND

(2) Wall transformers 1309-ND

(2) Panel mounts jacks CP-6-ND

(2) Two BNC panel jacks

(3) BNC cables (two 3 ft long, another of sufficient length to reach trigger source)

Table 7. Components of Optical Multichannel Analyzer System

Part Description	Model No.
InstaSpec V intensified CCD	78521
MS125 1/8 m spectrograph	77400
Mounting flange	77439
Grating — 600 l mm^{-1}, 400 nm blaze	77414
100 μm slit	77223
Multiple I/O accessory	77159
SRS delay generator	SP1000-439

3.3.3 Data Processing System

The data processing system regulates all components of the hazardous waste sensor, collects data from each component, runs automatic system calibrations, converts collected data into contaminant-species concentrations, and displays measurement results in real time as well as stores them for later retrieval and archiving. Our prototype instrument will use a portable computer for this purpose. A commercial instrument would undoubtedly incorporate a single-board computer with operations programmed into EEPROM memory.

Our system will have IBM-compatible portable PC with Windows 95-based software. Several data acquisition and control boards will be installed inside the computer. Software to interface between primary instrumentation, the boards, and the computer is being developed using the National Instruments LabView®, object-oriented programming language. This system produces a virtual instrument that has a screen display much like an instrument panel. The virtual instrument is controlled from a graphical user interface (GUI) on the computer's screen by clicking the computer's mouse on virtual buttons, or by entering numbers into specially designated blocks on the screen. An example of one such instrument panel is shown below in our description of the Pb monitor.

The two-filter radiometer design will employ a high speed analog/digital conversion board manufactured by National Instruments (HTMIO16E-1). We used this device in our Pb monitor described below. We have also developed GUI and menu-based operating and analysis routines for this instrument using National Instruments Lab Windows CVI® software. This provides real-time viewing of the metal atom concentration as well as automatic recording of the data to file. More details on the software are given below in Section 3.4.

Much of the software needed to control the Oriel InstaSpec® optical multichannel analyzer is provided by the manufacturer. We will augment this software with more sophisticated data analysis software that will allow extraction of metal atom concentrations from the more congested spectra that result either from more complex atomic emitters such as U or Th or from simultaneous emission from several metals. We will use a chemometrics approach to analyze such spectra. Chemometrics is a non-linear data analysis method that uses known spectral features (basis sets) to fit an observed spectrum and obtain the relative contributions of each component. At PSI we have developed a variant of this method that we call spectral fitting for the analysis of complex molecular spectra. We are therefore very familiar with these data reduction techniques. For the alpha prototype we will purchase a commercial chemometrics routine since it will be more efficient to couple such software into our instrument.

One area where this approach will be particularly useful is in dealing with background emissions, particularly those relating to ablated electrode material. While the Re electrodes have numerous attractive properties, some Re is ablated during the discharge and several spectral lines from this element are observed. We will store the wavelengths and relative intensities of these lines in the data acquisition computer to allow their subtraction from each spectrum. These sputtered-electrode emissions, however, are not just a background interference. They provide a measure of the intensity of each spark and can be used to normalize each emission-pulse event. This normalization procedure when implemented will significantly reduce the noise component of the fluorescence signals and will thereby greatly improve the overall sensitivity of our analytical procedure.

In order to optimize this software for our applications, the spectral line positions and relative intensities of all the observed lines for each metal that we observe in our SIBS device will be stored as an array. In addition the positions and relative intensities of the Re emission lines will be stored. The spectral bandwidth of the OMA spectrometer will also be entered as an input depending on the particular slit width being used. When a particular sample spectrum is recorded, the chemometrics software will apply the stored basis set and convolute this basis set with the spectrometer spectral bandwidth.

Finally, the data processing system will also be programmed to provide all other necessary control and housekeeping features. Signals will be sent from the computer to turn electronics instrumentation on or off. Important features relating to ambient conditions will be read by the computer from sensors sending such information to its data acquisition boards. The delicate timing pulses used to control the spark generation system and gating signals needed to control the detection electronics will all be operated by the computer software and set and controlled by the GUI used to interface the computer with the instrument's operators.

3.3.4 Calibration System

We described earlier our aerosol generator that can provide metal laden particulates of known concentrations. We will use this device to provide aerosols to the sensor head and spectra will be recorded. These data will be used to establish the basis sets for chemometrics software. The aerosol generator produces a monodisperse stream of aerosols of known concentrations of metals. As discussed above the generator is cross calibrated by a gravimetric method that involves capturing the aerosols on filter paper and weighing the mass of the captured aerosols.

This calibration source has the advantage that different discharge configurations can be attached to it and calibrated. It can also be used to simultaneously calibrate an optical system that uses an OMA or a set of interference filters. The aerosol calibration source was shown above in Figure 3. The calibration feed solutions are made from NIST-traceable ICP standards.

3.4. Engineering Design of Prototype Instrument

3.4.1 Hazardous Waste Monitor

Regardless of the method of analysis of the optical spectra (filter photometer or OMA) the basic design of the Hazardous Waste Monitor will be the same. The system components will be arranged as indicated in Figures 24 through 27. The timing and triggering electronics, the discharge power supply, the spectral dispersion and detection module, and the data acquisition and control system will be contained in a standard, half-height 19 in. equipment rack. The sensor head (shown above in Figure 20) that contains the electrodes and fiber optic collection optics will be contained in a separate, small portable module. Figure 28 shows an engineering drawing of this module. The sensor head will connect to the main instrument via an umbilical containing the optical fibers and the cables to power the spark system. This will allow placement of the sensor head at desired locations including areas remote from the operator. The system will require standard 110 V power service.

3.4.2 Lead Monitor

The prototype instrument we have developed in this phase of the program, and which we described in the previous section, will naturally bear some resemblance to the SIBS-based Pb monitor, a prototype of which we developed using internal funding. We will describe some of the operating characteristics of this instrument below, and show several pictures of its operation.

The data acquisition and control system for the Pb monitor is based on a fast (1.2 MHz) digital-to-analog board manufactured by National Instruments. This board allows us to acquire and process the data from the two channel radiometer with time resolutions of 2 μs/channel, and in addition, enables both signal averaging and general data processing. At PSI, we have extensive experience in GUI methods and have incorporated that into this unit. We will use National Instruments LabWindows CVI® software to construct the GUIs. We have developed numerous diode laser based sensors in the past that use this approach. The advantage this approach has is that one can write custom data reduction codes in "C", while the user interface is through the menu style GUI screens. The display windows will contain the raw data traces from both channels (400 and 405.8 nm), the difference between the two channels, and the integrated difference. This last quantity is directly proportional to the lead concentration and is displayed as a strip chart recording thus providing a real-time record of the lead concentration.

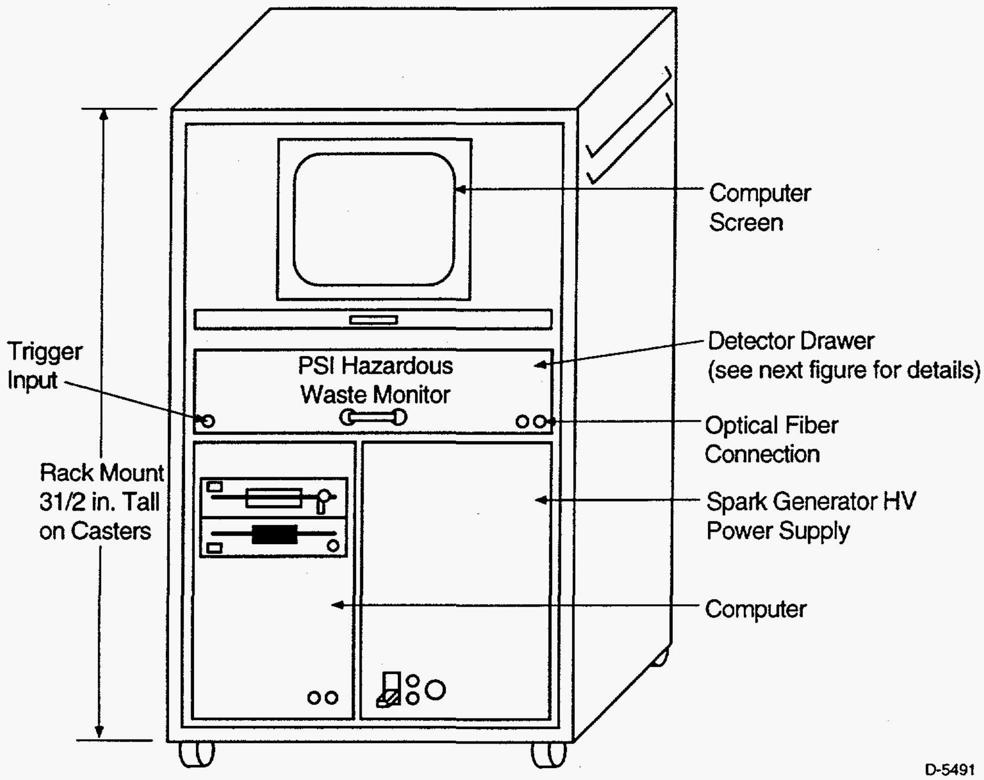

Figure 24. Diagram of complete hazardous waste monitor.

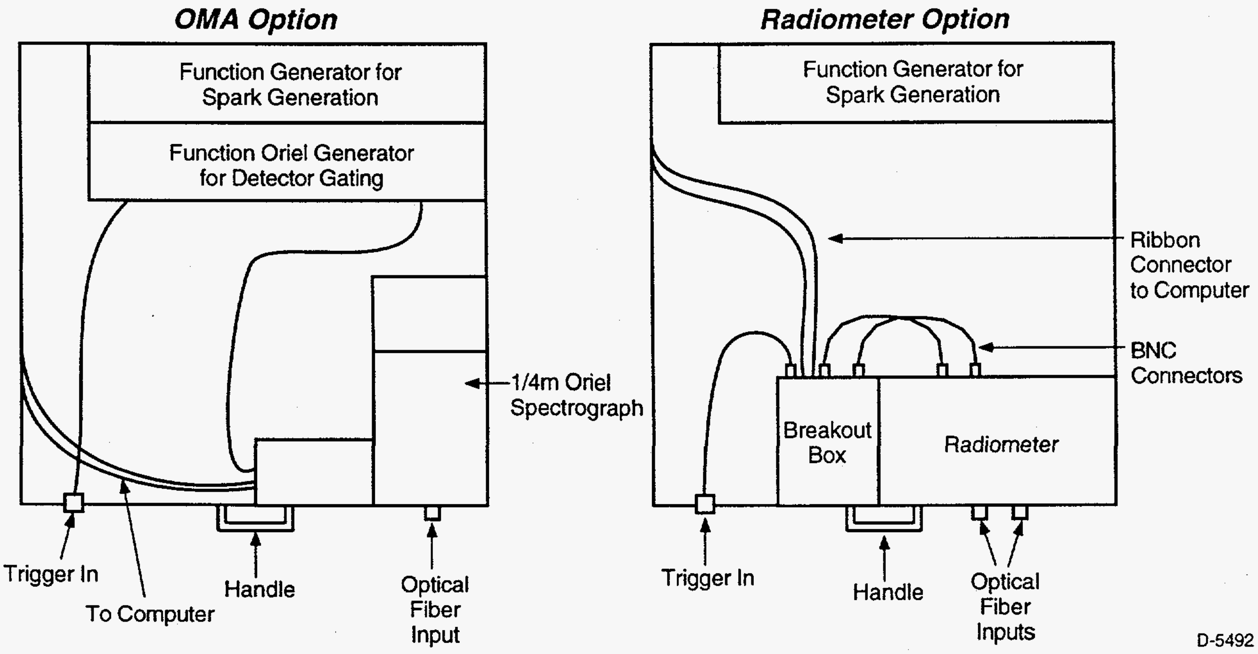

Figure 25. Details of the detector system drawers. Option A is when the OMA is used as the detector, and Option B is when a filtered photometer will suffice for detection.

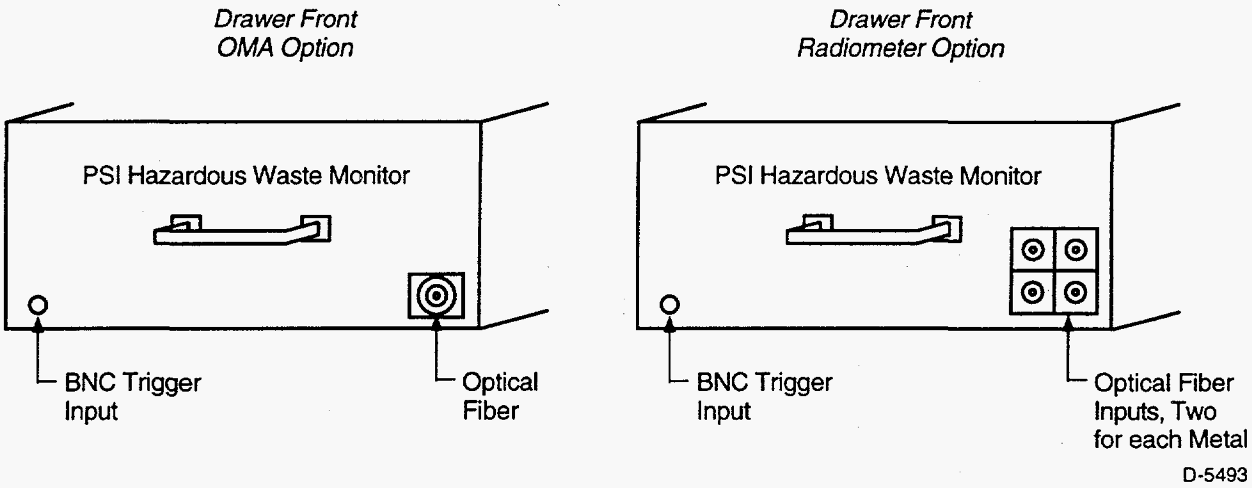

Figure 26. Details of the front of the detection system drawers.

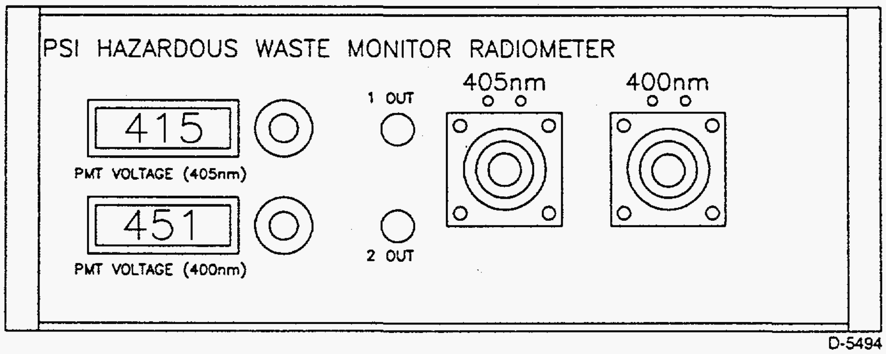

Figure 27. Engineering detail of front of radiometer module.

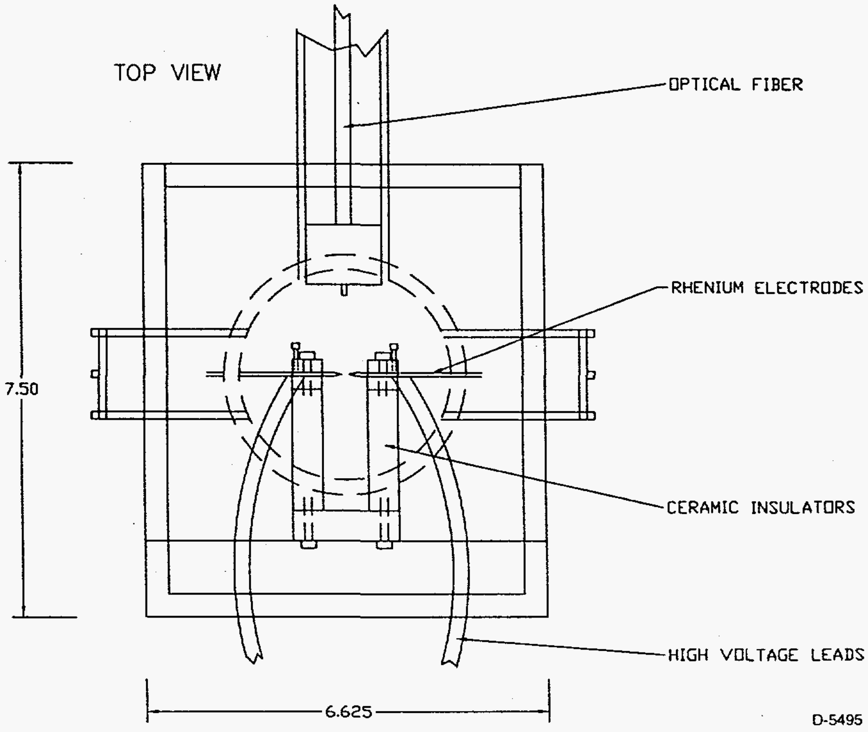

Figure 28. Engineering detail of spark chamber.

The lead monitor package consists of two GUI windows: a setup window and an acquisition window. Figure 29 shows the setup window. The left panel is used to display the temporal evolutions of the 405 and 400 nm traces. The right hand panel is used to display the difference between the SIBS intensity at these two wavelengths. This setup window is used to assure that the system is working properly and is ready to acquire data. The acquire window is shown in Figure 30. The left panel displays the difference between the SIBS signals at the two wavelengths for a user selected number of averages. The red and yellow cursors are used to select that part of the SIBS emission temporal profile that contains the Pb emission. From our previous work using the OMA, we know that this occurs between 40 and 100 μs after spark initiation. The right hand panel of the acquisition window displays the integrated area of the emission that occurs during the time window set by the cursors. The data traces shown are typical. The system has the capability of being triggered externally by the spark system in order to synchronize the data acquisition. The data are also written to file so that post processing can also be accomplished. This PC based approach has several significant advantages over our original idea of using a boxcar integrator. First, the user is provided with real time displays of the temporal evolutions of the SIBS emissions. One can use this information to optimize the time window to obtain the maximum sensitivity to lead. Secondly, the results are displayed in real time. Finally, since data are also written to file, more sophisticated data analysis can also be performed after the data the collection is complete.

A photo of the complete data acquisition system is shown in Figure 31. The radiometer containing the two miniature PMTs is on the left. The data acquisition and analysis component is on the right hand side of the photo. The lead monitor menu panel is active on the screen.

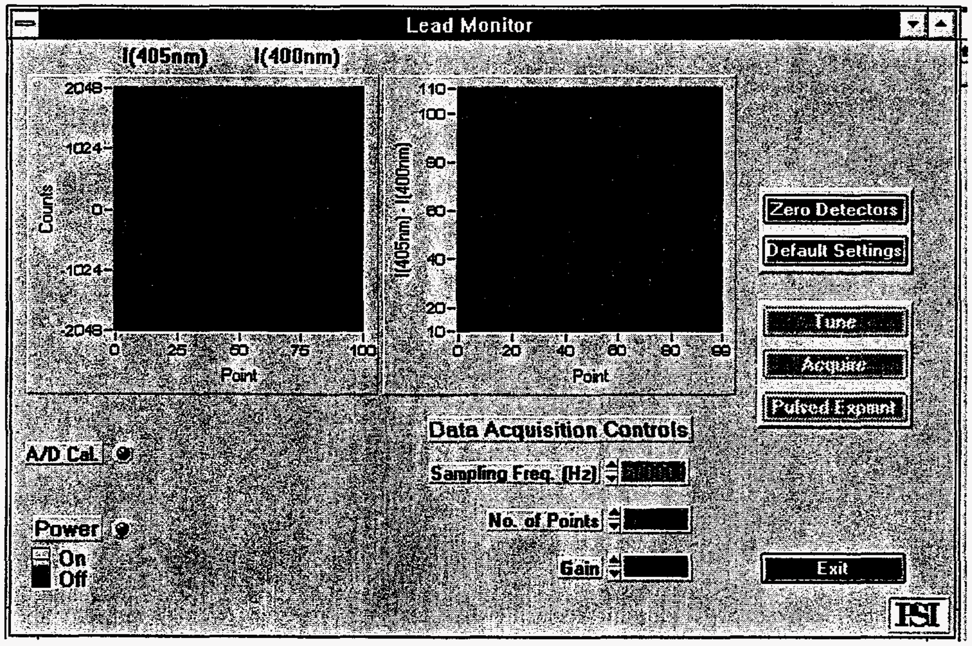

Figure 29. GUI setup screen for lead monitor.

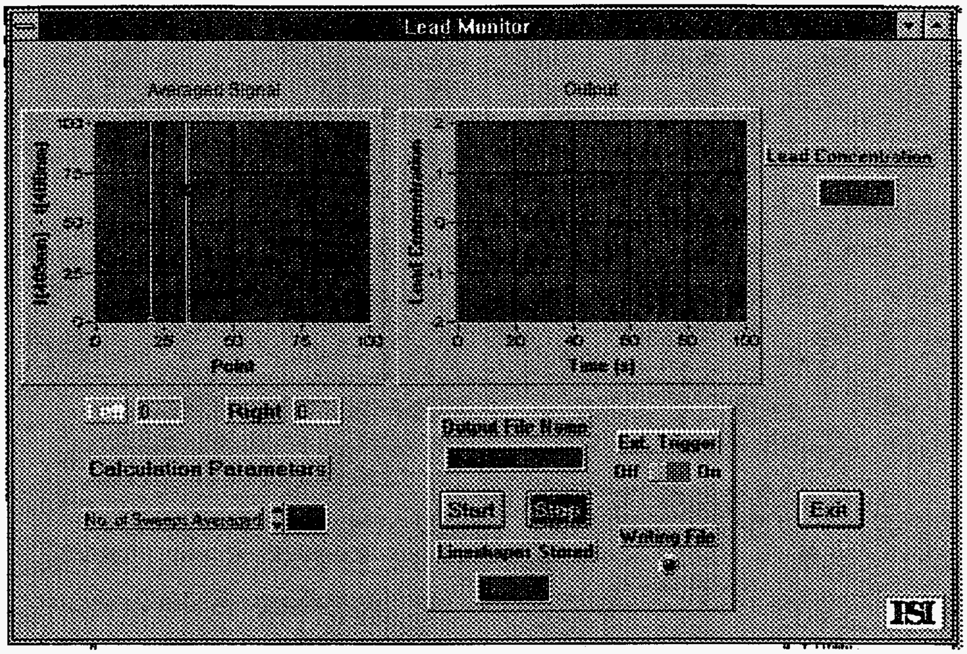

Figure 30. GUI acquisition screen for lead monitor.

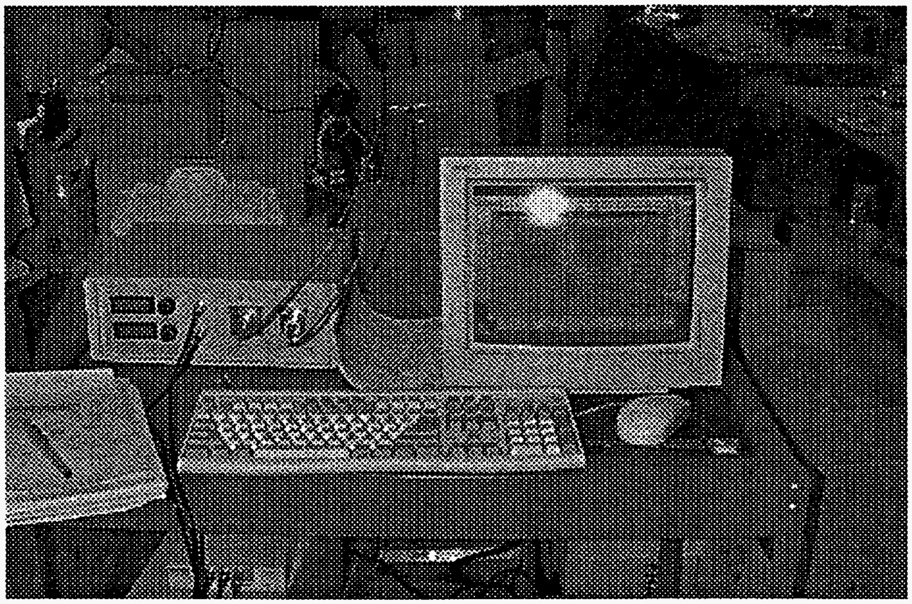

Figure 31. Photograph of fiber optic coupled radiometer and data acquisition computer. Components shown have been described in the text.

3.4.3 Operating Instructions for SIBS-based Hazardous Waste Monitor

3.4.3.1 Routine Operation

Spark Generator

Figure 32 details the components of the spark generation system and their assembly. Assemble the system as shown in the diagram. Note that it is necessary to complete the safety interlock circuit as shown in the figure. The high voltage (HV) cannot be triggered unless this condition has been met. To begin operating the spark generator, ensure that the generator is attached either to the calibration source or to the sampling air tube. This is necessary to ensure safety during the spark production. **This instrument operates with high voltage (>20 kV), and it is therefore critically important to keep the operator and observers away from the electrodes during operation.** The safety interlock on the HV and the complete enclosure of the spark chamber are the two safety features currently implemented. Additional safety features will be added to the commercial system.

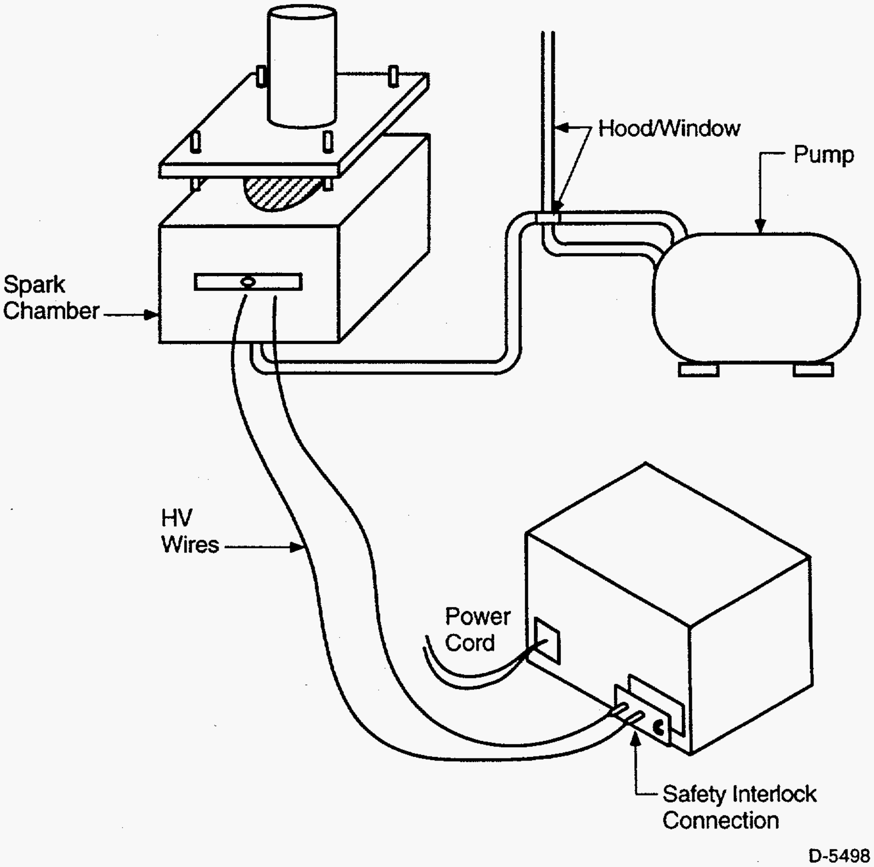

Figure 32. Power setup for SIBS apparatus showing connections between spark chamber and power supply. Figure 20 shows a detailed view of the spark chamber.

Set the desired repetition rate on the function generator associated with the spark power supply. The current configuration of the spark generator will allow pulse rates from 0.5 to 5 Hz. Faster rates will require more frequent electrode maintenance, and should therefore be avoided unless necessary to temporally resolve emission behavior. After setting the repetition rate, turn the power supply on. Sparks will be produced immediately. If they are not, see section on electrode maintenance.

The energy associated with each spark can be controlled through the use of the HV potentiometer on the front of the power supply of the spark generator. This will set the energy of the spark from about 1 to 5 J/spark. Larger energies produce larger sparks, with larger volume. This enables processing of more ambient or calibration aerosols, and therefore more sensitivity, but also ablates more of the electrode material. This will necessitate more frequent electrode maintenance. Irrespective of the energy level selected, once the instrument has been calibrated for a given set of conditions, these settings should not be changed, as this will invalidate the calibration.

Detection System

Multiple Filter Radiometer

Figure 33 shows the connections between the optical fibers and the data collection system to the radiometer body. Once assembly is complete, turn on both the computer and the main power to the radiometer. Select the "CVI" icon on the computer screen, and open it. From the available options, choose "lead.h" and then run the program. This will open the window shown above in Figure 29. When this window is turned on, the detectors can be zeroed. This should be done before the voltage to the PMTs is turned on. Following the zeroing procedure, the PMTs can be balanced. For a 5 J spark, the voltages necessary for high sensitivity will be near 400 V. While observing the left hand window, as well as the right hand "405 to 400 nm subtraction window", balance the PMTs until their temporal traces overlay each other. Because they will only be identical to each other in the absence of analyte, perform this balancing while generating sparks in clean air.

Once the PMTs are balanced, select the "acquire" icon. This will bring up the acquire screen, in which data are collected and stored. This screen was shown above in Figure 30. In this screen, averaging can be done, and files can be saved to the hard drive for later examination in a spreadsheet. In the figure, the output file has been called lead.out. Output files can be named any Windows acceptable name, followed by the suffix ".out".

This screen also allows the user to select the gate necessary to maximize the sensitivity of the method while eliminating the prompt emission of the spark plasma. Since the metal emission occurs for times longer than the duration of the spark, if the detection is delayed until the spark event is over, then the metallic atomic emission can be observed and quantified without the interference of the spark. In our experience with 5 J sparks, this is typically about 50 μs. With larger sparks, this delay may need to be longer. (Given the sampling rate of the A to D board, this will be "25" on the x-axis of the left hand screen.)

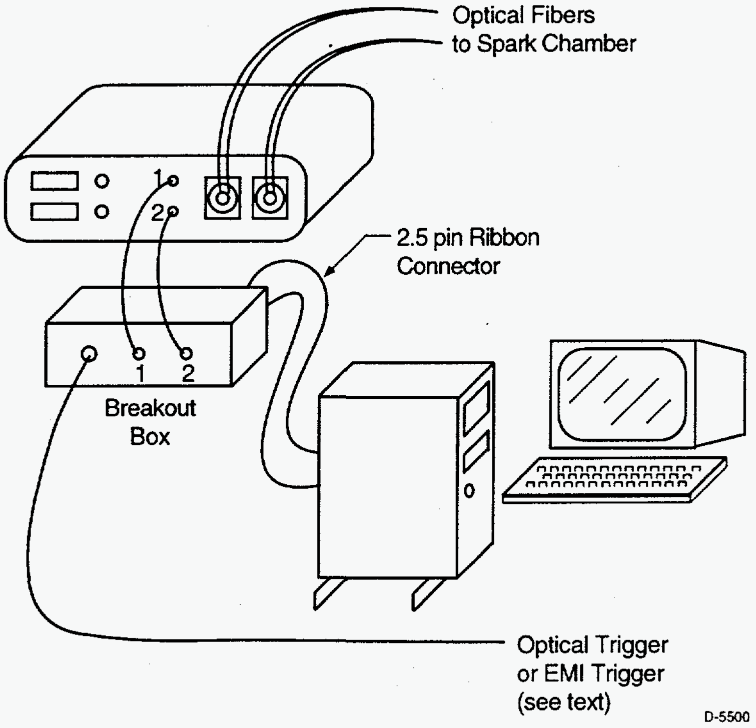

Figure 33. Detection setup for SIBS apparatus showing connections between radiometer head and data acquisition and control system.

Optical Multichannel Analyzer (OMA) Data Collection

If it is necessary to monitor more than a few metals with simple spectra simultaneously, it will be required to use the OMA detection option of the Hazardous Waste Monitor. This system is shown schematically in Figure 34. Assemble the system as shown in the diagram. The OMA is comprised of an intensified CCD camera with a pulser to operate the gating. It is important to heed the warning issued by the manufacturer and not expose the unit to full intensity room light while the intensifier is in operation. This could occur if the entrance slit of the monochromator were not coupled with the optical fibers. Full assembly of the system prior to turning the power on will eliminate this possibility.

The OMA must be operated according to the instructions of the manufacturers. The correct gating of the signal past the prompt spark emission is readily determined by optimizing the intensity of the metal to be monitored at it's characteristic atomic line or lines, while minimizing the background counts at a spectral location where the metal(s) of interest do not emit. Use care when performing this optimization, as the spark is extremely bright, and can injure the diode array if too short a gating period is applied. For the case of a 5 J spark, begin gating at least 25 μs after the spark event.

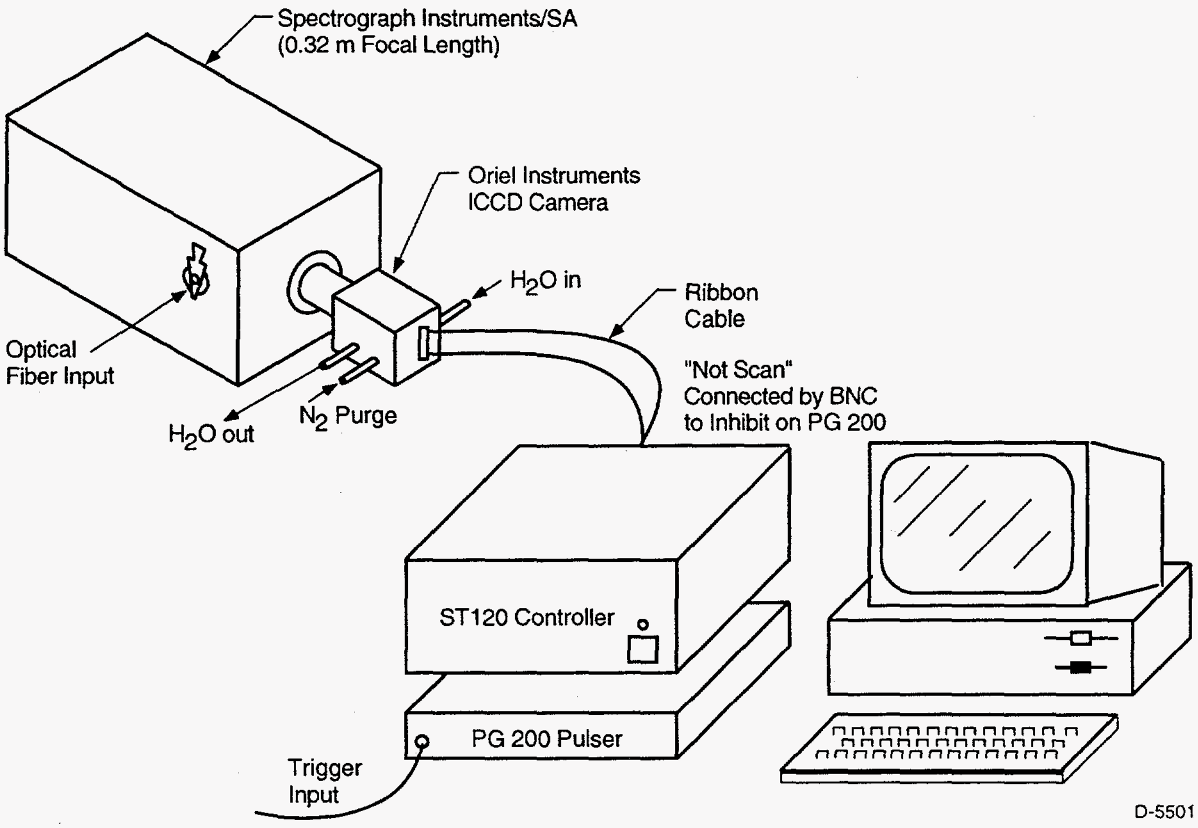

Figure 34. Setup for OMA-based detection.

Triggering

The unit may be triggered in a number of ways. Because a large electric field is generated with the spark events, it may be preferable to trigger the detection system from this field. This is accomplished by using a long (10 to 12 ft) BNC cable as an antenna, running it from a location near the spark chamber to the breakout box as shown in Figure 33. If this configuration does not result in satisfactory triggering (conditions such as erratic or double triggering will be easily diagnosed by going to a 1x averaging and ascertaining one signal input per spark), it is also possible to create a trigger signal with the use of a small photodiode. The device is configured to accept a trigger of 5 to 10 V, although this is can be changed by altering the appropriate line in the CVI code.

3.4.3.2 <u>Maintenance</u>

Electrode Maintenance

While the electrode material in the spark chamber has been chosen to be as durable as possible, with each spark event, some ablation of the electrodes will occur. Therefore, after using the spark generator for some duration (a function of repetition rate and spark energy), the electrodes will require maintenance. If sparking is difficult, first unplug the power supply to the spark generator. After disconnecting, pull the chamber down from the calibration system or away from the sampling tube. Using a tool with a plastic handle, discharge any charge remaining on the electrodes by touching all metallic surfaces inside the spark chamber. **Do not touch any surface inside the spark chamber until the unit has been both unplugged and discharged! To do so may cause serious injury!**

Following these important precautions, the electrodes may be serviced. Unless the gap between the electrodes is noticeably wider than upon installation, do not regap them. It is probable that there is material deposited upon them that is preventing full breakdown. Clean the electrode with fine grit wet-dry sandpaper, dampened with distilled water. After removing any discoloration, rinse carefully with distilled water on a Q-tip. Following two or three rinses, swab the electrodes with methanol, also on a Q-tip. Allow to fully dry before attempting operation.

If cleaning isn't sufficient to renew the electrode function, then (and only then) regap the electrodes. Perform this step by loosening the cap head screws that secure the electrodes in place. Gradually push the electrodes (tenths of millimeters) closer together, testing between each movement. Test by reassembling the unit, plugging in, and attempt sparking. **Whenever the unit is opened again after power has been applied, unplug and discharge the unit, even if sparking has not taken place!**

Optical Fiber Maintenance

If the intensity level changes suddenly with no apparent reason, it is conceivable that the ends of the optical fibers have become soiled. These fibers terminate inside the chamber and should be cleaned with a Q-tip and water, followed by a Q-tip dipped in methanol. When opening the chamber, unplug the power line to the spark generator power supply and discharge the electrodes in the manner described in the above paragraph.

3.4.3.3 Calibration Source

Since the aerosol generation source will have its own extremely detailed operations manual, only a brief description is listed here. The aerosol generator coupled to the drying column was shown in Figure 2 above. By feeding metallic compounds of known concentration through the droplet generator, and allowing the monodisperse droplets to fall through the heated drying column, known concentrations of metal aerosols in air are produced. When the spark chamber is attached to the generator, the aerosols can be used to calibrate the monitor. If the same air flow velocity is used during the testing, the calibration will extend to sampling in open air and in various sampling streams. The formulae that describe the relationship between the concentration of the compound in water to the concentration of the metal in the aerosol follow.

$$\frac{g_{(\text{metal})}}{\text{ml}_{(\text{water})}} = \frac{g_{(\text{compound})}}{\text{ml}_{\text{water}}} \cdot \frac{\text{AW}}{\text{MW}} \tag{4}$$

In this equation, AW refers to the atomic weight of the metal of interest, and MW designates the molecular weight of the water soluble compound used in introduce the metal. To calculate the concentration of the aerosol-phase metal in the spark chamber, the following relationship is utilized.

$$\mathrm{ppmw}_{(\mathrm{metal})} = \frac{v\left(\frac{\mathrm{m}\ell}{\mathrm{min}}\right) \cdot E \cdot \left(\frac{g_{\mathrm{metal}}}{\mathrm{m}\ell_{\mathrm{solution}}}\right)}{\rho \cdot s\left(\frac{\mathrm{cm}^3}{\mathrm{min}}\right)} \tag{5}$$

In this formula, v is the rate of introduction of the sample into the droplet generator. E is the passage efficiency of the heating column. ρ is the density of dry air, and s is the pumping speed.

Before calibrating the monitor, is it advisable to measure E by generating a dry aerosol of known density and allowing it to flow for a known time period onto a preweighed high-volume filter. By comparing the amount of compound collected on the filter with that introduced into the droplet generator, high E can be ascertained. Under conditions of low passage efficiency, refer to the manual provided with the aerosol generator.

3.5 Commercialization Plans

PSI is committed to the commercialization of the SIBS heavy metal technology. Our project has been accepted into DOE's "Dawnbreaker" program. The goal of the "Dawnbreaker" program is to develop and refine viable business plans through a cooperative effort between the small company, DOE, and industry and venture capital representatives. We are also receiving assistance from the Global Environment Technology Enterprise (GETE).

We have completed the first draft of the SIBS heavy metal detector business plan for submission to "Dawnbreaker." A copy of this report is attached as Appendix E. "Dawnbreaker" will be evaluating the draft, with revisions planned, over the next month.

We have determined that SIBS instruments address annual markets of at least $130M. PSI believes that these markets represent a significant opportunity. There are no currently available field instruments that provide an accurate measurement of heavy metals at an affordable price. As a result, current practice is largely to collect field samples for laboratory analysis. A range of products is under development to address:

- Industrial health monitoring in gun firing ranges and metals processing plants
- Continuous emissions monitoring from coal and oil fired utility plants and waste-to-energy facilities

- Field instruments for use by environmental engineers to characterize and monitor heavy metals in air, groundwater, and soils at environmental remediation sites

- Drinking water quality detection by municipal health officers and maintenance personnel using a hand-held monitor.

PSI has developed the SIBS technology with the aid of substantial funding from the U.S. Dept. of Energy (DOE). The company is seeking a minimum of $5M equity investment to be used to complete the development of its instrument products and introduce the products to target markets. Concurrent with raising that equity, PSI will establish the SIBS project as a separate spin-out corporation. PSI projects that SIBS instrument sales will grow to $36M in the fifth year following initial product introduction in 1999, at pre-tax profit margins surpassing 20%.

4. CONCLUSIONS

Under contract to DOE, Physical Sciences Inc. (PSI) of Andover, MA has developed a monitoring technology with wide application to DOE, commercial, and industrial problems. The PSI Hazardous Waste Monitor is directly applicable to gaseous, aerosol, and particulate species. An air sample containing contaminants is drawn into the unit and the concentration is directly determined in-situ without any extraction or sample handling procedures. The contaminant species that can be sensitively monitored include the most important RCRA metals targeted for regulation under the 1990 Clean Air Act. These are: lead, cadmium, chromium, mercury, arsenic, selenium, and antimony. In addition, the monitor can also detect radionuclides such as uranium and thorium.

For DOE the goal of this instrument is to provide a field-portable instrument capable of screening site contamination to facilitate rapid analysis and decision-making and to evaluate clean-up operations to verify compliance. Other possible applications within the DOE complex are process control in thermal treatment systems, real time offgas monitoring, and worker safety and plume monitoring. In the commercial and industrial sectors, PSI is actively commercializing this technology for application in firing range safety and as a continuous emission monitor (CEM) for utility and incinerator stack gases.

The PSI Hazardous Waste Monitor obtains its high sensitivity by using optical emission from both the metal analyte of interest. This emission is created by direct excitation of the analyte atomic excited states by SIBS. The spark also fully atomizes the sample. SIBS has three principal advantages over other technologies based on atomic emission. These are: lower cost, improved ruggedness, and ease of operation and maintenance. We believe these advantages will make our technology more competitive in both the DOE and commercial markets.

The PSI Hazardous Waste Monitor is at a state of development commensurate with our program with DOE-METC. We presently have a Phase B prototype that has been extensively tested at our own facility on a wide range of RCRA metals and radioisotope aerosols. We are also actively commercializing this technology with assistance from the Global Environment Technology Enterprise (GETE). We have established our proprietary position and are currently writing a business plan under the "Dawnbreaker" program, we are providing internal funding for developing and testing a lead monitor for firing ranges, and we are establishing the test program for Phase C to include one or more field tests under the large scale demonstration program. We believe these efforts demonstrate our commitment to developing a technology that will help DOE meet its goal of timely and cost-effective site cleanup.

5. ACKNOWLEDGMENTS

We appreciate the advice and support of our METC Project Managers, Mr. C. Edward Cristy (Phase A), Mssrs. Scott Renninger, Brian Frankhouser, and David Schwartz (Phase B). We are also grateful for efforts of Larry Vogel of the Global Environmental Technology Enterprise (GETE) for advice regarding commercial development and marketing of our technology. The overall program period of performance runs from October 1, 1993 to November 30, 1998.

6. REFERENCES

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APPENDIX A

Summary of Phase A Results

The primary goals of the first phase of the program were two fold:

- To demonstrate the variety of hazardous species that can be detected by the technique of ANET excitation of atomic and molecular fluorescence;
- To demonstrate that sensitivity limits for detecting several of these species are at parts per billion (ppb) levels.

Species to be investigated included heavy metals, organics and chlorinated organics, and/or transuranic surrogates.

To achieve the stated Phase A goals, we designed a program where we first focused on the ANET technique by studying parameters important to the production and quenching of nitrogen metastables in an atmospheric pressure, D-B discharge. These metastables are the primary excitation species in the active nitrogen. The second component of the program was qualitative and quantitative studies on the detection of several hazardous species including heavy metals, both chlorinated- and non-chlorinated-organic molecules, and uranium compounds. The third component of the program was to investigate the effects of adding small quantities of dust to the D-B discharge region. The two issues to be resolved in this part of the investigation were whether the presence of dust in the discharge region would compromise the operation of the D-B discharge and whether species adhering to dust could be detected.

We demonstrated a linear relationship between the intensity of the ANET excited fluorescence and the concentration of the additive in the discharge region for detection of the heavy metals Hg, Cr, and Se. Our results indicated a sensitivity for Hg and Se detection below 1 ppb. The sensitivity for Cr detection appeared to be somewhat higher, and we have reinvestigated this species during the current phase of the program

All hydrocarbons studied can be detected in a D-B lamp in nitrogen at atmospheric pressure by observing emission from the CN(B - X) system at 388 or 420 nm. Furthermore, if the hydrocarbon is chlorinated, one observes CCl emission at 278 nm in addition to that from CN. The relationship between the mole fraction of added hydrocarbon and CN or CCl band intensity was also linear, and sensitivities at both wavelengths were at the parts per billion level.

Adding Uranyl compounds to the discharge region resulted in the appearance of three rather broad bands appearing at 486, 510, and 534 nm in the spectrum. We think these spectral features indicate uranium oxide excitation in the D-B discharge, probably UO_2, but possibly UO.

APPENDIX B

Active Nitrogen Energy Transfer (ANET) Investigations

Our initial approach for detecting hazardous waste was to excite atomic and molecular fluorescence by the technique of active nitrogen energy transfer (ANET). The active nitrogen is made in a dielectric-barrier (D-B) discharge in nitrogen at atmospheric pressure. Only a few emission lines or bands are excited for each hazardous species (see Figure B1), so spectral resolution requirements are greatly simplified over those of other spectroscopic techniques. We showed that this approach had great promise in the first phase of the program. Furthermore, the D-B discharge is compact, 1 to 2 cm in diameter and 1 to 10 cm long, and the discharge power requirements are quite modest. Thus an instrument based on ANET can readily be made portable.

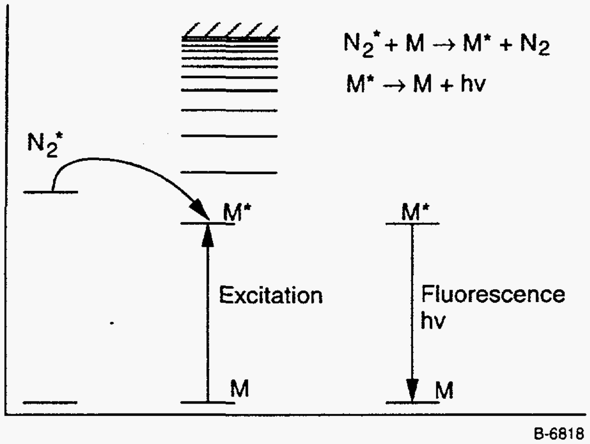


Figure B1. ANET excitation mechanism.

Our principal goals for this second phase of the program were to develop and breadboard test instrument components and to design a prototype instrument suitable for construction and evaluation in the final phase of the program. A secondary goal was to extend the ANET technology to encompass a greater number of hazardous species, primarily additional heavy metals and radionuclides.

The major problem to overcome in this second phase of the program was to develop procedures for sample handling and analysis. We established ANET as a very sensitive detection technique, but the problem of extracting samples quantitatively, and transporting them to the ANET discharge region is a difficult one. We devised a system which uses a small, compact solid-state laser to ablate material from the samples. The throat of our laser-delivery system also houses the D-B discharge used to generate the active nitrogen. Thus, the ANET excitation takes place directly in the sampling region. Light from the discharge is then transported to an optical multichannel analyzer where it is detected. The whole analytical process could be run under control of a small portable computer, and all procedures and processes could, therefore, be automated

We begin this appendix by providing some details related to the ANET process. We will then present data on the detection of several additional species by ANET which we were unable to address during the program's first phase, and finally will discuss our development of the hybrid detection technique mentioned briefly above.

Active Nitrogen Energy Transfer (ANET)

From the beginning of this century, scientists have observed characteristic emissions from atoms and free radicals when atomic and molecular species were added to active nitrogen. A rich literature exists detailing the chemical reactions and energy-transfer processes that occur to excite these emissions.[1-6] Basically, metastable nitrogen molecules (molecules having internal energies of about 6 eV which they cannot easily release via radiation) in the active nitrogen transfer their energy to the various acceptor species. These acceptor species then fluoresce at wavelengths characteristic of the acceptor. Most of these studies relied upon the recombination of nitrogen atoms at relatively low pressures to generate the metastable nitrogen molecules. For analytical applications, this approach has the disadvantage that considerable power is required to dissociate atomic nitrogen. In addition, because these systems operate at pressures on the order of 1 to 10 Torr, a vacuum system is required and sampling under ambient conditions becomes much more difficult.

We conceived and began developing ANET as an alternative to active nitrogen analytical techniques using an atomic-nitrogen recombination source. Our approach is to generate the metastables in a D-B discharge operating at atmospheric pressure and total powers of a few Watts. Thus our system requires neither a large power source nor a vacuum system. In addition, we believe that the overall metastable number densities generated in the D-B discharge are several orders of magnitude larger than those in the atom-recombination system, which means that ANET has the potential to be several orders of magnitude more sensitive.

Dielectric-Barrier (D-B) Discharge Technology

A D-B discharge is a high voltage a.c. discharge between two electrodes, at least one of which is separated from the discharge region by a dielectric-barrier (D-B) (insulator) such as glass[8-11] (see Figure B2). A typical discharge will run at voltages between 3 and 30 kV at frequencies from line frequency to 100 kHz. Gas pressures are typically an atmosphere and gap spacings are on the order of a few millimeters. In its simplest form, the discharge can be powered by attaching the electrodes to the output of a high voltage, step-up transformer, such as a neon-sign transformer, plugged into a variac.

The D-B discharge (also referred to as an ozonizer discharge) is not a single discharge in the sense of a continuous arc or glow discharge, but rather a collection of innumerable micro-discharges between the dielectric and the other electrode. These microdischarges consist of short duration (typically 10 to 100 ns) current pulses (100 to 1000 A cm^{-2}) localized in roughly cylindrical filaments, typically 100 μm in radius. The mean electron energy in a microdischarge is on the order of 1 to 10 eV which is ideal for metastable generation. At any given instant in time, the microdischarges are distributed uniformly across the face of the dielectric. This uniformity provides a relatively stable excitation throughout the discharge volume.

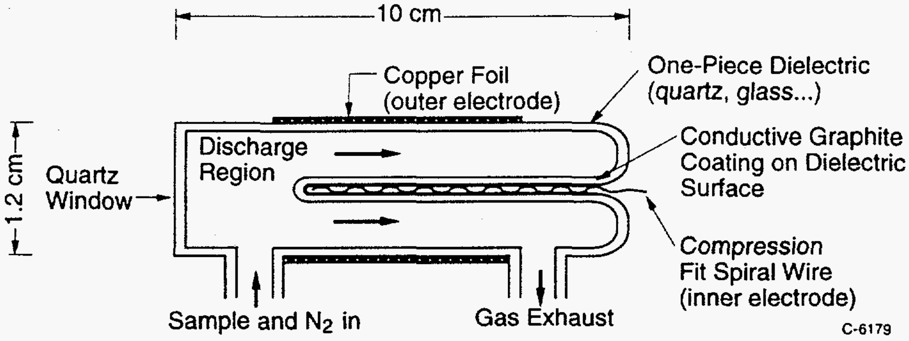


Figure B2. Dielectric-Barrier discharge lamp.

The Chemistry and Physics of ANET

D-B discharges in pure nitrogen have been shown to be efficient sources of metastable $N_2(A\ ^3\Sigma_u^+)$,[12-15] even at pressures of 1 atm, thus providing the active nitrogen source necessary for the selective analyte excitation of ANET. If the analyte species is an atom, such as elemental mercury or lead, the excitation occurs directly. When molecular species are added to the discharge region, the $N_2(A)$ generally reacts with the molecule, producing molecular fragments, which it subsequently excites. For example, $HgCl_2$ is dissociated to $HgCl^*$ which emits around 540 nm, organic molecules are broken down into CN radicals which emit near 388 and 420 nm, and chlorinated organics to CCl molecules emitting at 278 nm.

The chemical processes responsible for exciting fluorescence from species M in a D-B discharge are summarized by the following reactions:

$$N_2 + e^- \rightarrow N_2^* + e^- \qquad (1)$$

$$N_2^* + N_2 \rightarrow N_2 + N_2 \qquad (2)$$

$$N_2^* + M \rightarrow M^* + N_2(X) \qquad (3)$$

$$M^* \rightarrow M + h\upsilon \qquad (4)$$

$$M^* + N_2 \rightarrow M + N_2 \qquad (5)$$

$$M^* + Q \rightarrow M + Q' \qquad (6)$$

$$N_2^* + Q \rightarrow N_2 + Q', \qquad (7)$$

where, Q represents a species in the discharge that quenches electronic energy in either the N_2^* or the electronically excited analyte fragment.

Although the D-B discharge is a pulsed discharge, one can treat it as if it were a continuous discharge if observations are averaged over a number of discharge cycles. Then, because of their short radiative and quenching lifetimes, the excited species in the discharge region are effectively in steady state and we can write

$$I_{M^*} = k_4[M^*] = k_3[M][N_2^*]/(1 + (k_5/k_4)[N_2] + (k_6/k_4)[Q]). \tag{8}$$

Equation (8) shows that for constant metastable number density and total pressure, the fluorescence intensity will be linearly proportional to the additive number density, provided the number densities of any potential quenchers remain constant. This generally will be the case. In previous investigations, the linearity of active-nitrogen excited fluorescence intensity with analyte number density has been demonstrated experimentally to cover four to five orders of magnitude for many species.

The exciting species in active nitrogen responsible for exciting fluorescence from additives generally is considered to be $N_2(A\ ^3\Sigma_u^+)$, although other nitrogen metastables have been invoked from time to time.[1] $N_2(A)$ carries about 6 eV of internal energy. Based on the reaction scheme above, its effective steady-state number density is given by

$$[N_2^*] = k_1[e^-][N_2]/(k_2[N_2] + k_3[Hg] + k_7[Q]) \ . \tag{9}$$

The radiative lifetime[16] of $N_2(A)$ is about 2.5 s. Thus, the primary mechanism for its deactivation will be quenching rather than radiative decay.

Quenching of either the analyte fluorescence or the nitrogen metastables can be an issue affecting the sensitivity of ANET. Although rate coefficients for quenching $N_2(A\ ^3\Sigma_u^+)$ and many analyte emissions by a number of important species are known,[7, 17-19] one should determine the effects of quenching in a D-B discharge *in situ* to ensure that unexpected processes do not complicate the analysis. Our observations related to metastable nitrogen quenching in the D-B discharge[20] are generally consistent with more direct quenching measurements. While our Phase A investigations showed air quenching could be a problem in our system, we shall be able to circumvent this particular complication in the present situation by performing our ablation/ excitation an a nitrogen atmosphere. That is, we will first flood the surface being tested with pure nitrogen prior to sampling so we may exclude oxygen from the surface.

Detection of Additional Species Using ANET

This section describes out work on extending ANET technology to the detection of additional species. All of this work involves using volatile compounds of the metals being tested. We had originally thought the ANET technology would be able to vaporize small particulates, and thereby allow detection of species in aerosol form. This turned out not to be the case, however.

Experimental

The apparatus to perform this work is shown in Figure B3. Low concentrations of the metal compounds are generated by passing nitrogen through a trap containing a small sample of volatile compounds of the metals being investigated. The trap and its contents are maintained at a reduced temperatures to ensure the vapor pressure of the compound is low enough to achieve the desired concentration range in the discharge. The effluent of the trap is further diluted by a pure nitrogen stream. The mixture then flows into the atmospheric pressure discharge. The discharge glow is observed by a spectrometer/optical multi-channel analyzer combination.

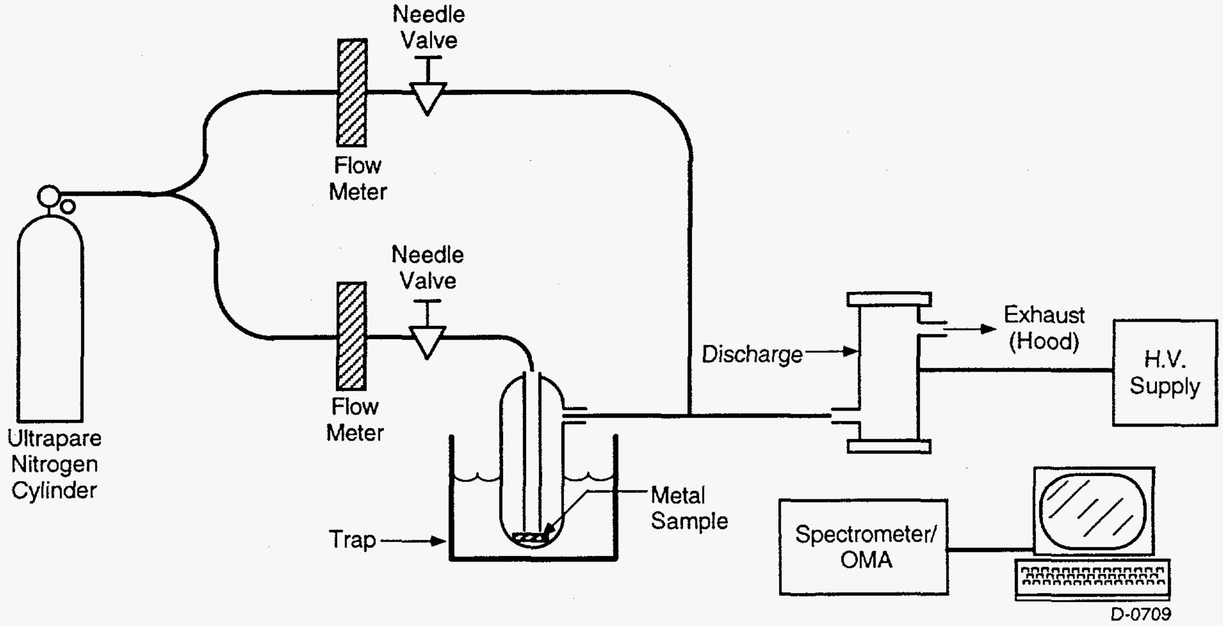


Figure B3. Schematic of apparatus for ANET excitation studies.

We used a quartz lamp with an annular geometry and a quartz window, similar to that depicted above in Figure B2. The electrodes of this lamp were attached to the secondary of an automotive ignition coil. This arrangement powers the lamp with 12 to 15 V square wave pulses at frequencies between 45 Hz and 300 kHz. This situation will lend itself well to compact battery operation, and is therefore preferable to the use of 60 Hz ac wall current. The lamp was situated about 2 cm in front of the collection system. For some studies we powered the lamp with 8 kV sine wave pulses at 60 Hz line frequency. This arrangement proved more reliable than the circuit based upon an automotive ignition coil. Operation with the particular coil we had was erratic, and the coil eventually failed. Presumably a higher quality coil would alleviate such problems in the future.

The fluorescence excited by the energy transfer in these experiments was dispersed with 0.32 cm focal length monochromator (2400 grooves/mm grating, blazed at 250 nm) and detected with an optical multichannel analyzer (Princeton Instruments) having an intensified linear diode array. Good signal-to-noise could be achieved with accumulation times about 10 s. Data were stored in a computer for later analysis.

Summary of Experimental Results

Figures B4 through B18 display ANET excitation spectra and sensitivity calibration curves for compounds of Pb, Sb, As, and Cr that were studied in this part of the program. Table B1 summarizes the results.

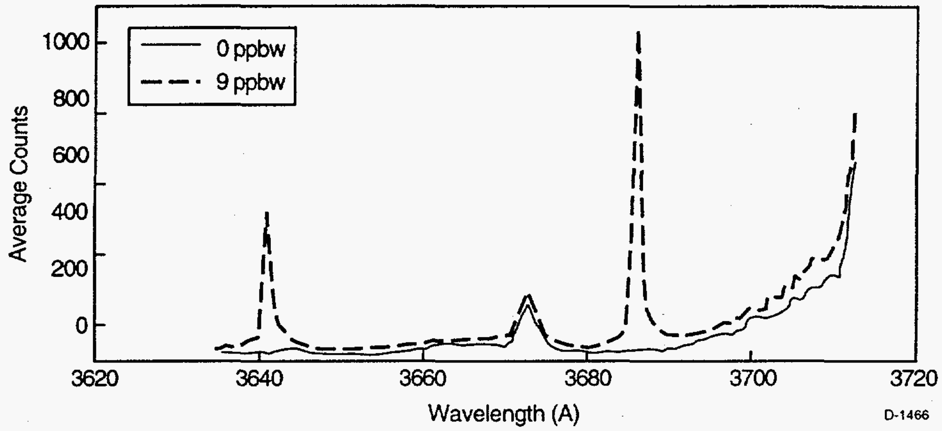


Figure B4. Spectrum between 362 and 372 nm of a dielectric-barrier discharge in nitrogen in the absence and presence of trace amounts of tetraethyl lead.

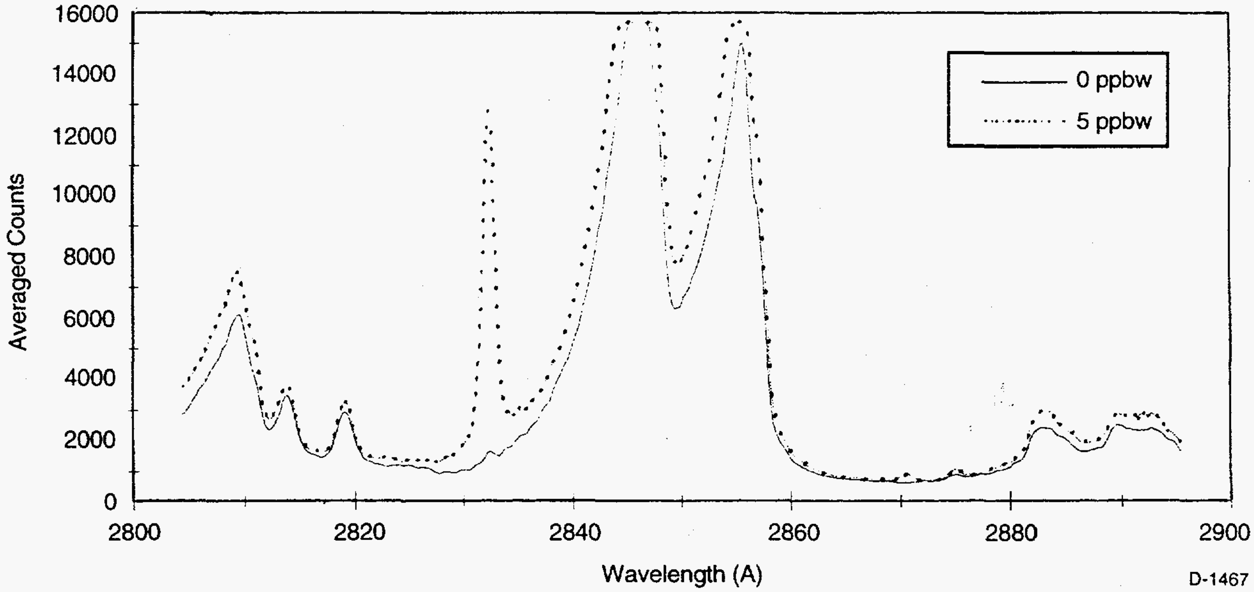


Figure B5. Spectrum between 280 and 290 nm of a dielectric-barrier discharge in nitrogen in the absence and presence of trace amounts of tetraethyl lead.

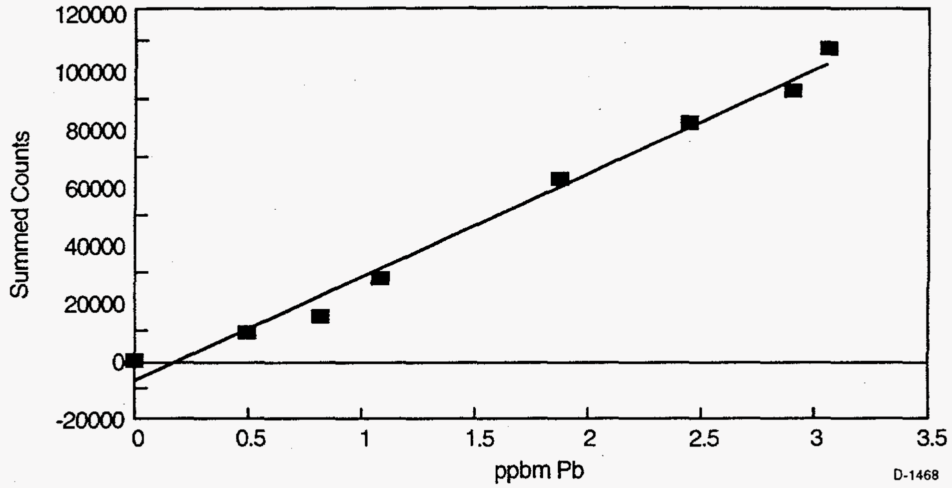


Figure B6. Variation in the intensity of the 283.3 nm Pb line as a function of Pb concentration in the dielectric-barrier discharge.

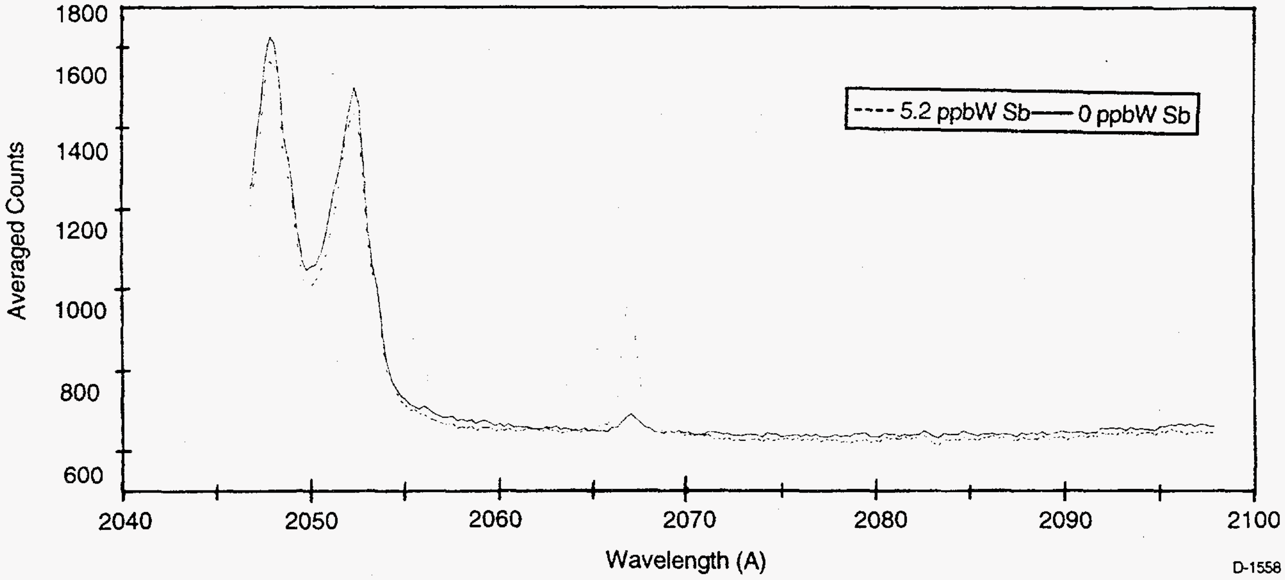


Figure B7. Dielectric-barrier discharge spectrum between 204 and 210 nm in the absence and presence of 5.2 ppb Sb.

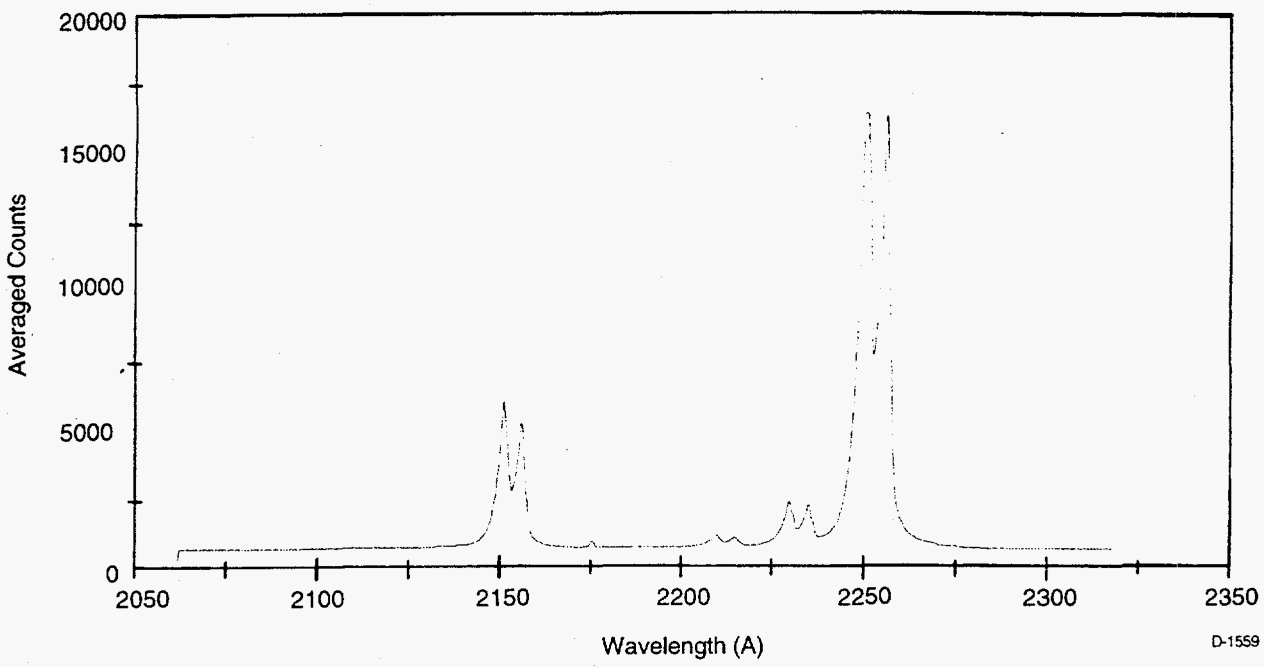


Figure B8. Dielectric-barrier discharge spectrum between 207 and 230 nm in the presence of traces of Sb. The weak feature near 217.5 nm is an atomic Sb line.

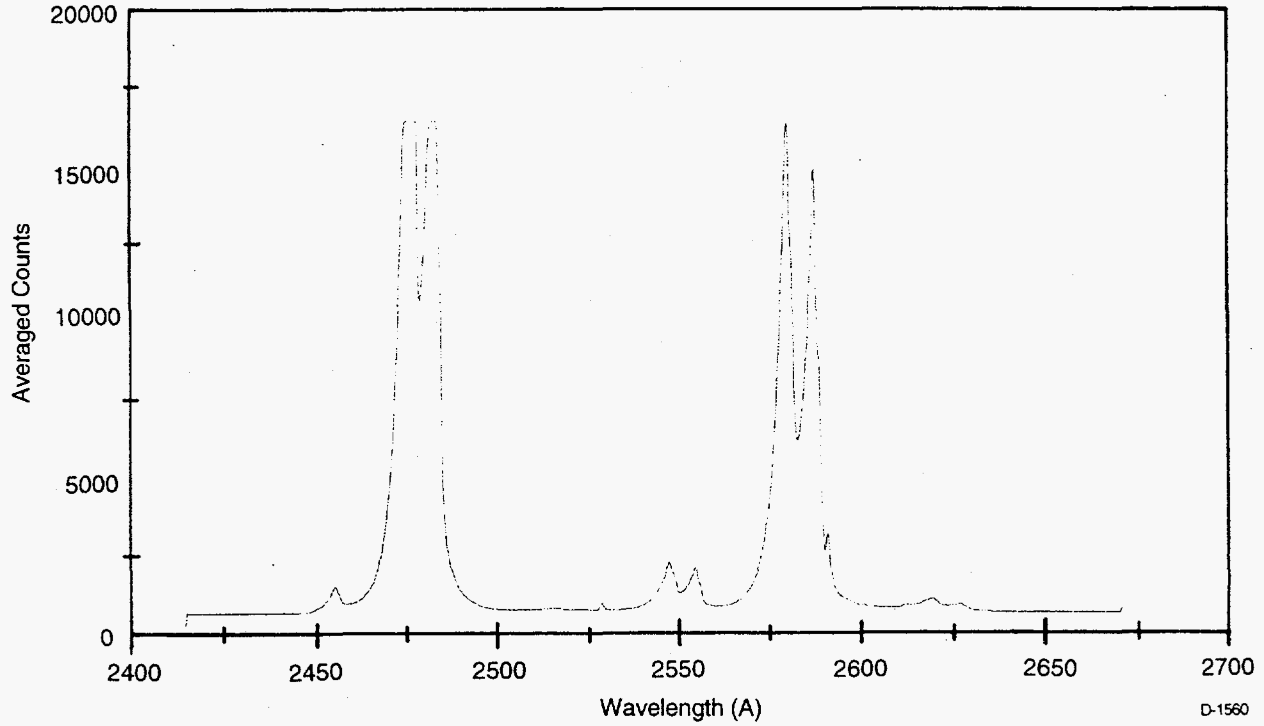


Figure B9. Dielectric-barrier discharge spectrum between 245 and 265 nm in the presence of traces of Sb. The weak feature near 253 nm is an atomic Sb line.

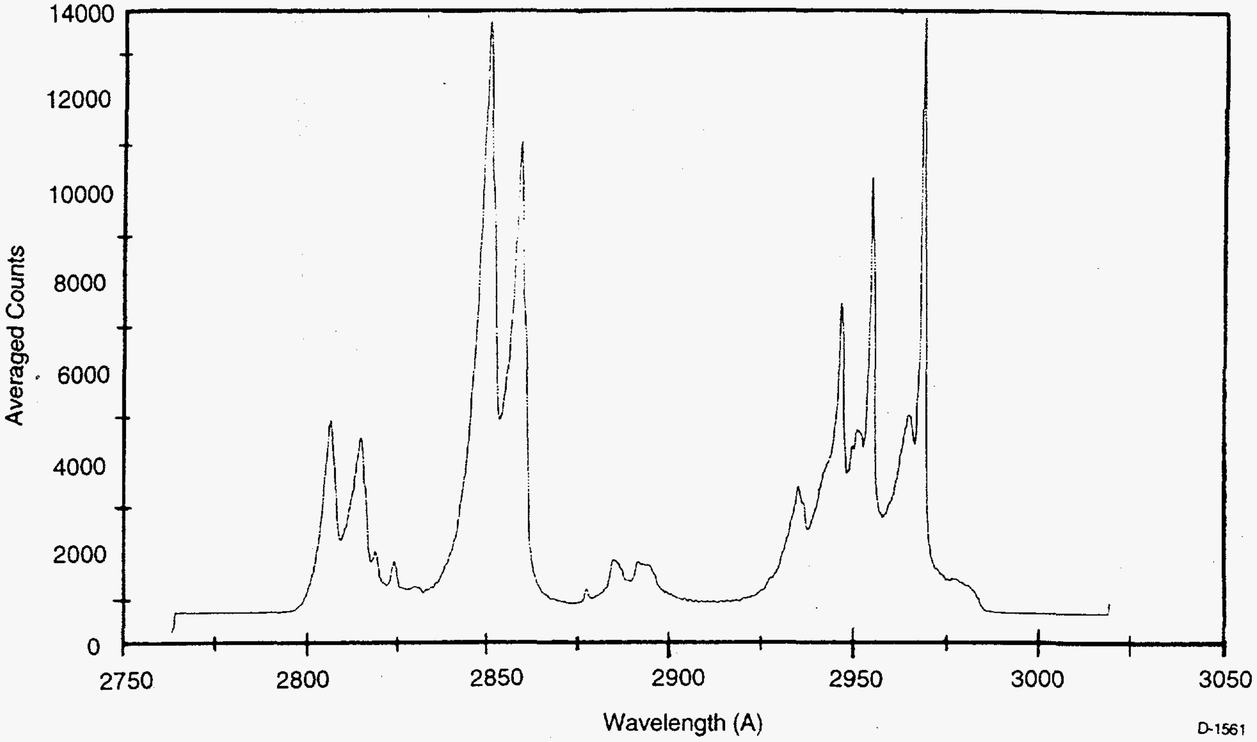


Figure B10. Dielectric-barrier discharge spectrum between 275 and 300 nm in the presence of traces of Sb. The weak feature near 288 nm is an atomic Sb line.

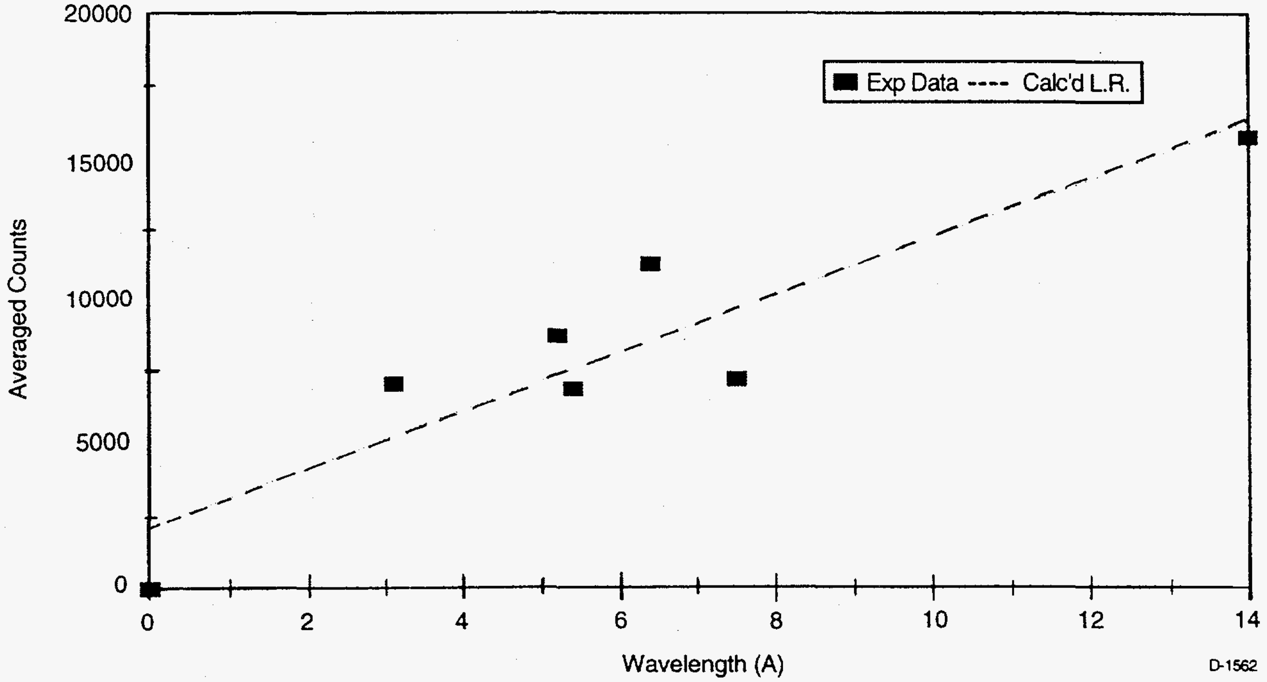


Figure B11. Correlation between 206.8 nm emission intensity and Sb concentration in a dielectric-barrier discharge.

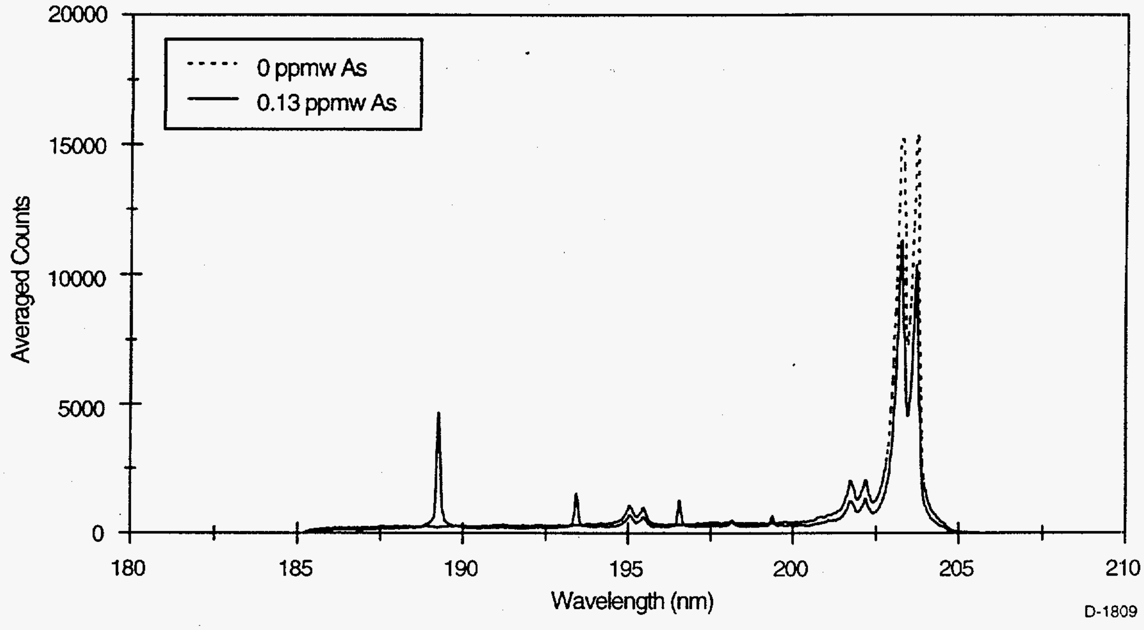


Figure B12. Dielectric-barrier discharge spectrum between 185 and 205 nm in the absence and presence of 130 ppb As.

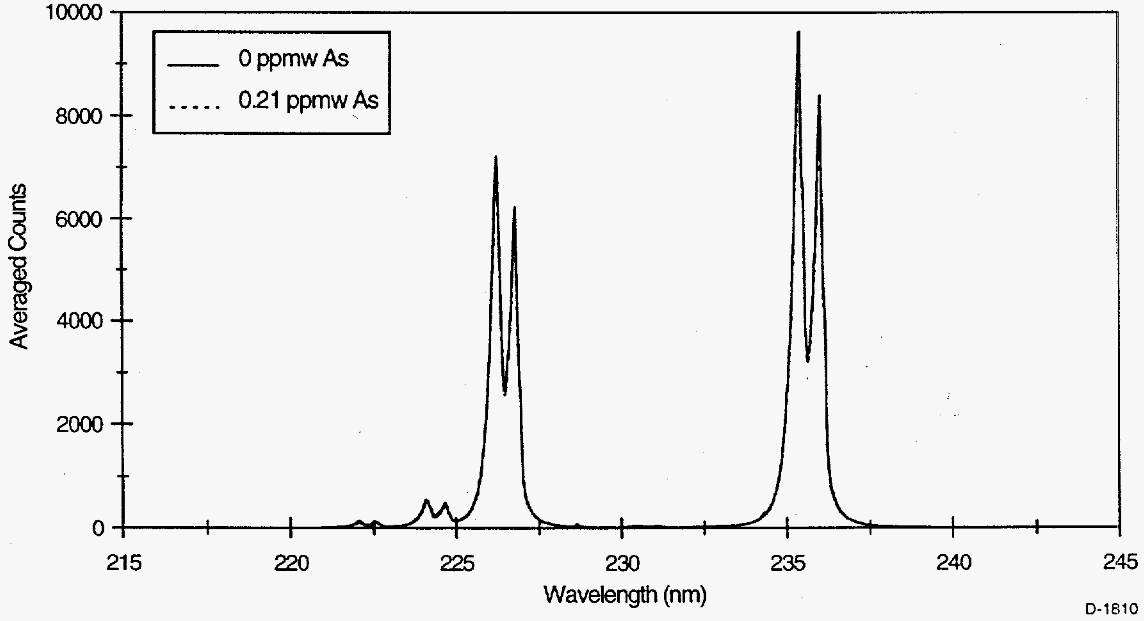


Figure B13. Dielectric-barrier discharge spectrum between 220 and 240 nm in the presence of traces of As. The weak feature near 228.8 nm is an atomic As line.

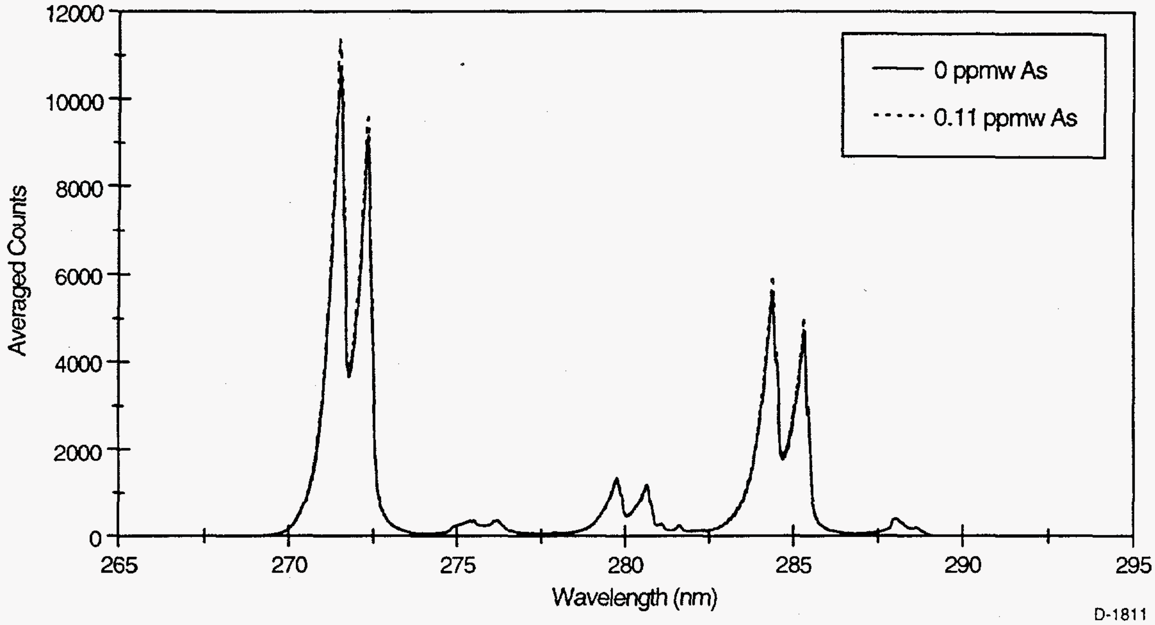


Figure B14. Dielectric-barrier discharge spectrum between 270 and 290 nm in the presence of traces of As. The weak feature near 278 nm is an atomic As line.

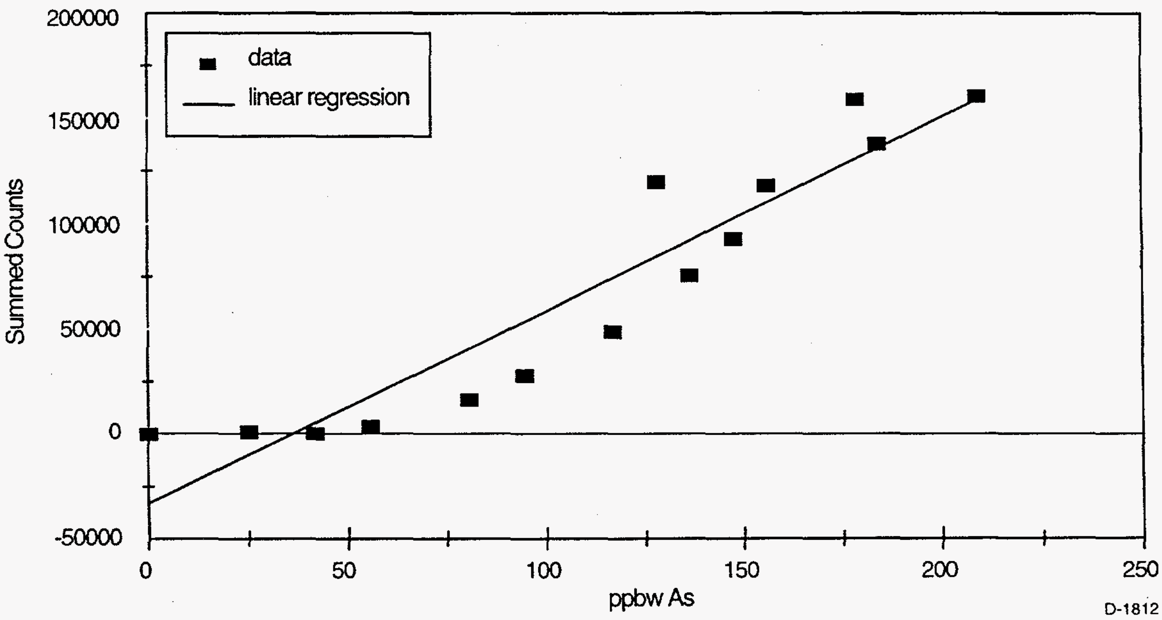


Figure B15. Correlation between 189.0 nm emission intensity and As concentration in a dielectric-barrier discharge.

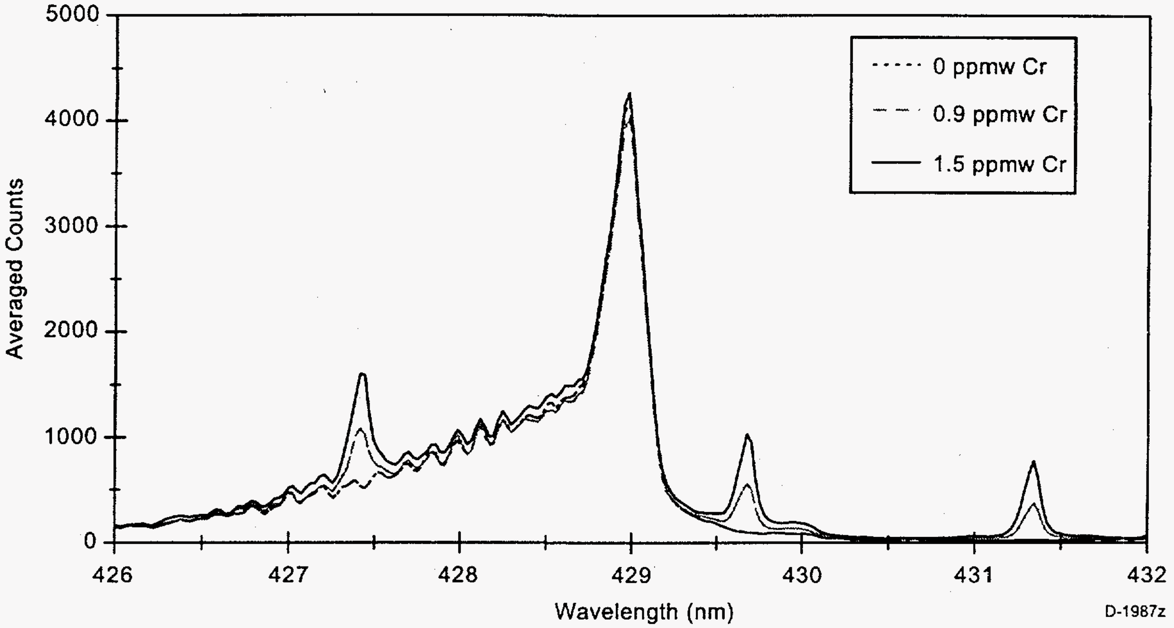


Figure B16. Dielectric-barrier discharge spectrum between 426 and 432 nm in the absence and presence of 0.9 and 1.5 ppmw $Cr(CO)_6$.

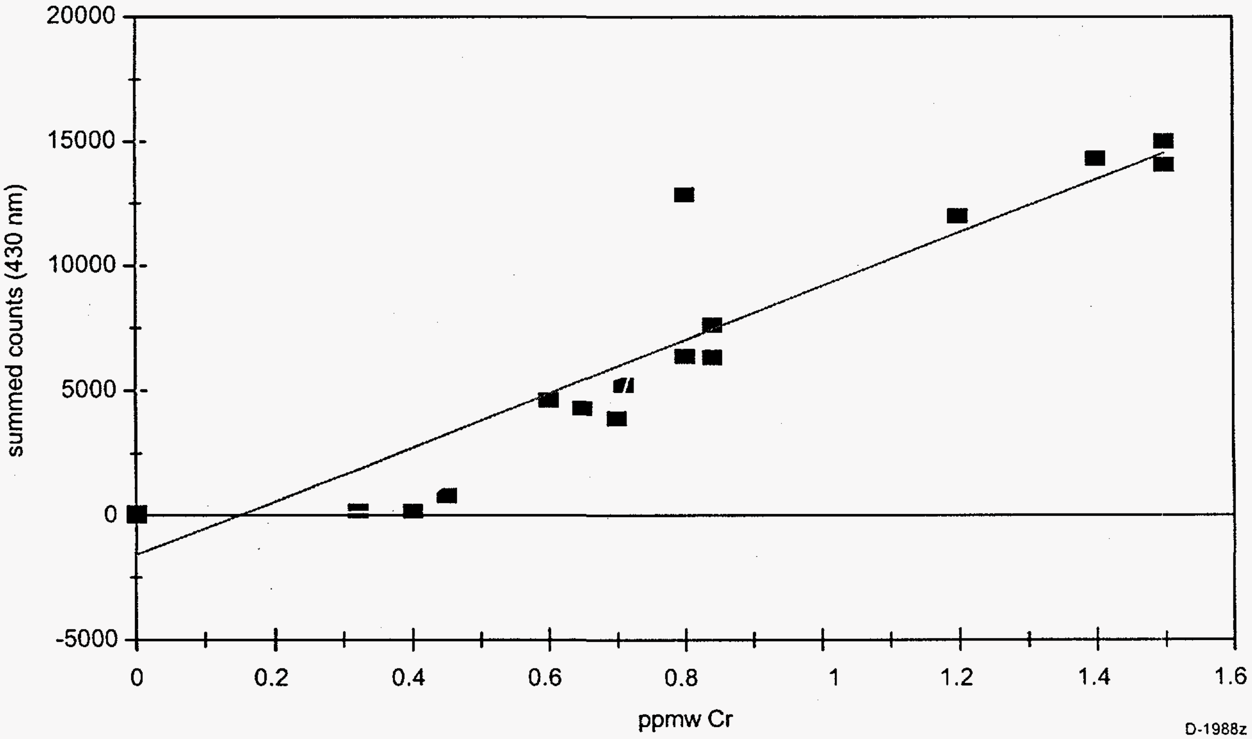


Figure B17. Correlation between 429.7 nm emission intensity and Cr concentration in a dielectric-barrier discharge when $Cr(CO)_6$ is the Cr source.

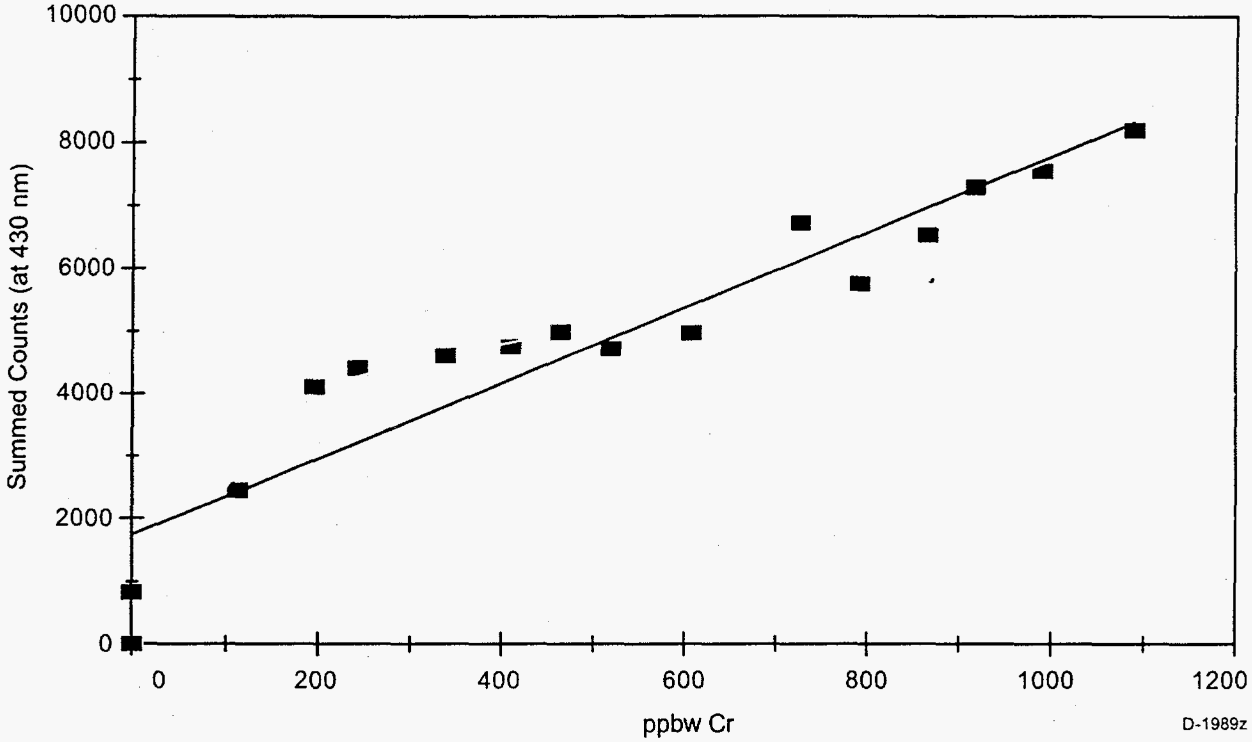


Figure B18. Correlation between 429.7 nm emission intensity and Cr concentration in a dielectric-barrier discharge when CrO_2Cl_2 is the Cr source.

Table B1. Results of the ANET Sensitivity Studies

Species	Compound Introduced	Sensitivity in N2 (ppbw)	Sensitivity in Air (ppmw)
Pb	$Pb(C_2H_5)_4$	0.002	0.008
Sb	$SbCl_3$	0.05	0.20
As	AsH_4	0.055	0.22
Cr	$Cr(CO)_6$	5	20
	CrO_2Cl_2	8	30

Discussion of Experimental Results

We wish briefly to discuss the range of sensitivities of the ANET technique. In the scope of this discussion, it is important to remember the mechanism of metal atom excitation. The electronic excitation of the metal species is due to energy transfer from the N_2 ($A^3\Sigma^+_u$) that is generated in the dielectric-barrier discharge. This transfer of excitation is followed by the subsequent fluorescence of the atom, whose emission is used both to identify and to quantitate the metals present in the sample. The intensity of this emission is dependent upon the rate and efficiency of this energy transfer. In order for efficient energy transfer between two species to take place, two criteria must be met: there must be a close energy match between the reagents and the products and there must be no change in the total spin angular momentum of the system. This latter criteria is called the Wigner spin conservation rule.[a]

Due to the multitude of vibrational levels that are active in the electronically excited nitrogen, the first criterion is expected to be the easiest to fulfill. The second criterion is the one that is likely responsible for the ANET sensitivity range. This point can perhaps best be illustrated by example. In the case of the very sensitive mercury line at 253.7 nm, the total spin of the system is conserved:

$$N_2\,(A^3\Sigma_u^+) + Hg\,(^1S) \rightarrow N_2\,(X^1\Sigma_g^+) + Hg\,(^3S)$$

In the emission following Hg excitation by ANET, the 365.0 and 404.6 nm lines are also observed, but at intensities about a thousand times less than the 253.7 nm line. This is because these lines do not exhibit spin conservation. It is interesting to note that all of metals that are most readily detected by ANET-type systems (Zn, Hg, Cd, Ag, Se and Cu) have either singlet ground states or accessible triplet-quintet or doublet-quartet transitions.

In the case of the metals Pb, As, Sb and Cr, there simply are no energetically accessible transitions with the necessary change of spin angular momentum in the metal atom ($\Delta S=+2$). Hence, even in the event that there is good energy matching between reactants and products, and plenty of accessible transitions, energy transfer to these metals will be less efficient because of this constraint. The associated emission intensities, while perhaps still visible, will be diminished.

This effect seems to be somewhat ameliorated in the case of the Pb. This could well be the influence of spin-orbit coupling in the heavier atom, allowing the Wigner constraint to be overcome to some degree.

Attempt to Monitor Beryllium

In view of the previous argument, beryllium should be one of the more readily seen elements, as it has the possibility for $\Delta S=+2$ transitions within the available energy window, an appropriate transition deeper in the UV, away from D-B features and a singlet ground state. However, there are few volatile Be compounds available for study. Using $BeCl_2$ we briefly attempted to observe Be atomic lines in the D-B discharge. Even by heating our sample lines, we were not able to detect Be at an approximate vapor pressure of 10^{-9} Torr. This probably reflects the difficulty in achieving homogenous heating rather than any other physical or chemical effect. It is easy to imagine a scenario in which the beryllium chloride is deposited on the walls of the sample delivery tubes in "cold spots" before it arrives in the excitation zone.

Process Development Tasks

An instrument using ANET to monitor hazardous wastes in real-time will have five essential components:

1. A sampling system for collecting the sample from contaminated material, mixing it with nitrogen, and transporting it to the discharge region

2. A discharge system for exciting the N_2 metastables which, in turn, excite contaminant fluorescence

3. A detection system for separating contaminant fluorescence from other features excited either in the discharge or by the N_2 metastables

4. An *in-situ* calibration system to ensure the accuracy of the hazardous waste measurements

5. A data processing system for controlling the various instrument components, for collecting the data, for converting the raw data into hazardous waste concentrations in the sample, and for reporting and archiving hazardous waste analysis results.

We will now consider each of these issues in some detail.

We will begin by describing the basic principles of the instrument operation. Figure B19 shows a block schematic of the instrument where the component subsystems are identified. The surface to be tested is first flooded with pure nitrogen to eliminate oxygen from the system. Then the sample is removed from the surface and transported in a flow of nitrogen to the discharge system In the discharge chamber, the N_2 metastables, and subsequently the contaminant fluorescence, are excited. Light from the discharge is dispersed by a small monochromator and detected with a photomultiplier or intensified photodiode array. The detected signals are read and processed by a computer system, and results are displayed and stored. The computer system can also provide feedback signals for active control of remediation processes.

A calibration system will be included that can inject known quantities of contaminant into the diluted sample flow prior to its entry into the discharge cell. In addition, we will be monitoring an emission feature of the discharge that is diagnostic of the N_2 metastable number density. This allows for correction of the fluorescence data for variations in excitation strength either because of pulse-to-pulse variations in discharge strength or because of residual quenching of the metastables by impurities remaining in the sample stream.

Sampling System

Our initial focus is the detection of contaminants adhering to building materials or other surfaces. While ANET is a sensitive technique for air-borne species, such species must first be liberated from the surface into the gas phase and then transported to the discharge region. In some instances, the contamination might lie on the surface to be sampled in the form of dust particles. In other instances, however, the contamination might be closely bonded to the surface either as a component of a surface coating, e.g., paint, or even trapped beneath a surface coating.

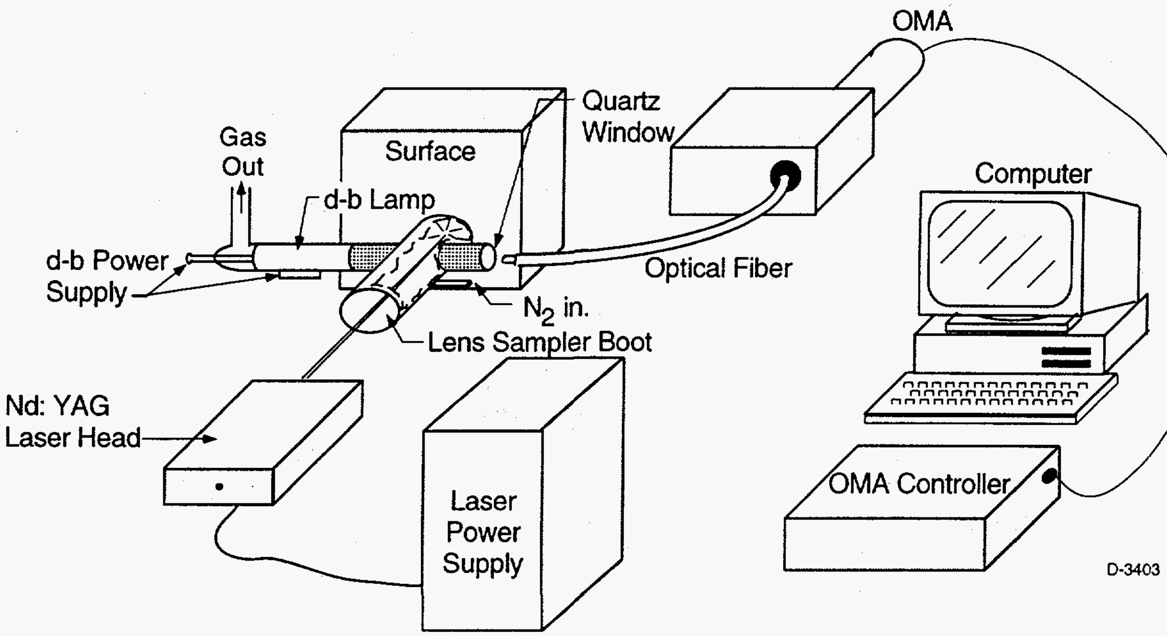


Figure B19. Schematic of analysis system integrating laser ablation sampling with ANET detection.

We can think of three primary methods for removing contamination layers of material from a surface that might prove suitable for the present application. Mechanical means for sample removal from surfaces might include miniature impingers, somewhat along the idea of a small jackhammer, or abrasive removal, e.g., via a jet of solid CO_2 pellets. A second means of sampling would be to ignite an electrical spark at the surface which would remove material either through generating heat from the spark-induced plasma, or from a shock-wave created by the spark. A third method, somewhat related to the second, would be to use a laser to ablate material from the surface.

Using mechanical means for sample extraction will result in a sample that is essentially an aerosol. The other two techniques described above can result in a sample that is a mixture of vapor and fine particulate. In the first phase of this program, we showed evidence that ANET was not seriously compromised by the presence of some fine particulate in the discharge region. These results seemed to indicate further that the ANET microdischarges themselves might be potent enough to vaporize some of the particulate in the discharge region. We have since found that the ANET discharge is not generally suitable for detecting species adhering to particulates. Since electrical and laser ablation of the sample both can provide some of the sample in the vapor phase, one of these two approaches appeared to be viable.

Our examination of the benefits and liabilities of these two latter approaches indicates that laser ablation appears to offer the most reproducible and compact method for sample extraction. We have found a miniature Nd:YAG laser can readily ablate paint that contains lead from concrete blocks. The laser head is about half the size of a shoe box, and produces output pulses at a rate of 10 Hz. The laser plasma itself contains emissions from the added contaminant. Examining laser-induced plasmas for diagnostic emissions is commonly known as laser-induced breakdown spectroscopy or LIBS. Generally, LIBS systems use a much larger laser than the one we have been using, and they generally require a much more sophisticated detection system that what we have been using. In addition, LIBS systems tend to be much more expensive that ANET based systems, and significantly less sensitive. Thus, we think that incorporating an ANET detection system with a laser-based ablation system offers the greatest potential for sensitivity, compactness, and limited cost.

Figure B19 shows the hybrid laser-ablation/ANET system schematically, while Figure B20 gives a more detailed view of the probe region. The laser is fired through a lens at the end of the sample tube and is directed through the 2.5 mm gap that comprises the discharge region. The other end of the sample tube seals the surface to be tested with an o-ring. A flow of nitrogen sweeps into the sampler at the gas surface and purges air from the region. The nitrogen flow also entrains the vapor and particles that are the result of the laser spark and carries them through the discharge. Since the top electrode of the db lamp is constructed of conductive mesh, we are able to observe the signal associated with the discharge through it. This observation takes place about 15 mm away from the laser spark, and substantially reduces the interference of the prompt emission from direct excitation by the laser-induced plasma. Light from the D-B lamp is collected by a fiber-optic bundle and transported to an optical multichannel analyzer (OMA) where the light is dispersed and subsequently detected.

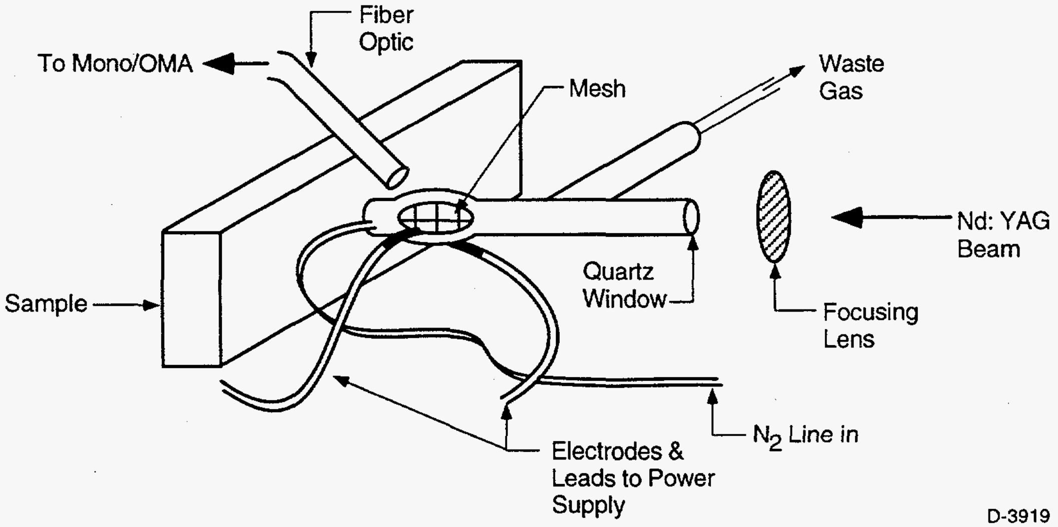


Figure B20. Schematic of the probe region of a system combining laser ablation of contaminants from surfaces with their detection by ANET.

Detection System

The detection system monitors contaminant fluorescence, primarily at ultraviolet wavelengths, and N_2 Herman infrared (HIR) fluorescence between 695 and 710 nm. We showed in the Phase A program that the HIR fluorescence can be related directly to the concentration of N_2 metastables produced in the discharge. Monitoring the HIR emission, therefore, provides a means of compensating for variations in metastable concentrations that might occur with variations in air in the sample or with pulse-to-pulse irregularities in the D-B discharge itself. The spectral resolution necessary to separate the atomic fluorescence from neighboring emissions in the D-B discharge is about 0.4 nm, about an order of magnitude less than required in commercial ICP or LIBS systems. Spectral resolution requirements in the near infrared are less stringent, so using an interference filter at 700 nm may be useful. A spectrometer is necessary to obtain adequate spectral resolution in the ultraviolet, however, and works well to isolate other important wavelengths.

A compact spectrometers having a 10 to 15 cm focal length and a standard 1200 g mm^{-1} has a first-order resolution of about 8 nm mm^{-1}. Since aberrations in small focal length spectrometers limit their usefulness to slit widths greater than 100 to 150 μm, the best first-order resolution one can expect is about 1 nm. Adequate resolution is therefore readily available using a somewhat higher density grating (1800 to 2400 g mm^{-1}) with fluorescence monitoring in second or third order. Such spectrometers are readily available with computer-controlled, stepper-motor based grating rotation mechanisms have been made sufficiently rugged to with stand the rigors of space flight. A computer-controlled filter wheel situated at the monochromator's entrance slit enables switching between filters appropriate to the spectral region observed. The system collects data from a few discrete wavelengths in a spectral region; then slews to the next wavelength region and repeats the procedure. A UG-5 glass filter adequately transmits ultraviolet radiation with wavelengths longer than about 225 nm while completely blocking that at wavelengths between 400 and 650 nm. For visible wavelengths, a long-pass colored glass filter effectively blocks second-order uv radiation while transmitting that at longer wavelengths.

A compact photomultiplier assembly detects fluorescence at the exit slit of the monochromator. Emissions from the discharge extend for a periods of tens of nanoseconds after the initiation of the discharge pulse if they are excited directly in the discharge, but will extend up to 100 to 200 μs if excited by metastable transfer. To enhance discharge emission relative to dark current the photomultiplier's output is integrated for periods of about 150 μs after the discharge pulse. The data acquisition system then reads the voltage output of the integrator and averages the result with those of a number of previous pulses.

Discharge System

Our discharge system is similar to that used previously.[21] It is powered by applying 15-V, square wave pulses to a high-energy induction coil. The discharge frequency is controlled by one of the data acquisition and control system's timers. Digital pulses from the computer trip a gate, which in turn, opens a transistor switch able to sink adequate levels of current at 15 Vdc to the coil's primary. The high-voltage output of the coil's secondary connects to the D-B discharge lamp. We have found this system to be compact and quite rugged and reliable in operation.

As mentioned above, we can use observation of the Herman infrared (HIR) emission around 700 nm as a monitor of the metastable number densities in the discharge region. We can use such measurements to normalize observed atomic emissions for variations in the strength of the discharge or variations in metastable number densities due to quenching effects. Figure B21 shows an example of HIR emission in a D-B discharge with several different amounts of added air. It can be seen that the air does diminish somewhat the HIR emission.

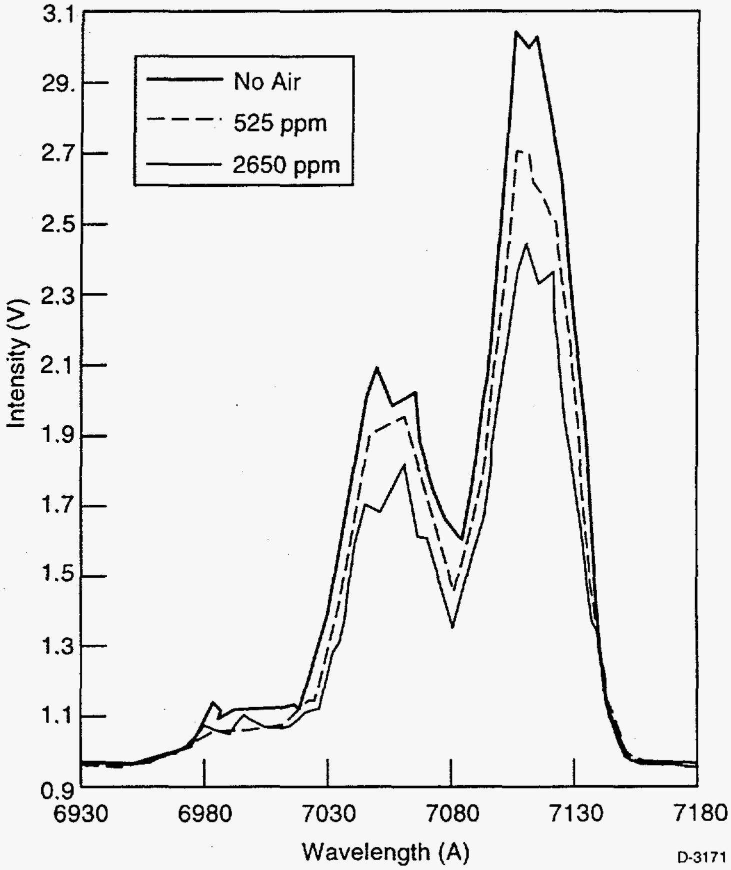
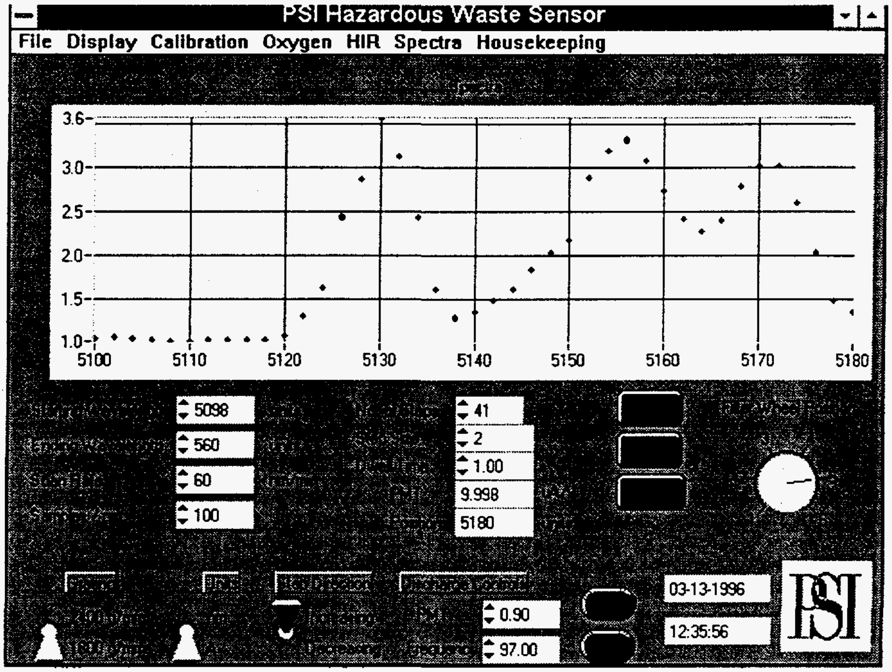


Figure B21. Herman infrared (HIR) emission in a D-B discharge with varying amounts of added air.

Data Acquisition and Control System

The data acquisition and control system regulates all components of the hazardous waste sensor, collects data from each component, runs automatic system calibrations, converts collected data into contaminant-species concentrations, and displays measurement results in real time as well as stores them for later retrieval and archiving. For the current program prototype, we are using a portable computer for this purpose. A commercial instrument would undoubtedly incorporate a single-board computer with operations programmed into EEPROM memory.

Our system uses an IBM-compatible portable PC with Windows 95-based software. Several data acquisition and control boards are installed inside the computer. Software to monitor and control the boards is being developed using the National Instruments LabView®, object-oriented programming language. This system produces a virtual instrument that has a screen display much like an instrument panel. It is controlled from the screen by clicking mouse the computer's mouse on virtual buttons, or by entering numbers into specially designated blocks on the screen. An example of one of our instrument panels is shown in Figure B22.



D-3595

Figure B22. Virtual instrument control panel created with LabView programming.

<u>Results of Tests Using the Hybrid Approach</u>

We studied the hybrid laser ablation/ANET system to detect lead paint on surfaces. In our initial tests we used lead nitrate doped, latex house paint. We encountered considerable difficulty because the prompt emission from the laser-induced spark was quite large compared to the ANET signal, and in addition highly variable. Thus it was difficult to discriminate between the two.

We attempted to alleviate this problem by removing the D-B discharge region somewhat from the surface being tested. There are limits, however, to how far one extend the scale of the dielectric discharge lamp to reduce these interfering emissions. This limitation is due to diffusion losses of analyte to the wall of the discharge cell. The loss of analyte material also makes it necessary to flow the N_2 carrier gas at fairly high flow rates (about 3 L/min). This in turn creates the necessity of using a variable (higher) frequency power supply for the dielectric discharge lamp to ensure that the ablated material encounters as many excitation events from the discharge as possible during its passage through the cell. This new discharge power supply can run at rates up to several kHz, and has a variable duty cycle (up to >95%) to permit full recharging of the discharge coil at the higher frequencies.

Figure B23 shows some illustrative spectra which were obtained with the OMA controller in “free running” continuous mode while the laser was pulsing at 10 Hz. For control purposes, spectra from only the dielectric barrier discharge lamp, spectra of the db lamp with ablation laser running and spectra from the ablation laser only were compared. Many spectra were averaged to reduce the sample-to-sample variability. Clearly, under these conditions, the majority of the lead emission in the vicinity of 368 nm is a result of the laser-induced spark. However, there is some

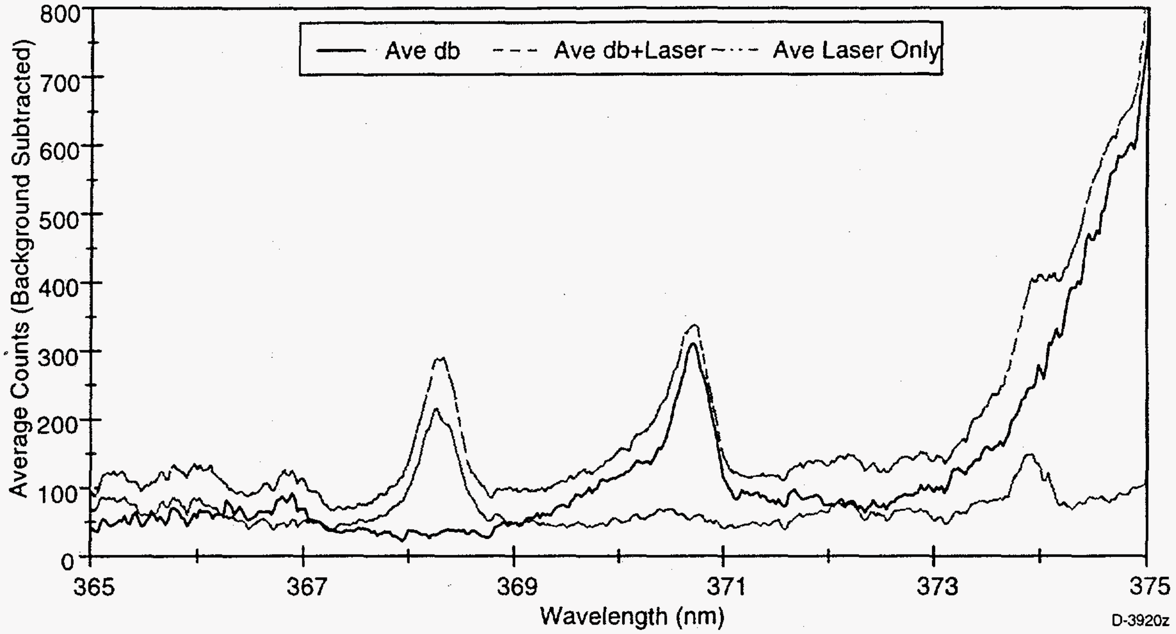


Figure B23. Spectra between 360 and 380 nm excited by a D-B discharge in N2 at atmospheric pressure, by laser ablation of a lead-based paint, and of the two excitation processes occurring simultaneously.

additional signal that is a result of the presence of the dielectric barrier discharge. The effect can best be seen when the spectrum of the db discharge only and the spectrum of the ablation laser only are subtracted from the spectrum taken with both the laser and the db discharge operating. This difference spectrum is shown in Figure B24. The feature at 368.3 nm, the location of the Pb ($7s^3P_0^\circ \rightarrow 6p^3P_1$) transition is the only prominent feature remaining in this difference spectrum.

Another interesting result is shown in Figure B25. In this instance the laser operation results in the removal or organic species, i.e. the organic paint binder, from the surface being irradiated. The presence of the organic material in the sample going through the D-B discharge is signaled by the presence of the CN (B-X) emission bands between 385 and 389 nm.

In order to discriminate better the spectral contribution from ANET excitation to that from the ablation pulse, we would need to collect data in a gated mode. In this experiment, the collection of the data would be suspended until after the laser-induced spark has cooled completely (≈500 µs). Data collection would end when the "plug" of ablated material exited the discharge region. The timing for this process is complex but crucially important. If data collection is delayed for too long after the ablation pulse, the ablated material will have already passed through the D-B discharge lamp. On the other hand, if the delay is too short, interference from the prompt emission is considerable, and furthermore, the ablated materials might not have had time to flow from the surface to the db discharge region.

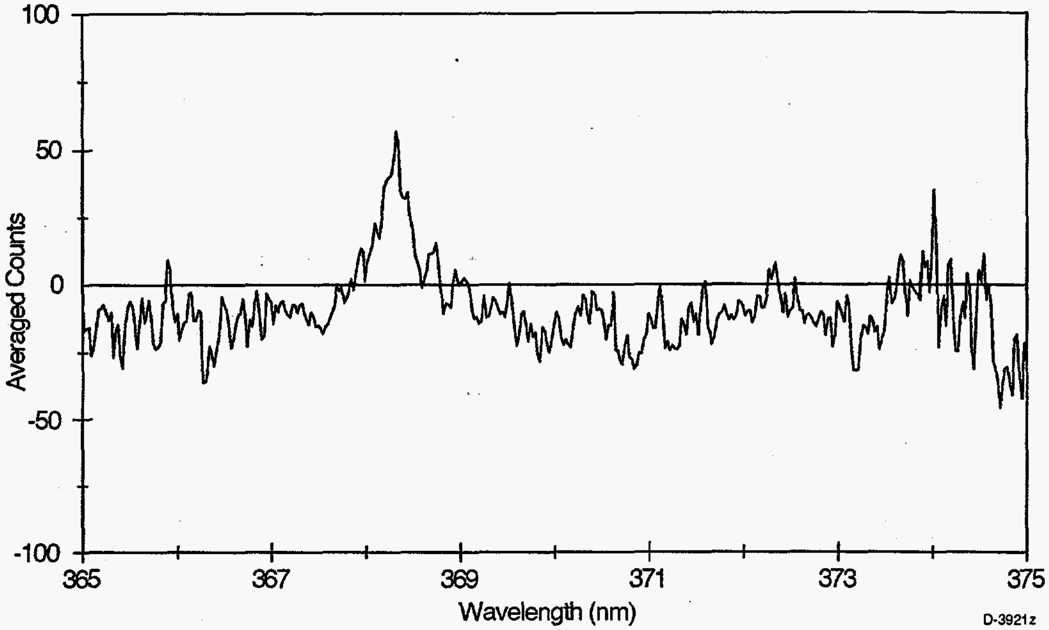


Figure B24. Difference spectrum of residual radiation when a spectrum of laser ablation of Pb-based paint and one of a D-B discharge in N_2 at atmospheric pressure are subtracted from a spectrum excited by the two processes acting together.

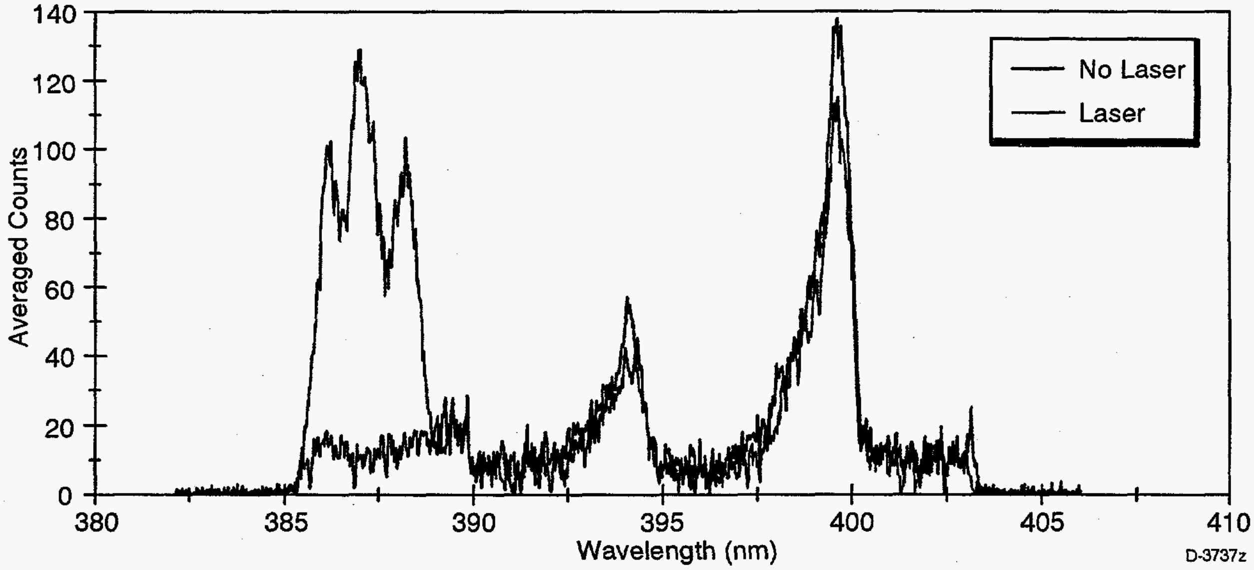


Figure B25. ANET spectra between 385 and 405 nm in the absence and presence of laser-ablated material from a latex-paint covered surface. The new bands appearing between 385 and 390 nm are bands of the CN (B- X) system which is a sensitive emission diagnostic of the presence of traces of organic materials in an ANET discharge.

Conclusions from the ANET Studies

During the course of these investigations we demonstrated the ability of the ANET technique to sensitively detect several more heavy metals. We also developed a number of processes and procedures for integrating ANET detection into a hazardous waste monitor. We eventually abandoned our efforts regarding the ANET technology because we felt the SIBS technology was more easily applied to a greater number of DOE needs. In addition, the basic SIBS technology implementation is far simpler to engineer, than the hybrid laser ablation/ANET system we had developed and thus holds greater promise for near term application to DOE needs.

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APPENDIX C

Results and Analysis of Analytical Testing Survey

Prepared by:
Mark E. Fraser

Executive Summary

Current Technology and Uses

- We received a total of eight responses from seven sites. Hanford and Savannah seem to be conspicuously absent.
- More of the respondents are performing risk/site assessments than are doing actual D&D.
- Current uses include D&D, site assessment, environmental restoration, waste management and emissions and effluent monitoring. It seems likely that a new technology will be required to be multi-purpose to satisfy all or most of these applications.
- If we exclude organics, a multi-species monitor is competing with ICP, AAS, AES, and radiochemistry.
- Five out of the eight respondents have analytical testing costs exceeding $500K; Fernald spends $8M to $10M and it expects these costs to rise to $25M/year after 1996. Because of their high costs, Fernald uses their own contractor staff.
- The majority of the other respondents send their work to outside labs.
- Turn-around time and cost are the two principal limitations of current technology. Often samples take 6 weeks to be analyzed.

New Technology Development

- New analytical technology is expected to first realize direct savings with testing. A secondary expectation is that faster and more efficient D&D operations will result.
- Getting analytical data faster is common to almost all of the respondents.
- The amount of savings required ranges from any amount to 10% to nearly half of their analytical expenditures.
- Fernald and WETC responded with amounts nearly equal to half of their expenditures. It is possible that they mean this to be an eventual goal rather than the barrier to introduction.
- Mound points out that the savings must factor in initial costs and regulatory approval.
- The new technology must highly accurate, sensitive and reliable (i.e., it must meet regulatory requirements).
- In addition, it must perform on-site in real time.
- In general the costs of the technology are not ranked high.
- Surprisingly, speciation and multi-species are ranked low.
- Regulatory approval and the mechanism of introducing the technology are key issues we need to address.

Conclusions

The respondents are generally dissatisfied with their current analytical protocols. This does not result from any inherent deficiencies in the technologies but from cost and turn-around time. The biggest advantages a new technology can offer are less cost, on-site use and real time analyses. This will allow faster D&D operations and real time decision-making, with direct and derivative cost savings.

Our technology will have to be as good as current techniques. We will have to be accurate, reliable, sensitive, and approved for the particular species and applications. The mechanism of regulatory approval and introducing our technology to a site are key issues to be addressed. Regulatory approval can be a long and expensive process. It can also be a Catch-22 with approval witheld until site testing and site testing awaiting approval. It seems logical, therefore, to negotiate one or more beta site tests with no obligation to the users. Important data necessary for regulatory approval can be obtained while useful performance and enhancement feedback is obtained.

Primary business, scientific and engineering details not covered in this survey include the following categories:

Scientific Issues

Preferred suite of contaminants versus ANET capabilities.
Necessary sensitivities.
Sample preconcentration, digestion and extraction.
Current sample collection methods; will we stay with these?
Speciation required or only total concentration?

Engineering Issues

Decon procedures.
Field portable versus Lab use.
Performance constraints (power, size, weight, consumables).
User environment - derived operational constraints.
Desired user interface.

Business Issues

How many units on each site and overall.
Unit cost.
Cost/benefit analysis for the labs.
Required amortization rate.
Purchase versus leasing.
Regulatory approval procedure.
Site introduction and beta testing.
Liability.
Site/unit support and user training

Survey Respondents
(total of eight responses from seven locations)

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Mound - Miamisburg OH
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Environmental Engineer
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(2 responses)
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? Oak Ridge ?	POC	Unknown Cover of fax missing Fax - (423) 574-9786

The ANET technology is highly specific for metals detection but responds to organics as a class. I have therefore organized the species of interest responses into three tables. The first shows the organics grouped into several classes rather than by specific compounds. The second table shows the detailed responses for all of the inorganic metals. The last table lists the radioactives.

Summary of Survey Results

Table 1
Question 1 - Current Applications

Uses	Fernald	Mound	Oakland 1	Oakland 2	Nevada	Idaho	WETC	? Oak Ridge ?
Decontamination	✔	✔		✔				✔
Decommisioning	✔	✔				✔		✔
Risk/site assessment		✔	✔	✔	✔	✔		✔
Env. Restoration	✔	✔						
Waste management		✔					✔	
Effluent/emissions monitoring		✔		✔			✔	

Conclusions:

- More of the respondents are performing risk/site assessments than are doing actual D&D.
- Three other applications turned up in the "other" category. These are: environmental restoration, waste management and effluent and emissions monitoring.
- Any new technology must be multi-purpose and able to perform all or most of these applications.

Table 2a

Question 2 - Species of Interest

Organics

Species	Fernald	Mound	Oakland 1	Oakland 2	Nevada	Idaho	WETC	? Oak Ridge ?
Volatile organics (e.g., benzene)								several compounds in water and sludge
Chlorinated Solvents		1-1500 µg/l groundwater	0.5-5000 ppb ground water					several compounds in water and sludge
Semivolatiles (inc. PAH's)		0-2000 mg/kg soil						several compounds in water and sludge
Herbicides, Pesticides and PCB's		10-5000 mg/kg soil			variable, building materials and soil			several compounds in water and sludge
Oils and Fuels		0-100 g/kg soil			variable, above and below state limit of 100 mg/kg of soil	wide range in soil and tank sludge	0-10,000 ppb? In soil and water	several compounds in water and sludge
Explosives (RDX, HMX, etc.)			up to 300 µg/l ground water					

Conclusions:

- Oils and fuels turn up in a surprising number of sites
- Chlorinated solvents occur in many but not all sites
- Herbicides, pesticides and PCB's were also a surprise, being present at three of the sites

Table 2b

Question 2 - Species of Interest

Inorganics

Species	Fernald	Mound	Oakland 1	Oakland 2	Nevada	Idaho	WETC	? Oak Ridge ?
Aluminum							0-1000 ppb? In soil and water	
Arsenic				0.001-20 mg/l in sewage	variable, on building materials and in soil		0-100 ppb? In soil and water	not stated, in water and sludge
Barium					variable, on building materials and in soil		0-1000 ppb? In soil and water	
Beryllium				0.1-10 mg/kg in soil		wide range as metal and metal oxide in tank sludge, soil, and on solid parts		
Cadmium				0.001-20 mg/l in sewage	variable, on building materials and in soil		0-100 ppb? In soil and water	
Calcium							0-1000 ppb? In soil and water	
Chloride								not stated, in water and sludge
Chromium			5-250 ppb as chromate in ground water	0.001-20 mg/l in sewage	variable, on building materials and in soil		0-1000 ppb? In soil and water	
Copper				0.01-20 mg/l in sewage			0-1000 ppb? In soil and water	

Species	Fernald	Mound	Oakland 1	Oakland 2	Nevada	Idaho	WETC	? Oak Ridge ?
Fluoride								not stated, in water and sludge
Iron							0-1000 ppb? In soil and water	
Lead		10-5000 mg/kg as oxide in soil		0.001-20 mg/l in sewage	variable, on building materials and in soil		0-100 ppb? In soil and water	
Magnesium							0-500 ppb? In soil and water	
Manganese							0-1000 ppb? In soil and water	
Mercury				0.001-20 mg/l in sewage	variable, on building materials and in soil	1-100 ppm, elemental in tank sludge and soil from spills	0-100 ppb? In soil and water	not stated, in water and sludge
Molybdenum							0-1000 ppb? In soil and water	
Nickel			5-100 ppb in ground water	0.01-20 mg/l in sewage			0-100 ppb? In soil and water	
Nitrate			up to 200 mg/l in ground water				0-100 ppb? In soil and water	not stated, in water and sludge
Phosphate								not stated, in water and sludge
Potassium							0-100 ppb? In soil and water	
Selenium					variable, on building materials and in soil		0-100 ppb? In soil and water	not stated, in water and sludge
Silver				0.001-20 mg/l in sewage	variable, on building materials and in soil		0-100 ppb? In soil and water	

Species	Fernald	Mound	Oakland 1	Oakland 2	Nevada	Idaho	WETC	? Oak Ridge ?
Sodium							0-10,000 ppb? In soil and water	
Sulfate							0-10,000 ppb? In soil and water	not stated, in water and sludge
Thallium								not stated, in water and sludge
Zinc				0.01-20 mg/l in sewage			0-1000 ppb? In soil and water	

Conclusions:

- The most important prevalent species, appearing at four or more sites, are As, Cr, Pb, and Hg
- The second tier, appearing at three sites, are Cd, Ni, Se, and Ag
- Some new compounds are Al, Ca, Cu, Fe, Mg, Mo, Mn, K, Na, and Tl
- These responses show the inorganic metal list to be extensive and site specific

Table 2c

Question 2 - Species of Interest

Radioactives

Species	Fernald	Mound	Oakland 1	Oakland 2	Nevada	Idaho	WETC	? Oak Ridge ?
Uranium	20-2000 pCi/g as oxides in soil, concrete, building materials and in water	1-1000 pCi/g as inorganic in soil	up to 110 pCi/l in groundwater as $UO_2(CO_3)_3^{-2}$	1-1000 μg/? as oxide (235 and 238 isotopes) in soil, sewage				Uranium total and isotopes 234, 235 and 238 in water and sludge
Cs-137	>1.4 pCi/g as oxides in soil					barely detectable to several Rad/hr ? As radioactive particles on steel, concrete and in soil		isotopes 134, 135, and 137 in water and sludge
Tc-99	>30 pCi/g as oxides in soil and concrete							in water and sludge
Thorium	isotope 230 > 200 pCi/g as oxides in soil, pit waste and other waste; isotope 232 >1.5 pCi/g as oxides in soil, pit waste, and other waste	1-300pCi/g as inorganic in soil (isotope unspecified)						isotopes 228, 230, and 232 in water and sludge; additional isotopes 231 and 234 in sludge
Pu-238, 239		0-3000 pCi/g as inorganic in soil and 1-300 nCi/g in sediments and sludge		10^{-6} to 10^{-2} pCi/ml as oxide in soil and sewage				isotopes 238, 239 and 240 in water and sludge

Species	Fernald	Mound	Oakland 1	Oakland 2	Nevada	Idaho	WETC	? Oak Ridge ?
Tritium		0.02-100 nCi/l as oxide in groundwater	2000-2,000,000 pCi/l in groundwater and soil moisture	100-20,000 pCi/l as water and gas in soil, vegetation, stack and experiment emissions				
Co-60						barely detectable to several Rad/hr ? As radioactive particles on steel, concrete and in soil		
Neptunium								isotope 237 in water and sludge
Americium								isotope 241 in water and sludge
Protactinium								isotope 234 in water and sludge
Sr-90						barely detectable to several Rad/hr ? As radioactive particles on steel, concrete and in soil		
Radiation					varies, on building materials and in soil			gross alpha, beta in water and sludge

Conclusions:

- We already knew that Uranium and Plutonium would be prevalent.
- I was surprised that Thorium, Tritium, and Cesium would also be so important.
- Many of the respondents are really more interested in total radioactivity and total fission products rather that speciation.

Table 3
Question 3 - Current Analytical Techniques

Species	Fernald	Mound	Oakland 1	Oakland 2	Nevada	Idaho	WETC	? Oak Ridge ?
GC, GC-MS		✓	✓	✓	✓		✓	✓
ICP	✓	✓	✓	✓	✓		✓	✓
AAS, AES		✓	✓	✓	✓	✓	✓	✓
MS	✓	✓	✓	✓				✓
Ion Chromatography								✓
Wet Chemical		✓		✓		✓	✓	✓
IR								✓
Raman								
X-ray		✓		✓		✓		✓
UV-Vis		✓	✓					✓
Electrochemical		✓						
Radiochemical		✓	✓	✓	✓	✓		✓

The results grouped by application are:

Metals
ICP - 7
AAS, AES - 7
Wet chemistry - 5
X-ray - 4
Electrochemistry - 1

Organics
GC, GC-MS - 6
MS - 5
Ion chromatography - 1
IR - 1
UV-Vis - 3
Raman - 0

Radioactives
Radiochemistry

Conclusions:

- If we exclude organics, a multi-species monitor is competing with ICP, AAS, AES, and radiochemistry.

Table 4

Questions 4 and 6 - Analytical Performance and Costs

Performance or Cost	Fernald	Mound	Oakland 1	Oakland 2	Nevada	Idaho	WETC	? Oak Ridge ?
In-house, own staff		10%	5%	10%		90%		95%
In-house, contractor staff	100%							
Out-of-house		90%	95%	90%	100%	10%	100%	5%
Annual costs	$8-10M	>$500K	>$500K	>$500K	$50-100K	$50-100K	$100-200K	>$500K

Conclusions:

- Five out of the eight respondents have costs exceeding 500 k$; Fernald spends 8-10 M$ and it expects these costs to rise to $25M/year after 1996.
- Due to their extremely high costs Fernald uses their own contractor staff.
- The majority of the rest send their work out.

Table 5

Question 5 - Limitations of Current Analytical Technology

Limitation	Fernald	Mound	Oakland 1	Oakland 2	Nevada	Idaho	WETC	? Oak Ridge ?
Turn-around time	✔		✔			✔	✔	✔
Need field instruments	✔	✔						
Cost		✔		✔		✔	✔	
Improve sensitivity, preconcentration		✔		✔				
Regulatory acceptance					✔			
Prior knowledge needed					✔			
Complexity					✔			
Poor product field support					✔			

Conclusions:

- Turn-around time and cost are the two principal limitations of current technology. Often samples take six weeks to be analyzed.

Table 6

Question 7 - Enhanced Operations with New On-site Analyses

Operation	Fernald	Mound	Oakland 1	Oakland 2	Nevada	Idaho	WETC	? Oak Ridge ?
Analytical Cost Savings	✔	✔	✔	✔	✔	✔	✔	✔
Faster D&D	✔	✔		✔	✔	✔		✔
D&D Cost Savings	✔	✔			✔	✔		

Conclusions:

- New analytical technology is expected to first realize direct savings with testing. A secondary expectation is that faster and more efficient D&D operations will result.

Table 7

Question 8 - Necessary Advantages for New Technology

Advantage	Fernald	Mound	Oakland 1	Oakland 2	Nevada	Idaho	WETC	? Oak Ridge ?
Analytical Cost Savings, amount	$12M/yr	$100K needed to offset initial costs and approval	10%	10%	Yes, amount unspecified	Any amount	$50K	Yes, amount unspecified
Enhanced D&D	Faster take-down of bldgs	Reduced radiological exposure		Faster data	Faster data w/ real-time decision ability	Faster turn-around		
Other		Faster turn around of data	20% reduced sampling costs		Must meet QA criteria for field methods		Faster results	

Conclusions:

- Getting analytical data faster is common to almost all of the respondents
- The amount of savings required ranges from any amount to 10% to nearly half of their analytical expenditures.
- Fernald and WETC responded with amounts nearly equal to half of their expenditures. It is possible that they mean this to be an eventual goal rather than the barrier to introduction.
- Mound points out that the savings must factor in initial costs and regulatory approval.

Table 8

Question 9 - Important Attributes for a New Monitor Technology
0 = No Response or No Importance, 1 = Some Importance, 2 = Very Important, 3= Critical

Attribute	Fernald	Mound	Oakland 1	Oakland 2	Nevada	Idaho	WETC	? Oak Ridge ?
Sensitivity	1	2	3	3	2	1	2	3
Dynamic Range	0	2	2	2	1	1	2	2
Accuracy	2	3	3	2	3	1	3	3
Reliability	3	3	3	2	3	1	3	2
Multi-species	1	1	2	1	1	1	1	0
Portability	2	2	1	1	1	2	1	1
Real-time	3	1	2	2	2	2	2	2
Speciation	1	1	1	2	1	1	1	2
Initial Capital Cost	0	1	2	1	1	2	2	2
Operating Cost	1	1	3	1	1	1	2	1
Maintenance Costs	1	1	2	1	1	0	2	1
On-site Use	3	2	2	2	2	2	2	1
Ease of Use	2	1	2	1	1	2	2	2

Attribute Results with Scores by Logical Groupings:

Top 5		Middle 5		Bottom 3	
Accuracy	20	Ease of Use	13	Speciation	10
Reliability	20	Dynamic Range	12	Maintenance Costs	9
Sensitivity	17	Portability	11	Multi-species	8
Real-time	16	Initial Capital Cost	11		
On-site Use	16	Operating Cost	11		

Conclusions:

- The new technology must highly accurate, sensitive and reliable (i.e., it must meet regulatory requirements).
- In addition, it must perform on-site in real time
- In general the costs of the technology are not ranked high.
- Surprisingly, speciation and multi-species are ranked low.

Final Question Results:

Question 10 - What do you feel are the most important issues for integrating a new sensor or monitoring technology into your operations?

Fernald - Must get site buy-in to use through a process of user involvement, including an uncertainty period without commitment requirements.

Mound - Data quality and overall costs are the prime issues associated with analytical testing programs.

Oakland 1 - Cost, ease of use, accuracy and sensitivity, and reliability.

Oakland 2 - Improve sensitivity and turn-around time

Nevada -
1. Training of potential users
2. Readily available support for field operations
3. Securing regulatory agency buy-off
4. Good correlation with confirmatory lab results

Idaho - Does it work?

WETC - EPA acceptability

Oak Ridge? - N.A.

Appendix D

Proposed Agenda for Fernald Site Visit

Introductions

Review of PSI Technology (Semi-formal presentation)

Scientific basis
Progress summary
Key issues

Review of DOE Facility Needs (Informal discussion session)

Current analytical protocols
Analytes and sample matrices
Sample collection and handling
Required sensitivities
Known interferences
Sample process rate
Costs

Needs of New Technology

Host site for Tc sampling and analysis
Guidance in calibration standard preparation

Refinement of DOE Requirements for the New Technology

Decontamination procedures
Field portable versus Lab use
Desired performance (contaminants, sensitivity, analysis time)
Physical constraints (power, size, weight, consumables)
User interface

Site Introduction and Implementation

Regulatory barriers
Cost/benefit
Purchase vs. lease options
Site introduction and beta testing
Liability
Support and user training

Summary and Conclusions

Site Walk-through

Appendix E

SIBS Heavy Metal Detector

Draft Business Plan

DRAFT

BUSINESS PLAN

SIBS HEAVY METAL DETECTORS

PHYSICAL SCIENCES INC
20 New England Business Center
Andover, Massachusetts 01810
508-689-0003

CONFIDENTIAL

1. Executive Summary

Physical Sciences Inc. (PSI), a developer of advanced opto-electronic instruments for broad applications in energy, environmental, industrial, medical and aerospace markets, has developed a spectroscopic instrument to measure toxic heavy metals in airborne, groundwater and soil field applications. PSI's Spark-Induced Breakdown Spectroscopy (SIBS) technology combines a powerful electrical spark discharge with spectroscopic detection of metal atomic emissions. PSI's propreitary approach enables sensitive detection of heavy metals (lead, Mercury, chromium, etc) in a rugged, affordable instrument.

The SIBS instruments address annual markets of at least $130 million. PSI believes that these markets represent a significant opportunity. There are no currently available field instruments that provide an accurate measurement of heavy metals at an affordable price. As a result, current practice is largely to collect field samples for laboratory analysis. A range of products is under development to address:

- industrial health monitoring in gun firing ranges and metals processing plants.

- continuous emissions monitoring from coal and oil fired utility plants and waste-to-energy facilities.

- field instruments for use by environmental engineers to characterize and monitor heavy metals in air, groundwater and soils at environmental remediation sites.

- drinking water quality detection by municipal health officers and maintenance personnel using a hand-held lead monitor.

PSI has developed the SIBS technology with the aid of substantial funding from the U.S. Dept. of Energy (DOE). The company intends to pursue additional funding support from the DOE to apply its instruments as detectors and monitors for the large clean-up efforts on the DOE complex.

The company is seeking a minimum of $5 million equity investment to be used to complete the development of its instrument products and introduce the products to target markets. Concurrent with raising that equity, PSI will establish the SIBS project as a separate spin-out corporation.

PSI projects that SIBS instrument sales will grow to $36 million in the fifth year following initial product introduction in 1999, at pre-tax profit margins surpassing 20%.

2. The Company & Technology

The Company. Physical Sciences Inc. develops propreitary advanced opto-electronic instrumentation for broad applications in the aerospace, energy, environmental, industrial and medical markets, and commercializes selected technologies working with corporate partners and spin-out companies.

The PSI SIBS division develops and markets spectroscopic instruments to measure toxic heavy metals (lead, mercury, chromium, cadmium, arsenic, antimony and beryllium) concentrations in airborne, liquid and soil applications. These detectors will be manufactured and marketed to customers in the environmental remediation, electric utility, metals processing and drinking water supply markets through distributors and established instrument companies.

Founded in 1973, Physical Sciences performs research and development for a wide range of federal government agencies and industrial clients. PSI has 110 employees, of whom 80 are technical professionals, mostly with advanced degrees, split about equally between engineering (ME, EE and computer sciences, Chem E, Aero) and the sciences (physics, chemistry). PSI's annual revenues are $16 million. The company's headquarters and primary R&D facilities are located in Andover, MA, with additional R&D operations in Alexandria, VA, Lanham, MD, Hunt Valley, MD, Boulder, CO and San Ramon, CA. PSI is a closely held company; over 30% of outstanding stock is now held by an Employee Stock Ownership Trust.

PSI has a diverse core R&D business, spanning electro-optical and spectroscopic instrumentation, electromechanical devices, chemical processes, aerospace simulation and instrumentation, and electrochemical processes and devices. PSI is a leading participant in the Small Business Innovation Research (SBIR) and other dual-use programs funded by the U.S. Government. PSI has received nearly $40 million in SBIR funds, which currently represent 50% of the companies R&D revenues. PSI is one of the top three recipients of SBIR awards in the country. The company is committed to commercializing appropriate technologies developed under government funding through internal projects, establishment of spin-out companies, strategic partner relationships and technology licensing. As a qualified small business, PSI retains ownership of all intellectual property developed under government funding, with the government retaining a non-exclusive license to use the technology for its own purposes.

PSI has created two development stage spin-out companies in recent years. One developed an electro-mechanical lithotripsy device for destruction of kidney stones and was pursued under venture financing through successful FDA approval. The other developed and marketed a line of tunable diode laser instruments for measurement of selected chemical compounds in utility and petrochemical plant applications; this company was successfully sold to an established provider of gas analyzer instruments in 1996.

The Product. The PSI SIBS heavy metal detector is a portable instrument for real-time on-site detection and measurement of the RCRA heavy metals (lead, mercury, chromium, cadmium, arsenic, antimony and beryllium). Using Spark-Induced Breakdown Spectroscopy (SIBS), the detector measures the total elemental concentration of heavy metals in the sample exposed to the spark, whether in gaseous, liquid or solid form. A powerful electrical spark discharge creates a small volume of hot plasma in which aerosol and solid particulates are quickly vaporized and all components are reduced to atomic form. Monitoring of atomic emissions in selected wavelength bands during the fraction of a second as the spark plasma cools provides the measurement of heavy metal concentrations. PSI's propreitary technologies for the spark discharge and spectroscopic data processing enable detection of heavy metals at sub-parts per million concentration, in a rugged and affordable field instrument.

PSI believes that the SIBS detector will meet an established need for real-time field and on-line measurement of heavy metals. Heavy metal detection and monitoring is currently accomplished, if at all, by collection of samples in the field or plant followed by analysis of the samples using sensitive x-ray fluorescence (XRF), atomic adsorption spectroscopy (AAS) or inductively-coupled plasma (ICP) laboratory instruments. While the analytical laboratory business has been quite competitive with declining costs in recent years, the effort to obtain field samples and the delay in waiting for lab results (often up to four weeks) hardly meet user needs.

Instruments based on the SIBS technology will offer the detection sensitivity required for numerous environmental and health monitoring applications, while enabling relatively simple, robust field instruments at affordable prices. SIBS instruments address current and projected annual markets of at least $130 million. PSI is currently testing a detector for airborne lead in gun firing ranges and metals processing plants. The company is also developing a Continuous Emissions Monitor (CEM) for incinerators, utility boilers and remediation plants for testing in a joint DOE-EPA evaluation in September; PSI is pursuing significant DOE funding to apply the CEM to the large-scale DOE facility restoration projects. Follow-on products include instruments for field measurement of heavy metals in groundwater and soils at environmental remediation sites, as well as a portable detector for real-time monitoring of water lead contamination in drinking water supplies.

3. Applications and Customers

Industrial Health Monitors. Airborne lead particles represent a serious threat to workers in the approximately 7,000 gun firing ranges in the U.S. There are also several thousand smelting and metal processing plants with occupational health concerns involving airborne heavy metals. Current strategies for dealing with occupation health issues are to employ excessive air circulations systems in these facilities, combined with occasional air sampling and lab analysis of airborne metals exposure. Use of a real-time on-site monitor would enable facility operators to significantly reduce worker exposure to toxic metals as well as to reduce their operating costs associated with the HVAC system.

In many cases, individual plant operators will be reluctant to install monitoring equipment for heavy metals without a proper economic motivation. Many operators may prefer not to know about the levels of toxic metal exposure in their plants. One approach to avoid such market resistance is to sell the SIBS monitors through the HVAC system providers, as part of the process control system to reduce operating expenses. Another approach is to sell through, or at the urging of, liability insurance providers.

Continuous Emission Monitors. The 1990 amendments to the Clean Air Act identified 189 hazardous air pollutants, including the RCRA metals. Although long delayed, the EPA may issue requirements for continuous emissions monitoring of heavy metals from the approximately 600 incinerators and 3300 large coal and oil fired utility and industrial boilers in the U.S. The major source of delay in promulgation of heavy metals emissions monitoring regulations has been the lack of acceptable technologies. We believe that the SIBS technology will be enabling for this application. PSI will be participating in a joint program between the DOE EM Office of Science and Technology and the EPA to test CEMs for monitoring hazardous metals in stack emissions from waste combustion and thermal treatment facilities. This evaluation program is scheduled for September 1997. Other prototypes slated for participation in these tests are based on laser excitation or employ extractive ICP technology, with projected selling prices of $250,000 to $300,000. A SIBS-based CEM will not require the expensive laser or extraction system and is projected to have a selling price below $50,000. Such a price is within the affordable capital purchase range for incinerator and utility operators, and the availability of the SIBS CEM should enable the EPA to mandate the instrument.

Although PSI's primary strategy for marketing the SIBS CEM instrument is to have the technology mandated by the EPA, many customers may wish to purchase the monitors to allay the concerns of neighboring communities and other stakeholders. The emission of mercury and other toxic metals by incinerators and utilities is a major source of community concern and is often a major issue in obtaining site approval for new installations. Continuous monitoring would be essential in meeting community concerns. Additionally, for DOE remediation projects, the DOE will likely be forced by the concerns of stakeholders and local permitting bodies to implement multi-metal CEMs, irrespective of CAA regulations to be issued by EPA.

Environmental Field Detectors. Environmental engineering firms currently rely primarily on sample collection/laboratory analysis for site characterization and remediation monitoring. Several companies are offering portable XRF detectors for analysis of soils and, to a lesser extent, of groundwater, but these products have experienced slow acceptance due to their marginal sensitivity for heavy metals. PSI will offer portable SIBS-based detectors to environmental engineering firms for on-site, real-time use. Field instruments will never completely replace the "gold standard" of analytical laboratory measurements. Combined with selected lab analysis for verification, use of field instruments will greatly enhance the productivity of remediation projects by providing real-time characterization of the site, better direction as to where to take samples for lab analysis, and avoiding the need for follow-up field measurements when lab results are received two-four weeks after the initial field measurements.

The requirement for a satisfactory field instrument are significant. Ruggedness, good portability, ease of operation, high reliability and good sensitivity are consistently cited by engineers, many of whom have experience with previous products that fell short in one or more of these categories. An affordable price is also very important, as the environmental engineering service market is now quite competitive in the U.S. and most potential customers are reluctant to make major equipment investments. The target price for a SIBS monitor for an individual heavy metal is $5,000 and that for a multi-metal instruments is $10,000. The first SIBS product will be an air emission monitor, with extensions to address the larger soil and groundwater markets to follow.

Development of the PSI SIBS technology has been largely sponsored by the DOE EM Office of Science and Technology. DOE is attempting to accelerate the development of advanced field equipment to accomplish waste cleanup and environmental remediation more cost effectively at DOE sites. One group of technologies identified with a potential for cost savings is those that allow characterization, monitoring and sensing of environmental contaminants in the field. Field deployable instrumentation can offer cost and time savings when compared with off-site laboratory analysis of field samples. Detection and monitoring of hazardous heavy metals was specifically noted as one of the key needs for DOE's Mixed Waste Focus Area, and one of DOE's three cross-cutting technology areas is concerned with Sensing, Characterization and Monitoring. These needs include both field instrumentation as well as CEMs for thermal treatment and vitrification plants.

Drinking Water Monitor. An eventual follow-on product is a hand-held instrument that can measure lead concentrations at drinking water levels (5-10 ppb). There is a significant market for such an instrument in schools and other public buildings, where copper pipes are a source of lead in the drinking water, resulting in a major health concern for children. Lead concentrations can build up in individual water dispensers on a daily basis, in an unpredictable manner. PSI's follow-on product is a hand-held lead detector in the $2,500-3,000 price range, to be sold to individual schools for continuous use by health or maintenance personnel to monitor water sources and flush or shut down problem sources when detected.

4. The Market

The global environmental instrumentation market was $2.5 billion in 1995 (Environmental Business Journal, Dec 1995), with lab instruments comprising 56%. The market is 49% U.S., 27% Europe and 24% Asia and elsewhere. Overall growth rate is projected to be 5-6%, with lab instruments being particularly flat (2-3%) and field instruments growing at the higher rate of 7-8%.

The following table summarizes the potential annual markets targeted for the SIBS heavy metal detector, assuming 100% market capture by our products. Additional international markets should be available for the industrial health monitor, water and soil field detectors, and drinking water monitor, once the products are successfully introduced into the U.S. markets.

Available Annual U.S. Markets for Heavy Metal Detectors

Market Segment	Served Available U.S. Market ($ millions)
Industrial Health Monitors	$6 M
Continuous Emissions Monitors	30
Field Instruments:	
Air	6
Water	14
Sludge	5
Soils	16
Drinking Water Monitor	50
TOTAL	$127 M

Industrial Health Monitors. There are about 7,000 military, state and local government, and private gun firing ranges in the U.S. There are several thousand additional industrial metals processing plants for which individual metal detectors could be installed. A total of 10,000 potential sites for an instrument with a target selling price of $3,000 results in a total potential market of $30 million. Assuming penetration of this market in five years then yields an annual potential U.S. market of $6 million.

Continuous Emissions Monitors. The U.S. CEM market has been very flat in recent

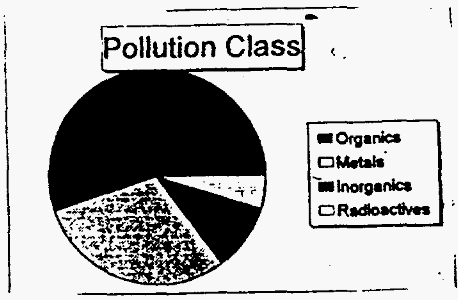
CEM requirements could be applied to the following U.S. plants:

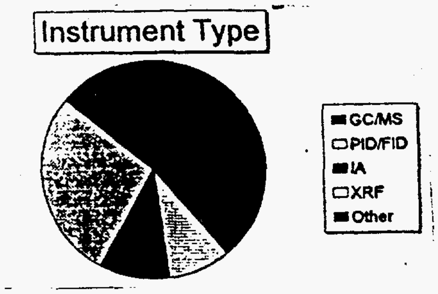
Available Market for Heavy Metal CEM Systems

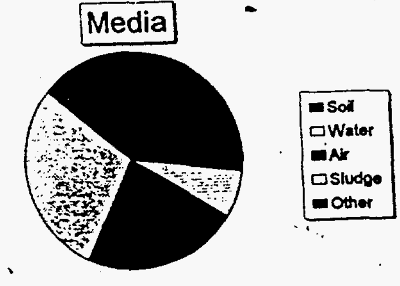
	Installations
Incinerators - RCRA Regulated	375
Utility Boilers - Coal/Oil Fired	1620
Industrial Boilers - Coal/Oil Fired - >500MBTU/hr	1700
TOTAL	3,695

3,700 sites at an average CEM unit price of $40,000 yields a total market of $148 million, or an annual market of about $30 million with a five year penetration. Inasmuch as European regulations limit emission of particulates rather than heavy metals, we do not expect a significant international counterpart to this U.S. market.

Field Instruments. According to a 1996 market study performed by the Unimar Group for the DOE in connection with the PSI heavy metals detector (available on the internet under http://cmst.ameslab.gov/CMST/About_Market_Study.html), the U.S. hazardous waste remediation market was about $12 billion in 1996. Environmental laboratory analytical services comprise about $1.6 billion of that total, with about $600 million for remediation, $380 million for water and waste water testing, and $80 million for air monitoring. The total environmental field instrument business is much smaller, about $140 million annually. The following charts show the breakdown of this $140 million by pollutant class, media and instrument type. Note that x-ray fluorescence (XRF) instruments are the only type intended to measure heavy metals for environmental field applications, representing current sales of about $12 million annually. The available markets for field instruments given in the table above are taken from the Unimar study. Note that larger markets could be opened if reliable and accurate field instruments could penetrate the much larger volume of testing performed in the analytical labs.







As compiled in the Unimar study, there are currently nearly 15,000 identifiable larger establishments considered likely to use field instrumentation. Over one-third of these are environmental consulting firms, with the remainder being split between government installations, utilities, chemical and petroleum plants, and water treatment facilities. Over 5,000 national and local engineering firms supply environmental remediation services, with combined revenues of $12 billion. The top 40 firms have over 30% of the business, and these larger firms have approximately 1,000 offices across the U.S.

Establishments Likely to Use Field Instruments

Environmental Consulting & Services	5,500
Government	2,500
Utilities	2,000
Chemicals	2,000
Petroleum	1,500
Water & Waste Water Utilities	800
Automotive	500
TOTAL	14,800

In addition, the Unimar study lists 12,000 "other" and presumably smaller establishments likely to use field instruments.

Drinking Water Monitors. The target market for portable drinking water lead monitors are school buildings - elementary through high school, plus day care centers. A $2,500 hand-held lead monitor could be sold direction to health or maintenance personnel at individual school buildings. There are approximately 100,000 schools in the U.S., representing a $250 million market opportunity if each school were to purchase one monitor. A five-year penetration cycle would result in annual available sales of $50 million. Additional units could be sold to municipal health officers to monitor day care centers and other smaller operations that would not be inclined to purchase a unit on their own. There may be further opportunities for this product internationally.

5. Industry Analysis

The relevant Standard Industrial Codes (SIC's) the the SIBS products are:

3823 - Industrial Instruments for Measurement, Display, and Control of Process Variables

3826 - Laboratory Analytical Instruments

The market for heavy metal detectors is strongly dependent on environmental and industrial health regulations. The National Institute of Occupational Safety and Health (NIOSH) and the Occupational Safety and Health Administration (OSHA) set limits in 1990 for workplace exposure to toxic metals vapors and particluates. For lead and most other heavy metals, these limits are in the 40-80 ppbw range.

The Clean Air Act Amendments of 1990 expanded the "air toxics" program (Title III) by identifying 189 "hazardous air pollutants", including 11 trace metals, and requiring the EPA to establish strict emissions standards and monitoring requirements for them. The EPA has identified a large number of major emissions sources throughout the U.S., to which continuous emissions monitoring requirements will be applied. To date the EPA has not promulgated regulations requiring the continuous monitoring of heavy metal emissions for major emissions sources, primarily from lack of validated measurement technology.

The largest single owner of real property in the U.S. is the federal government. Much of this land has been contaminated by various defense and energy related activities over the past decades. The U.S. Department of Energy has embarked on a massive program to clean up the hazardous wastes on the many DOE plants across the country. This ten-year effort is a major portion of the environmental market.

6. Competition

Industrial Health Monitor. The competition for this market is sample collection followed by laboratory analysis, with a two-four week response.

Continuous Emissions Monitors. The following table lists potential competing products for the CEM market. None of these products can be considered to be established for this application. All should be considered to be prototypes, to be tested in joint EPA/DOE tests in September.

The table lists the measured or projected detectivity levels for lead, as an example. The acceptable levels dictated by the Clean Air Act are 1-2 ppb. Only the TraceAir™ product quotes this level of sensitivity. The SIBS technology has not been optimized for CEM applications, and PSI anticipates further improvements in detection limits.

Competitive CEM Instruments

Product	Manufacturer	Sensitivity for Lead	Extractive/ In-Situ	Price ($K)
SIBS	PSI	~10 ppb	In-Situ	$40K
TraceAir™	Thermo Jarrell Ash	0.4 ppb	Extract	300K
LIBS	LANL/ADA,Laser Diagnostics, Miss. St.	≥15 ppm	In-Situ	200-300K
μWave Plasma	MIT	?	In-Situ?	<100K
HEST	Cooper Env Services	?	Extract	200-300K
XRF	Metorex	~10 ppm	Extract	?

TraceAir™ is an announced product, for which TJA reportedly has two orders. The underlying ICP technology was developed by Seltzer of China Lake Naval R&D. TraceAir was the only one of three prototype CEMs to perform satisfactorily in a 1996 EPA evaluation. This is a very capable product with high sensitivity. However, TraceAir requires extraction of a sample stream from the stack, introducing a number of complex engineering issues and resulting in a complicated, expensive system. We believe that the high price will severely limit the acceptance of TraceAir in the CEM market.

At least three groups are developing Laser-Induced Breakdown Spectroscopy CEM instruments: Los Alamos National Laboratory in conjunction with ADA Technologies (LASS), Laser Diagnostics, Inc., and Mississippi State University (DIAL). Prorotypes of LASS and DIAL participated in the 1996 EPA tests. LIBS technology is promising, and indeed is analogous to the SIBS technology, the primary difference being the excitation source. The candidate LIBS instruments employ Nd:YAG lasers with pulse energies of a fraction of a joule. These currently cost $50,000-100,000, driving the relatively high price of the LIBS candidates. PSI's SIBS technology enjoys a large advantage over LIBS in this regard: the SIBS electric spark produces more excitation energy (> 1J) at a very much lower cost. Also, the detection sensitivities reported by LASS do not match the levels achieved by PSI's SIBS system.

Not much is known about the microwave plasma analyzer developed by MIT's Plasma Fusion Laboratory or the Hazardous Element Sampling Train developed by Cooper Environmental Services. The latter is believed to work in conjunction with an XRF analyzer.

Metorex plans to test its XRF analyzer in the EPA/DOE evaluation, either separately or in conjunction with HEST. Metorex currently offers its Courier 10 for process applications, providing ~10ppm sensitivity. Analytical lab XRF analyzers provide ~ppb detection limits, but those employ more powerful x-ray source than would be practical in the field and are quite expensive.

Environmental Field Instruments. At least six companies offer commercially available portable XRF analyzers for detection of RCRA metals in soils and groundwater. These are typically in the $40,000-50,000 price range. Typical sensitivities are ~100 ppm, with several minutes required to process a sample. Many field engineers find this sensitivity to be inadequate, and the prices are higher than many firms can accept. The fundamental difficulty with field XRF units is that the x-ray sources do not have sufficient strength to provide rapid sensitive detection.

Competitive Field Instruments

Technology	Manufacturer	Sensitivity for Lead (ppm)	Measure Time	Price
SIBS	PSI	<1 ppm	<1 min	$10K
XRF	TN Spectrace, HNU, Etc.	~100	7-8	~50K
XRF	Metorex	<50	4	36K
XRF	Niton	≤130	2	12K
LIBS	LANL/ADA	>100	?	?

The inexpensive Niton XRF analyzer is interesting. That unit targets the lead paint detection market, but provides surprisingly competitive (relative to the other field XRF units) performance. The Niton device employs only one x-ray source, whereas the others all employ three sources to provide detection over a wide range of elements. As a result, the Niton analyzer provides competitive measurements for lead and mercury, but much less definitive data for arsenic, copper, zinc and chromium.

Los Alamos has developed a prototype LIBS detector for field anaylsis of soils. This device employs a 10-20 mJ laser pulse, which is far short of the 1 J produced by the SIBS spark discharge. The relative inefficiency of the laser as an energy source limits the ability of a portable LIBS analyzer to compete with the SIBS technology on the basis of sensitivity or price.

Drinking Water Monitor. The competition for this device consists entirely of sample collection followed by laboratory analysis.

7. Marketing and Sales Plan

Marketing Strategy. To the maximum extent possible, the marketing strategy for SIBS products is based on economic value to the customer. Because this is not always possible in the environmental businesses, we will employ several other approaches as well:

> Economic Value: The optimal approach is to offer products that provide obvious economic benefits to the customer. The SIBS environmental field instruments will be marketed on the basis of the cost savings that they provide to environmental engineering firms, through reduced lab testing charges, and the improvements in productivity by reducing delays due to the turnaround associated with lab testing. Also, the SIBS industrial health monitor will provide an economic benefit to the customer, when operated as part of an HVAC system to reduce operating expenses.
>
> Mandate SIBS Products: The primary motivation for the customers to purchase SIBS CEM products will be regulatory. PSI is working with the EPA to evaluate the SIBS technology, with the intention of being designated as Best Available Technology. Regulatory mandates may be also achievable for some applications of the health monitor.
>
> Community Relations: There are major benefits to government agencies and plant operators to be able to allay the environmental concerns of the neighboring community and other stakeholders. Neighbors can be very active politically, and potential generators of hazardous metals are guilty until proven innocent. CEMs may be politically necessary to obtain site approvals for remediation facilities, incinerators, coal and oil fired utility generating plants, and large smelting operations. Real-time monitoring of drinking water quality is motivated by genuine community health concerns.
>
> Other: PSI will continue to explore innovative channels to sell SIBS monitors. For example, we may be able to sell industrial health monitors through either liability or workers' compensation insurance providers.

Pricing Strategy. The straightforward and robust SIBS technology offers the opportunity to market very affordable instruments. SIBS instruments will be priced to open wide markets by providing obvious returns to customers. Target prices are based on perceived acceptable price ranges in each market segment to avoid significant customer price resistance and, in most cases, to keep SIBS prices within the purchase authority of individual plant operators or field engineers. PSI also has the opportunity to significantly undercut potential competition and thus acheive a large market share. Of course, detailed manufacturing designs will ultimately be required to ensure that the SIBS products can be produced profitably at the target price points.

> Health Monitor: The $3,000 target price for an instrument to monitor a single heavy metal compound is dictated by the fact that direct economic benefits will often not be obvious to customers.

CEM: A $40,000 price for an in-situ multi-metals monitor will enable the EPA to mandate this technology for a wide range of industrial generators, whereas it would be reluctant to do so at significantly higher prices.

Field Instruments: A $10,000 price point provides a rapid pay back to engineering firms, by reducing the $5,000-10,000 costs for lab testing that would be incurred per project on several projects per year. XRF field analyzers have not met sales expectations, in part due to $30,000-50,000 prices.

Drinking Water Monitor: At $2,500, this instrument will be within the expenditure range that can be justified within municipal health and school maintenance operating budgets without significant higher approvals. Health officers typically spend between one and few thousand annually on drinking water lead testing at analytical labs. Reduction of possibly elimination of lab testing expenses would justify the purchase of a SIBS lead monitor.

Sales Plan.

- PSI will sell the SIBS instruments to the U.S. markets through manufacturers representatives. This is appropriate to the relatively high unit volumes and moderate selling prices of the SIBS products, and is the standard approach in the environmental and process control instrument industry. The network would typically consist of 15-20 representatives located strategically throughout the U.S. A separate network will be required for CEMs, and perhaps for drinking water monitors.

- As one exception, PSI will employ 3-4 direct sales personnel to augment the rep network selling CEMs. The CEM product will often require demonstrations and an extended selling cycle, plus significant post-installation support.

- PSI will establish marketing arrangements with selected established instrument providers in Europe and the Far East to sell SIBS instruments to the appropriate international markets.

Advertising Plan. PSI will advertise SIBS products through periodical advertisments in selected trade journals, plus exhibits at appropriate annual conventions and seminars.

Trade Journals: Journal of Air & Waste Mgmt Assoc., Pollution Eng'g News, Applied Spectroscopy.

Exhibitions: Air & Waste Mgmt Assoc, Pittcon, PowerGen.

Sales Goals. We project that SIBS products will acheive 20% of the served available markets presented in the above section, with the exception of the CEMs markets for which we project penetrations of 50% of the incinerator market, 20% of the utility market and 10% of the market for other industrial boilers.

We further project that a period of 6 calendar quarters will be required for the rep organization to reach steady state sales following product release. This allows for four quarters for PSI's marketing manager to train the rep network, in groups of 3-4 reps per quarter, plus 2-3 quarters for individual reps to work through the selling cycle once trained. Similarly, it should take foreign distributors 6 quarters to take the products through their own introduction process.

Sales Goals - Units

	1999	2000	2001	2002	2003
Indust Health - US	112	388	440	480	530
- Intl		100	320	360	390
CEMs	4	100	148	163	179
Field Instr - US	14	133	485	838	925
- Intl			30	155	298
Drink Water - US			130	2800	4100
- Intl				300	1700

8. Research & Development Plan

PSI has already developed, under existing funding from DOE, an "alpha" version of an industrial health monitor for lead. The underlying research on the spark discharge and spectral detection methodology for individual metal compounds is complete. Testing of the α unit in a gun firing range is underway in the second quarter of 1997.

The planned sequence consists of "development" as opposed to "research", to extend the heavy metal detector technology to the various product versions. Each product extension consists of the following generic steps:

1. Design and assembly of an α prototype to test the performance of the conceptual product in the intended environment. This design effort will be carried out by existing PSI staff.

2. Testing of the α prototype for several periods over a six-nine month span to validate the design in the intended operating environment and obtain performance data for the β design.

3. Design and fabrication of a β unit, based on the α test experience. The β unit is a pre-commercial unit, intended for all of the "fit and function" of the commercial unit. PSI will compliment its internal engineering staff with outside professional design services to a significant extent for β designs to ensure meeting development schedule and manufacturability goals.

4. The β unit will be tested for at least six months in a real customer environment, much of that period without PSI oversight.

5. Revise the β design according to the test experience, document the resulting design, and obtain the required engineering certifications including Underwriters Laboratory, Canadian Standards Association, Federal Communications Commission , and Factory Mutual Laboratory. PSI will utilize outside consultants who specialize in preparing the required certification packages.

6. Commercial product release.

The following table lays out the product development schedule, leading to these target release dates:

Product Release Dates

Industrial Health Monitor	Jan 99
CEM	July 99
Field Inst - Air	Mar 99
- Water	Apr 00
- Soils	Jan 01
Drinking Water Monitor	Jul 01

SIBS PRODUCT DEVELOPMENT SCHEDULE

```
                            1997            1998            1999            2000           2001
                      Q1  Q2  Q3  Q4  Q1  Q2  Q3  Q4  Q1  Q2  Q3  Q4  Q1  Q2  Q3  Q4  Q1  Q2  Q3

Industrial Health
    Alpha Prototype          +----------------------<
    Beta Uint                     >=========+---------------<
    Certification                             >xxxxxxxx<
    Release                                           X

CEM
    Alpha Prototype        >=========+---------------------<
    Beta Unit                                 >======+-----------------<
    Certification                                     >xxxxxxxx<
    Release                                                    X

Field - Air
    Alpha Prototype ..        >======+--------------<
    Beta Unit                             >====+----------------<
    Certification                               >xxxxxxxxxx<
    Release                                               X

Field - Water
    Alpha Prototype                           >=======+--------<
    Beta Unit                                         >=======+------------------<
    Certification                                             >xxxxxxxxxxx<
    Release                                                                X

Field - Soils
    Alpha Prototype                                   >=======+------------<
    Beta Unit                                                     >=======+------------------<
    Certification                                                         >xxxxxxxxxxx<
    Release                                                                            X

Drinking Water
    Alpha Prototype                                          >=======+----------<
    Beta Unit                                                        >======+-------------<
    Certification                                                         >xxxxxxxxxxx<
    Release                                                                            X
```

Legend

```
Design     >======+
Test               +-------------<
Certify            >xxxxxxxx<
Release                     X
```

9. Manufacturing and Operations

The PSI SIBS division operates in space within the PSI 65,000 sq. ft. facility in Andover, Mass. It is anticipated this arrangement will be satisfactory until 1999, at which time the SIBS products enter volume production and the SIBS operations will require more significant space. In the meantime, PSI will make space available to the SIBS project as required from time to time and will allocate rent to SIBS at the going commercial market rate for R&D space. Beginning in 1999, the SIBS division will lease separate R&D space, mostly likely in the Andover area.

The company's manufacturing strategy is to outsource the manufacture of component parts and subassemblies. The PSI SIBS manufacturing process consists of assembly, calibration and QA/QC. This outsourcing strategy is common in the instruments business, and there is a large number of qualified vendors in the Massachusetts/New Hampshire area.

PSI plans to hire appropriate manufacturing personnel in early 1999, prior to commercial release of the SIBS products. The first hire will be a manufacturing manager who will be responsible for vendor selection, procurement, inventory control and scheduling. A quality engineer with experience in statistical quality control methods and testing procedures will be the second hire in 1999. PSI currently employs a limited number of technicians with extensive manufacturing assembly experience, but the company will have to hire several assembly personnel as manufacturing increases in later 1999 and 2000.

10. Management and Staffing

The SIBS project will continue to operate informally within the PSI core R&D operation until approximately mid-1998. During that period, the planned product development efforts will be largely funded by follow-on contract support from DOE. In early 1998, PSI will begin recruiting a Chief Executive Officer with specific previous experience at the CEO or VP Marketing level in the environmental or process control instrument industry. The goal is to have that CEO on board during the second quarter on 1998.

The first responsibility of that CEO in 1998 will be to hire an experienced VP of Marketing and Sales. The VP/Marketing should be hired in Q3 of 1998, in time to begin assembling the network of reps and limited direct sales personnel for the Industrial Health, CEM and Environment Field instruments.

The new CEO will also work closely with senior management from PSI to raise a first round of equity from venture capital sources. These funds will be needed in the summer of 1998, as shown in the Pro Forma financials of Section 12. Simultaneous with raising of outside equity, the SIBS project will be spun-out of PSI as a separate subsidiary corporation. Ownership in the spin-out corporation will be held by PSI and the new investors, with approximately 10% of stock reserved for stock options by the CEO and other key personnel.

PSI also anticipates the hiring of one or more product design engineers by the end of 1997, to supplement the PSI scientific and engineering staff that is more appropriate to alpha-stage engineering than to beta and final commercial designs.

The following chart shows the projected staffing for the SIBS project and planned spin-out corporation. The staff levels indicate the personnel that would be employed at the end of the indicated calendar years. Fractional number denote functions fulfilled by existing PSI personnel on an as-needed basis.

Projected SIBS Staffing

	1997	1998	1999	2000	2001	2002
Gen & Admin -						
CEO	0.3	1	1	1	1	1
Admin Ass't			1	1	1	1
Controller		0.1	0.2	1	1	1
		0.1	0.4	1	2	4
HR		0.1	0.2	1	1	1
Marketing -						
VP/Mkt & Sales		1	1	1	1	1
Product Mgr			2	3	4	4
Sales			1	3	3	3
Engineering -						
VP/Eng'g	0.5	1	1	1	1	1
M.E./Photonics	2	3.5	2.5	2.5	2	2
E.E.	1.5	3.5	2	2	2	2
Manufacturing -						
Mfg Eng			1	1	1	1
QA/QC			1	1	1	1
Purchasing				1	1	1
Assembly			1	6	12	25
TOTAL	4.3	10.3	15.3	26.5	34	49

11. Risks and Contingencies

The proposed development of SIBS heavy metal detectors involves numerous risks:

Limited Commercial Product Operating History: The PSI SIBS operation has a limited amount of operating history. There can be no guarantee that, if the Company is able to develop and construct the planned products, there will be substantial demand for its products or that, if there is demand, the company will be able to produce products at a profit.

Dependence on Environmental Regulations: A principal source of demand for the company's products is driven by environmental regulations, some of which have yet to be formulated. Products are developed only when appropriate regulations have been implemented for environmental monitoring and hence will create demand for instrumentation products.

Intellectual Property Rights: The company will protect its property by patents. However, there can be no assurance that it will be able to obtain useful patent protection for its technology, of that any patents to be issued will provide the company with signification protection against competition. Moreover, there can be no assurance that any patents issued to the company will not be infringed upon or designed around by others.

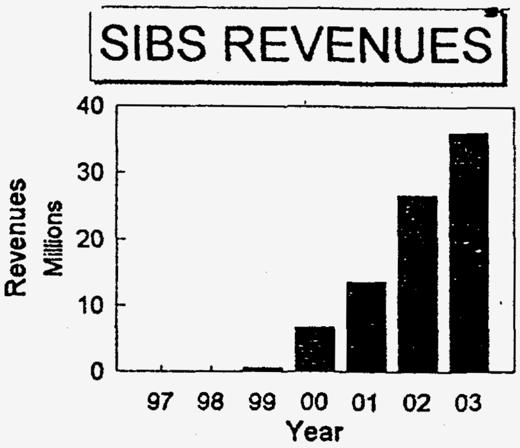
Technological Developments and Competition: The company's products will compete in fields characterized by rapid technological progress and intense competition. New developments in technology may have a material effect on some or all of the company's products. There are other companies with greater resources and commercial experience.

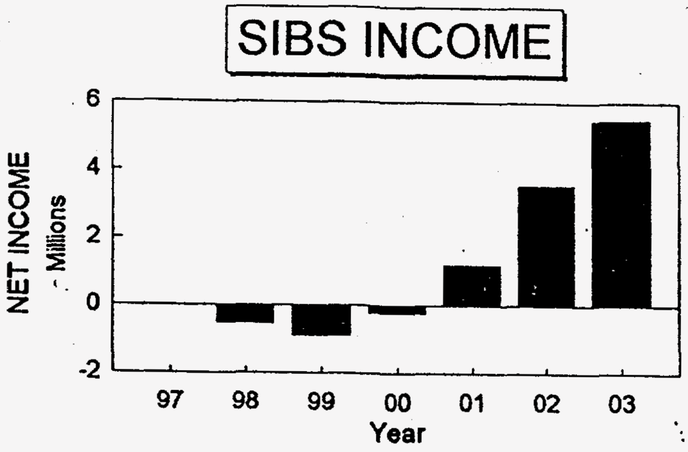
Dependence on Key Suppliers: The company depends on key suppliers for parts, components and subsystems as an integral part of the manufacturing strategy. These affect price and schedules. The company plans to develop alternate sources for all key components.

Need for Additional Funds: In order to continue or complete development and market introduction of the potential commercial products described herein, the company may choose or be required to raise additional funds. There can be no assurance that funding can be obtained on favorable terms, if at all.

12. Financial Projections

The following PRO FORMA Financial Projections are based on the sales forecasts on Section 7 above and the noted selling prices. Most notably, the SIBS heavy monitor business will grow to a $36 million five years after product introduction, generating over $5 million in net profits. To achieve this, investment of $1.5 million is required in mid-1998 to complete product development and testing, plus an additional $1.5 million in 1999 to fund market product introduction and nearly $2 million in 2000 for working capital purposes.





PRO FORMA STATEMENT OF OPERATIONS
($ Thousands)

	1997	1998	1999	2000	2001	2002	2003
REVENUE	0	0	636	6,794	13,675	26,720	36,150
Cost of Goods Sold	0	0	492	3,609	6,419	12,304	16,150
GROSS PROFIT	0	0	144	3,185	7,256	14,416	20,000
Margin %	-	-	*23%*	*47%*	*53%*	*54%*	*55%*
SG&A	61	272	989	2,879	4,631	7,551	9,667
Eng'g,R&D	189	860	655	684	676	1,100	1,600
OPER INCOME	(250)	(1,132)	(1,500)	(378)	1,949	5,765	8,733
Plus R&D Funding	200	250	-	-	-	-	-
Interest Inc (Exp)	0	0	0	0	38	80	225
Prov for Inc Taxes	20	353	600	151	(780)	(2,306)	(3,493
NET INCOME	(30)	(529)	(900)	(227)	1,207	3,539	5,465

PRO FORMA BALANCE SHEET
($ Thousands)

	1997	1998	1999	2000	2001	2002	2003
Cash		643	439	450	888	1,949	5,332
Receivables	60	0	88	944	1,900	3,711	5,021
Inventory	0	0	124	1,321	2,659	5,196	7,029
Plant & Equip	10	30	50	200	400	750	1,085
Less Accum Depr	1	5	13	38	98	212	392
Net P&E	9	25	37	162	302	538	693
Patents, Other	10	40	75	120	130	140	150
TOTAL ASSETS	80	708	763	2,997	5,879	11,534	18,225
Accts Payable	20	30	85	883	1,778	3,474	4,700
Accrued Taxes	(20)	(373)	(973)	(1200)	(420)	0	0
Capital Stock	110	1,610	3,110	5,000	5,000	5,000	5,000
Retained Earnings	(30)	(559)	(1459)	(1686)	(479)	3,060	8,525
TOT LIAB & EQ	80	708	763	2,997	5,879	11,534	18,225

PRO FORMA STATEMENT OF CASH FLOW
($ Thousands)

	1997	1998	1999	2000	2001	2002	2003
Cash Flow from Operations:							
Net Income (loss)	(30)	(529)	(900)	(227)	1,207	3,539	5,465
Plus Depreciation	1	4	8	25	60	114	180
Changes in:							
Receivables	(60)	60	(88)	(856)	(956)	(1811)	(1310)
Inventory	0	0	(124)	(1197)	(1,338)	(2537)	(1833)
Plant & Equip	(10)	(20)	(20)	(150)	(200)	(350)	(335)
Patents, Other	(10)	(30)	(35)	(45)	(10)	(10)	(10)
Payables	20	10	55	798	895	1,696	1,226
Accrued Taxes	(20)	(353)	(600)	(227)	780	420	0
Net Cash used in Operations	(109)	(856)	(1704)	(1,879)	438	1,061	3,383
Cash Flow from Investing Activity	110	1,500	1,500	1,890			
Net Change in Cash	1	644	(204)	11	438	1,061	3,383
Cash - Beg of Year	0	1	645	441	452	891	1,952
Cash - End of Year	1	645	441	452	891	1,952	5,335