DOE/MC/30175-96/C0588

Portable Sensor for Hazardous Waste

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<u>**Contract Number:**</u>

DE-AC21-93MC30175

<u>**Conference Title:**</u>

Environmental Technology Development Through Industry Partnership

<u>**Conference Location:**</u>

Morgantown, West Virginia

<u>**Conference Dates:**</u>

October 3-5, 1995

<u>**Conference Sponsor:**</u>

U.S. Department of Energy, Office of Environmental Management,
Morgantown Energy Technology Center

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Introduction

We are beginning the second phase of a three and a half 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. Our monitor will be a compact, portable instrument that will allow real-time, *in situ,* monitoring of hazardous wastes. This instrument will be able to provide the means for rapid field screening of hazardous waste sites to map the areas of greatest contamination. Remediation efforts can then focus on these areas. Further, our instrument can show whether cleanup technologies are successful at reducing hazardous materials concentrations below regulated levels, and will provide feedback to allow changes in remediation operations, if necessary, to enhance their efficacy.

Our approach is 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, so spectral resolution

requirements are greatly simplified over those of other spectroscopic techniques. The dielectric-barrier discharge is compact, 1 to 2 cm in diameter and 1 to 10 cm long. Furthermore, the discharge power requirements are quite modest, so that the unit can be powered by batteries. Thus an instrument based on ANET can readily be made portable.

During the first phase of the program we demonstrated that a variety of hazardous species could be detected by the technique of active nitrogen energy transfer (ANET) excitation of atomic and molecular fluorescence. 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 are 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 is to extend the ANET technology to encompass a greater number of hazardous species, primarily additional heavy metals and radionuclides.

We begin this current phase by surveying several DoE sites to better coordinate the capabilities of our monitor with their specific needs. Following this we will establish procedures for sample handling and analysis, and

develop systems and software needed to automate these processes. System components and processes being examined include sample collection and introduction, active nitrogen source stability, fluorescence detection and analysis, and measurement, calibration, and test procedures.

The second element of the program is 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.

At the end of this current phase we will 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.

The third, and final, phase of the program will involve 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. At the conclusion of the program we will transfer the developed ANET technology to Spectrum Diagnostix (SDx), a subsidiary of Physical Sciences Inc. (PSI). They have commercialized several instruments initially developed at PSI on SBIR programs.

Approach

The technique we chose for detecting hazardous species with high sensitivity was excitation of atomic and molecular fluorescence by active nitrogen energy transfer (ANET). The active nitrogen is made in a dielectric-barrier (D-B) discharge in nitrogen at atmospheric pressure. Figure 1 illustrates our instrument concept schematically. Samples are fed into the D-B discharge region where the active nitrogen is generated, and where it transfers its energy to species in the sample, thereby exciting fluorescence from them. The pertinent fluorescence is then isolated by a small spectrograph or interference filter and is detected by a photomultiplier or diode array placed behind the filter or spectrograph. Signals from the detector are then processed by a computer and a report is generated. The computer control allows both real-time reporting and data storage for subsequent processing or archiving.
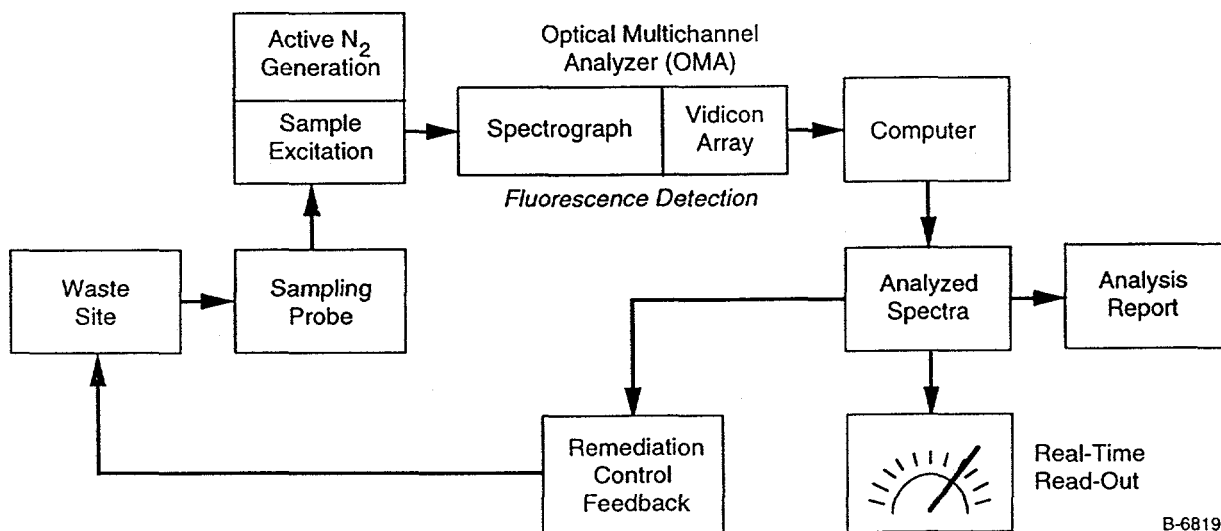
Figure 1. Block Diagram of ANET Analysis System.

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ANET excitation generates only a few emission lines or bands for each hazardous species (see Figure 2). Thus, spectral resolution requirements are greatly simplified over those of other spectroscopic techniques. The dielectric-barrier discharge is compact, 1 to 2 cm in diameter and 1 to 10 cm long. Furthermore, the discharge power requirements are quite modest, so that the unit can be powered by batteries. Thus an instrument based on ANET can readily be made portable.
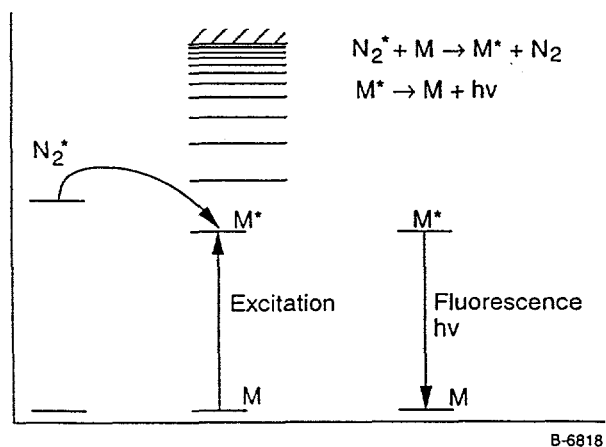

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Figure 2. Schematic Descriptin of ANET Excitation Mechanism,

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 2 to 10 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 dielectric-barrier 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 dielectric-barrier 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 Discharge Technology

A dielectric-barrier 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 (insulator) such as glass[8-11] (see Figure 3). 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 dielectric-barrier discharge (also referred to as an ozonizer discharge) is not a
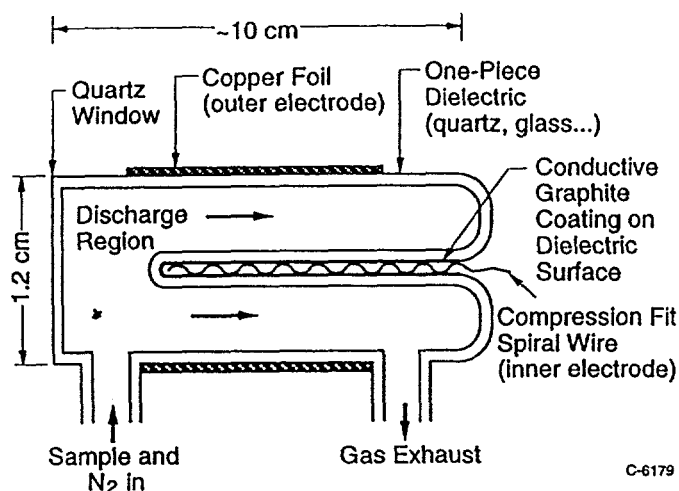
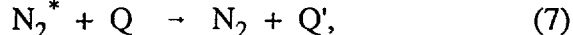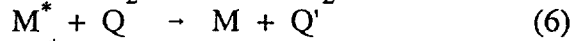Figure 3. Schematic Diagram of Dielectric-
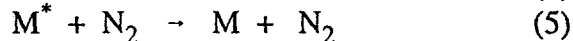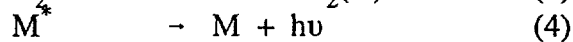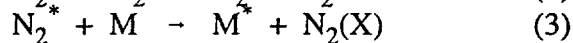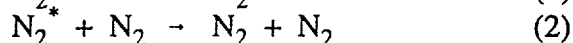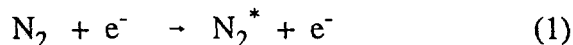Barrier Discharge Lamp

single discharge in the sense of a continuous arc
or glow discharge, but rather a collection of in-
numerable microdischarges 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 micro-
discharge 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.

The Chemistry and Physics of ANET

Dielectric-barrier 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
one atmosphere, 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, 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
dielectric-barrier discharge are summarized by the
following reactions:

$$N_2 + e^- \rightarrow N_2^* + e^- \tag{1}$$
$$N_2^* + N_2 \rightarrow N_2 + N_2 \tag{2}$$
$$N_2^* + M \rightarrow M^* + N_2(X) \tag{3}$$
$$M^* \rightarrow M + h\upsilon \tag{4}$$
$$M^* + N_2 \rightarrow M + N_2 \tag{5}$$
$$M^* + Q \rightarrow M + Q' \tag{6}$$
$$N_2^* + Q \rightarrow N_2 + Q', \tag{7}$$

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 dielectric-barrier 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

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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:

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

The radiative lifetime[16] of $N_2(A)$ is about 2.5s. 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 quenching was a problem in our system, we were able to demonstrate that it did not seriously compromise the overall sensitivity of the ANET technique for detecting important hazardous species. Even accounting for quenching effects, our detection sensitivities were at ppb levels or below.

Project Description

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 active nitrogen energy transfer (ANET) excitation of atomic and molecular fluorescence;

- to demonstrate 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, dielectric-barrier 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.

Experimental. Our Phase A program was essentially a laboratory study to prove our concept for monitoring hazardous waste. We demonstrated that a variety of hazardous species that could be detected by ANET and determine the sensitivities at which ANET could detect the various species.

Our apparatus is shown schematically in Figure 4. It consists of a dielectric-barrier discharge lamp, power source, optical multichannel analyzer, and gas handling lines.
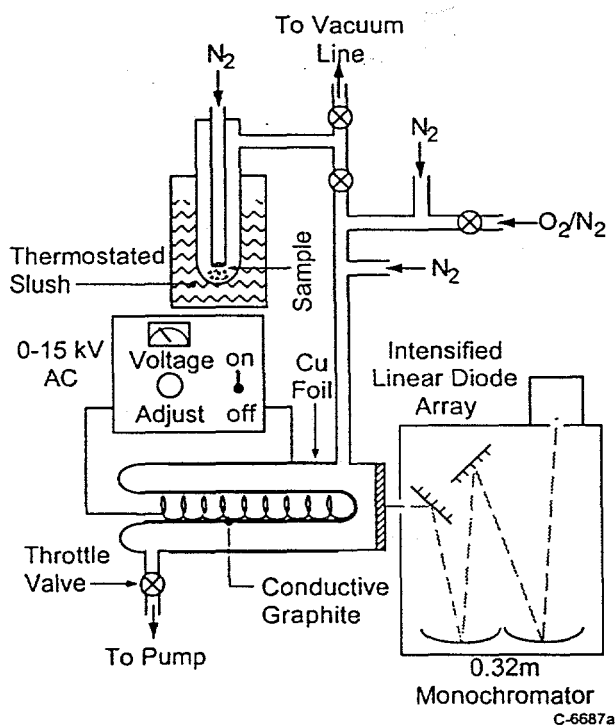

Figure 4. Schematic of Laboratory Apparatus

Most of our lamps were fabricated from a single piece of quartz having a 12 mm o.d. body with an axial protrusion inside the 12 mm tube, thus giving the lamp an annular discharge region. We used several lamps with various protrusion diameters ranging from 3 to 8 mm o.d. The end

opposite the protrusion is sealed with a quartz window. The outer electrode is formed by wrapping copper-foil tape around the outside of the lamp body. We painted the inside of the axial protrusion with a layer of conductive graphite or nickel to form the inner electrode. A wire, wrapped loosely with copper turnings to contact the conductive inner surface, was inserted into the protrusion and connected to the power supply. This configuration provides a clean discharge region since all surfaces are quartz.

For most experiments, we powered the discharge with 15 kV neon sign transformer having a center-tap-grounded secondary winding. The voltage to the primary was controlled by a variac operating off standard 60 Hz ac power. For a few measurements we connected the electrodes to the secondary of an automotive ignition coil which was powered with 12 to 15 V square-wave pulses at frequencies between 45 Hz and 3 kHz. This power source has great potential because it lends itself to battery operation.[21]

Samples were placed in a cold finger immersed in a bath that was thermostated for vapor pressure control. A small flow of nitrogen through the cold finger transported the samples into the discharge region. The concentration of the analyte in the discharge region was equal to the product of the compound's vapor pressure in the cold finger and the dilution factor between the N_2 flow through the cold finger and that through the D-B lamp as a whole. The temperature of the thermostated bath generally was quite cold, e.g., slush baths of chloroform (-63°C) or ethanol (-110°C). At these temperatures the vapor pressures of most species studied were on the order of 10^{-5} Torr or below. The bath temperatures were measured with a thermocouple or thermometer.

We used a Princeton Instruments ST210 Optical Multichannel Analyzer (OMA) system to

detect the fluorescence. This system consisted of a 0.32 m monochromator, generally with a 2400 groove mm^{-1} grating and an intensified linear diode array. The lamp was sufficiently bright, that relatively high resolution spectra ($\Delta\lambda$~0.1 nm) could usually be accumulated with good signal to noise in only 10 seconds. Data were stored in a computer for later analysis.

Results from the Phase A Program. The primary activity in Phase A was to characterize the D-B discharge spectroscopically both in the absence of added species, to provide an understanding of the basic operation of the discharge itself, and in the presence of added species. When species were added, we characterized the fluorescence spectrum resulting from their addition, and in some instances, determined how fluorescence intensities characteristic of the additives varied as a function of concentration of the added species.

Our Phase A laboratory study of hazardous species' detection in a D-B discharge in N_2 at atmospheric pressure showed the overall sensitivity for Hg and Se detection to be at sub part-per-billion levels, and that for organic species to be on the order of a few parts per billion. Furthermore, ANET could differentiate between chlorinated and non-chlorinated organic species, could detect several different heavy metals simultaneously, could differentiate elemental mercury from mercury tied up as chloride, and could detect species adhering to particulates. Finally, we observed molecular emission upon adding uranyl compounds to the D-B discharge. We think it most likely that the emission arises from the UO_2 molecule, although emission from UO is also a possibility.

Figure 5 shows the spectral region in the vicinity of the Hg 253.7 nm emission line. The mercury line is prominent in the spectrum, and is surrounded, but well separated from, several bands of the NO(A $^2\Sigma^+$ -- X $^2\Pi$) system. These bands are also excited by energy transfer from metastable nitrogen[22]. The NO is formed in the discharge in reactions involving traces of oxygen in the nitrogen.

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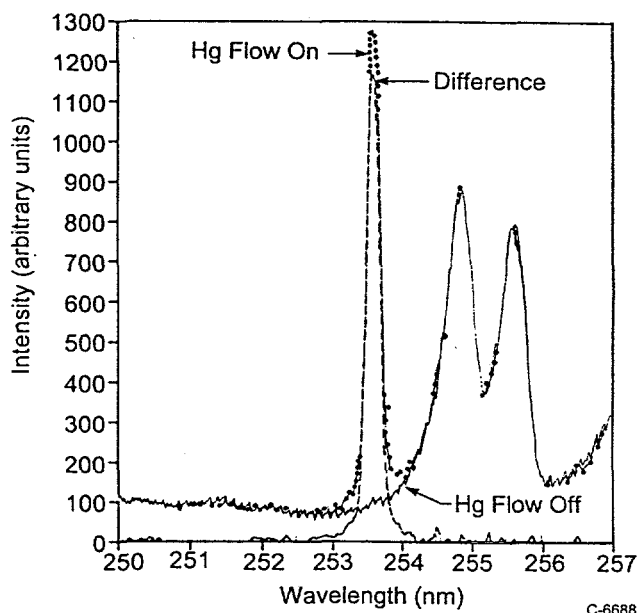
Figure 5. Spectrum of Dielectric-Barrier Disharge in the Absence and Presence of Added Hg

Figure 6 illustrates the linear proportionality between the mercury intensity in the D-B discharge lamp and the mole fraction of Hg added to the lamp. These data, when combined with results of quenching measurements allowed us to estimate a detection sensitivity of 0.07 ppb for Hg in air.
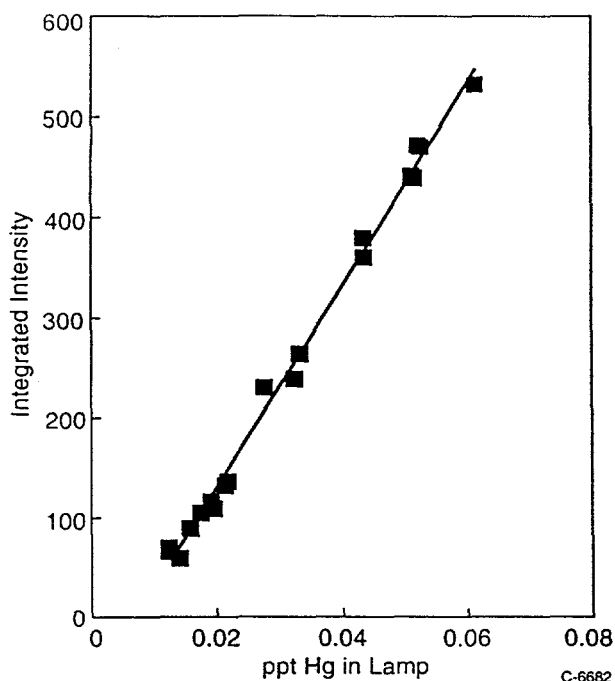
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Figure 6. Intensity of Hg 253.7 nm Emission Excited by ANET as a Function of the Mole Fractin of Hg in a D-B Discharge

Measurements with Cr and Se compounds also showed a linear relationship between the intensity of the ANET excited fluorescence and the concentration of the additive in the discharge region. Our results indicate a sensitivity for Se detection in air below 1 ppb. The sensitivity for Cr detection appeared to be somewhat higher, but we think our concentration estimates were erroneous. We will investigate this problem in more detail in the Phase B 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. Figure 7 illustrates this at 388 nm for the case of chloroform addition. Figure 7 shows the spectra generated in the D-B lamp in the absence of any added chloroform, with about 0.05 ppb added chloroform, and the difference between the two spectra, which is a spectrum of just the CN emission. We have

observed identical spectra from a number of hydrocarbons including hexane, acetone, methanol, isopropanol, 1,2-dichloroethane, trichloroethylene, 1-chlorobutane, and even bromotrifluoromethane.

Figure 7. Spectrum of a dielectric-barrier discharge lamp in nitrogen at atmospheric pressure in the absence of any added chloroform, with 0.05 parts per billion of added chloro-form, and the difference between the two spectra.

The presence of chlorinated hydrocarbons is signaled by the appearance of CCl emission at 278 nm in addition to the just discussed CN emission. Figure 8 illustrates this in the case of chloroform. Figure 8 shows the spectra generated in the D-B lamp in the absence of any added chloroform, with 0.01 ppb added chloroform, and the difference between the two spectra, which is a spectrum of just the CCl emission. To date, all
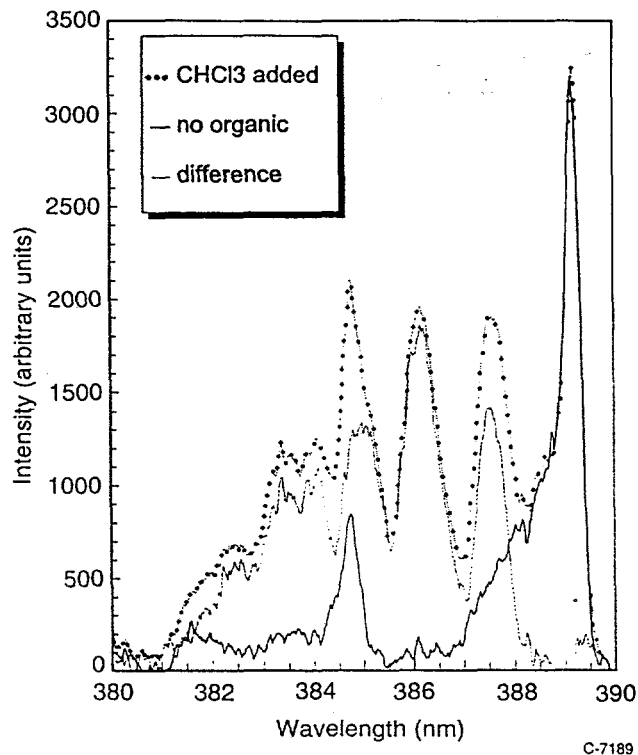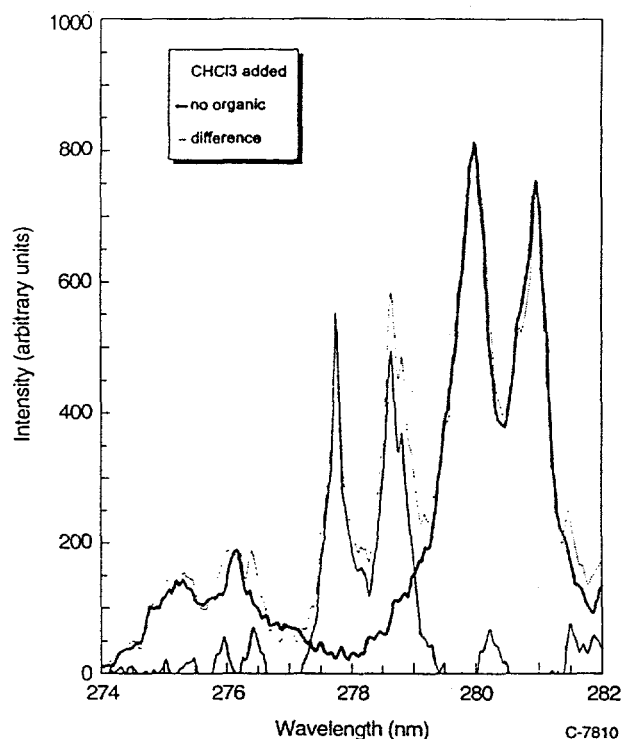
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Figure 8. Spectrum of a dielectric-barrier discharge lamp in nitrogen at atmospheric pressure in the absence of any added chloroform, with 0.01 parts per billion of added chloroform, and the difference between the two spectra.

chlorinated hydrocarbons studied have shown this fingerprint.

The relationship between the mole fraction of added hydrocarbon and CN or CCl band intensity was also linear. Our observations on hydrocarbon excitation, when corrected for quenching by air, indicated sensitivities at both wavelengths of about 5 parts per billion.

Figure 9 shows the spectrum resulting from the addition of uranyl acetate to the discharge region along with a background spectrum and the difference between the two. Several of the features in the background spectrum are easily identified as being part of the nitrogen second-positive system. The three rather broad bands

appearing at 486, 510, and 534 nm in the spectrum with added uranyl acetate, however, are not readily identifiable. A repeat measurement over the same region using uranyl nitrate in the lamp resulted in a very similar spectrum. We think, therefore, the spectrum in Figure 9 is from uranium oxide, probably UO_2, but possibly UO. Surveying a fairly wide range of wavelengths failed to show atomic line emissions from U. Since most uranium waste is likely to be oxidized, this probably isn't a serious drawback. Unique spectral features identify uranium as being present.
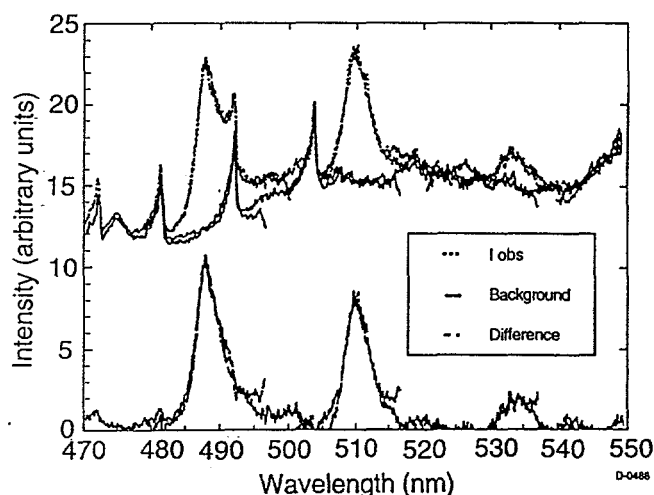
Figure 9. Spectrum of a dielectric-barrier discharge in nitrogen at atmospheric pressure in the absence of any added uranyl acetate, with a small quantity of added uranyl acetate, and the difference between the two spectra. Each spectrum shown is a composite of four separate spectra. We tentatively ascribe the difference bands to the UO_2 molecule.

Objectives of Phase B Program

The work in the first phase of this program successfully demonstrated that ANET technology holds great promise for development into a sensitive, multi-element hazardous species

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monitor. Our plans for the second phase of the program are to develop a breadboard prototype system and characterize the ANET process under more realistic conditions. During the third phase we will build a working prototype of a commercial instrument and test it in the field.

The Phase B program has three primary components:

- process development
- design engineering
- technology extension.

The purpose of the process development task is 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, active nitrogen source stability, fluorescence detection and analysis, and measurement, calibration, and test procedures.

The most crucial issues are sampling, calibration, and testing. The other issues, fluorescence detection and analysis, active nitrogen source stability, and measurement procedures, were explored in some detail in Phase A. Implementing these components into the breadboard system should be straightforward.

The sampling and testing issues, however, will ultimately determine the success or failure of the ANET technology. Designing a system that abstracts samples truly representative of the hazardous environment is crucial. Only if this is accomplished can the true hazardous species concentrations be determined accurately. There-fore, sample entrainment, speciation, calibration and matrix effects are of primary import.

The design engineering task has two elements. The first of these is 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. Each component needed will be enumerated, and commercial suppliers will be identified. We will investigate the efficacy of in-house construction of some components versus their purchase from commercial OEM suppliers. Final component suppliers will be determined by balancing various factors, including adaptability, quality, size, weight, and cost.

The second element of the design engineering task is to design of a prototype haz-ardous waste monitor. This design will balance a number of considerations including power management and portability. The location of each component will be studied in relation to the others to identify configurations that promote simple operation and servicing while retaining compact-ness in the whole instrument. At the end of the program's second phase we will have a detailed set of drawings and specifications for the construction of a first-generation, or alpha-, prototype instrument.

The third component of the program is to demonstrate the applicability of the ANET technology to detecting a number of hazardous species not investigated in Phase A. The activities on this task will involve not only identifying unique finger prints for each of the species to be investigated, but also to determine quantitative limits for their detection. The species we shall investigate in this task include the heavy metals, Sb Be, Cd, Cr, Pb, and Hg, and the radionuclides, Tc, Th, and U.

Results

This section outlines our progress to date on the process development, engineering development, and technology extension tasks.

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 and diluting it with nitrogen;

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; and

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.

In our developmental work, we are considering each of these issues in some detail before beginning to purchase and assemble components.

Before describing our strategy for each of the design issues, however, we'll first describe schematically the basic principles of the instrument operation. Figure 10 shows a block schematic of the instrument where the component subsystems are identified. The sample is removed from the surface being tested and diluted by a two-state ejector pump system. The diluted sample then flows into 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, an on-line oxygen monitor may be incorporated, if necessary, so that O_2 levels in the discharge cell can be accurately known. This allows the fluorescence data to be corrected for O_2 quenching. We are developing a more direct monitor of quenching so we may be able to dispense with the O_2 monitor in the final version of the instrument.

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 0.1 to 10 ppbw

- automatic, *in situ* calibration of all contaminant species

- at least six months between repair and maintenance operations

Contaminated Surface

5-10 Slpm N$_2$

5-10 Slpm N$_2$

Flow Controller #1

Flow Controller #2

Pump/ Diluter #1

Pump/ Diluter #2

Sample Probe

Sampling System

Calibration System

O$_2$ Monitor

Hg | N$_2$ | HgCl

Calibration Module

Flow Controller #3

0-1 Slpm N$_2$

Discharge System

Pulsed HV Supply

Exhaust into Stack

Optical Detection System

Spectrograph

PMT

Data Processing and Analysis System

Data Acquisition and Control
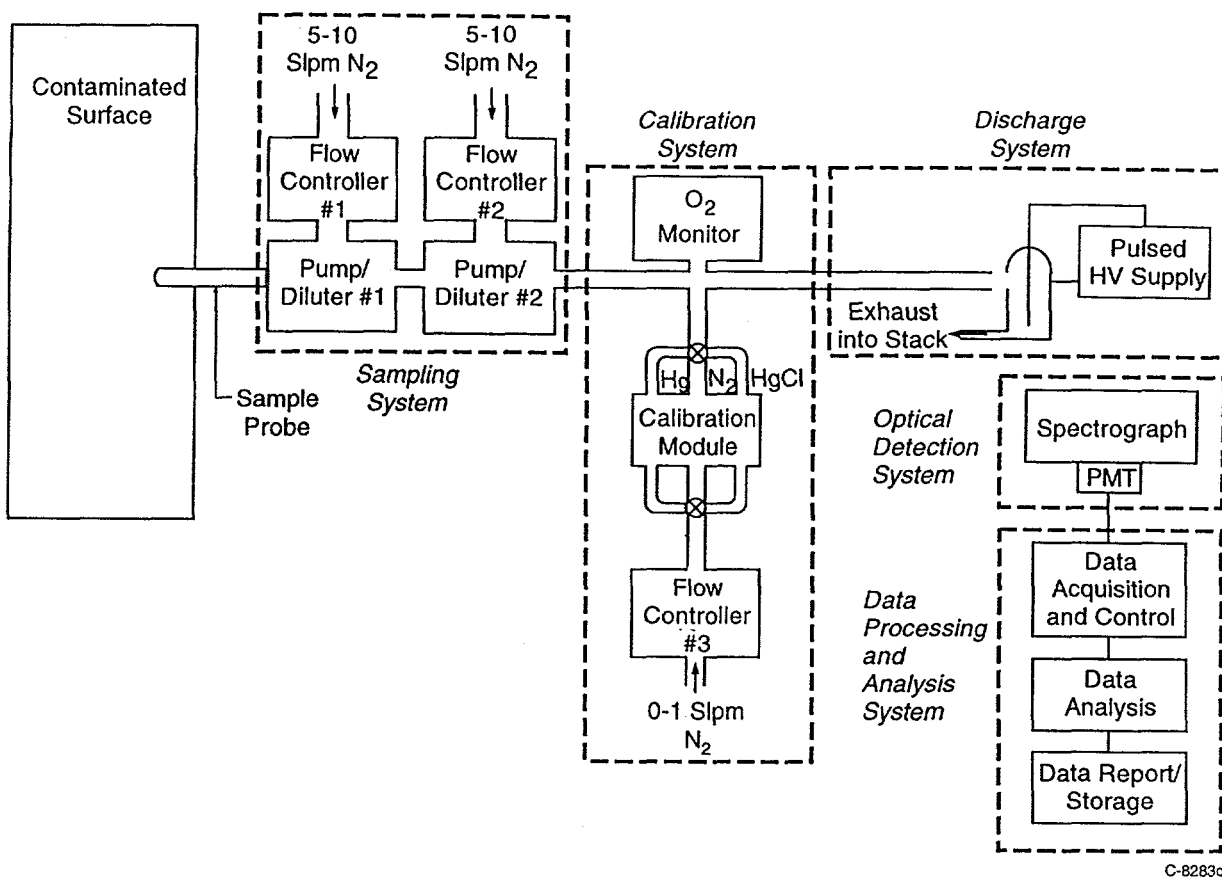
Data Analysis

Data Report/ Storage

C-8283g

Figure 10. Block Schematic of ANET-Baset Hazardous Waste Monitor

- analysis and display of results in less than one minute

- size, <50x50x100 cm (ca. 10 ft^3)

- weight <75 kg

- power <1.5 kW.

Sampling system. The primary constraint on the sampling system design is that our technique requires a high level of sample dilution, on the order of 1 part in 10^4. In addition, system components must be compatible with species being detected and mechanical simplicity is desirable. These three considerations can be readily satisfied with a gas ejector pumping system.

An additional possible constraint might be the necessity of sampling particulates.

Gas-driven ejector pumps can provide the necessary vacuum to draw the sample into the probe. The rate at which gas is drawn into the probe is limited by a small orifice in the probe upstream from the ejector pump. For a pressure drop across the orifice of roughly a factor of two or greater, the rate of flow through the orifice is independent of the ejector-pump flow rate, but is determined only by the pressure and temperature on the high-pressure side of the orifice (critical flow). The required levels of dilution obtain from a balance between the efficiency of the ejector-pump system and the diameter of the critical orifice. In practice, a two-stage ejector-pump system is allows for

larger orifices (~100 μm) which reduces the chance of orifice clogging.

Materials compatibility for most species can generally be satisfied with glass, teflon, and sapphire components. We anticipate most components will either be made from or coated with teflon PFA.

Detection system. The detection system will monitor contaminant fluorescence, primarily at ultraviolet wavelengths, and N_2 Herman infrared (HIR) fluorescence between 695 and 710 nm. We showed in the Phase I program that the HIR fluorescence can be related directly to the concentration of N_2 meta-stables 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. The spectral resolution necessary to separate the atomic fluorescence from neighboring emissions is about 0.4 nm. Commercial interference filters with ultraviolet pass bands having this level of spectral isolation are still in developmental stages and are too expensive to be considered seriously. Spectral resolution requirements in the neear infrared are less stringent, so using an interference filter at 700 nm is a viable option. A spectrometer is necessary to obtain adequate spectral resolution in the ultraviolet, however, and works well to isolate other important wavelengths.

Compact spectrometers using diode array or CCD detectors are adequate for our purposes, but are not cheap. If possible, we would prefer to use a scanning monochromator with photomultiplier detection. Such a system is about an order of magnitude cheaper than a comparably sensitive diode aray or CCD system. In addition, stepper-motor based grating rotation mechanisms have been made sufficiently rugged to with stand the rigors of space flight, so should be able to survive in a relatively hostile field environment.

A compact instrument 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 spec-trometers limit their usefulness to slit widths greater than 100 to 150 μm, the best first-order resolution one can expect is about 1 nm. This is inadequate for atomic fluorescence detection even accounting for the much simpler spectrum generated by ANET. However, adequate resolution is available by monitoring ultraviolet fluorescence in second or third order.

We are considering a system comprised of a 110 mm focal length monochromator with an 1800 g mm^{-1} grating driven by a stepper motor mechanism controlled by the instrument's computer. A computer-controlled filter wheel situated at the monochromator's entrance slit enables switching between filters appropriate to the spectral region observed. The system would collect data from a few discrete wavelengths in a spectral region; then slew to the next and repeat 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 can be used to detect fluorescence. 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 dis-charge, but can extend up to 100 to 200 μs if excited by metastable transfer. To enhance discharge emission relative to dark current the photomultiplier's output can be integrated for

periods of about 150 μs after the discharge pulse. The data acquisition system would then read the voltage output of the integrator and averages the result with those of several previous pulses.
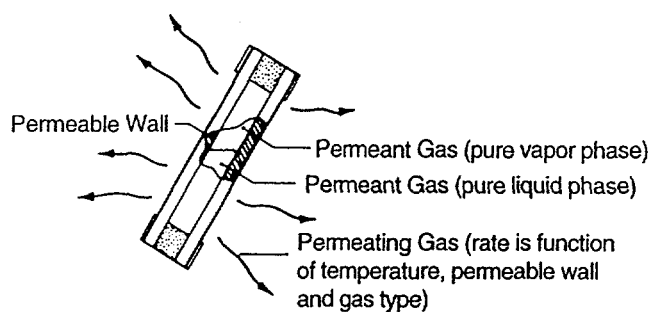
An alternative approach is to use an intensified photodiode array detector. Such a detector effectively monitors a group of wavelengths simultaneously. Thus one can collect all wavelengths in a given pass band at one time. This approach will increase the speed of data acquisition and may allow several contaminants to be detected simultaneously. In addition such a system can more easily correct for any drift in the discharge system. The disadvantage of a photodiode-array based system is that it is about an order of magnitude more expensive than comparably sensitive photomultiplier-based detection systems.

Discharge system. We expect to use a discharge system similar to that used previously.[12] We described the discharge cell above in presenting our Phase A results. It is powered by applying 15 V pulses to a high-energy coil. The discharge frequency can be controlled by one of the data acquisition and control system's timers. Digital pulses from the computer would trip a gate, which in turn, would open 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 would connect to the D-B discharge lamp.

Calibration system. The calibration system is comprised of two elements: accurately metered sources of contaminant species, and a sensor for O_2 in the sample gas. The contaminant sources allow *in situ* calibration of the monitor, while the O_2 sensor provides a means of compensating for quenching effects. Monitoring the HIR bands will probably suffice for

determining the quenching correction. In our first prototype, however, it may be prudent to have an additional support.

The simplest approach for the calibration system would be to use volatile contaminant sources. Accurately controlled vapor release sources can be made from either permeation tubes or capillary diffusion cells. Because their emission rate is temperature dependent, they would be housed in a unit providing independent temperature control for each source cell. An example of a permeation tube is shown in Figure 11. A few drops of a volatile liquid or solid containing a contaminant are placed inside a small cell having a permeable membrane as one of its walls. Cylindrical permeation tubes, for example, can be made from permeable tubing, often teflon or plastic, with the ends sealed by impermeable materials. It is important to have a solid or liquid phase inside the permeation tube so that the vapor pressure inside the source can be maintained at a constant level. This ensures a constant emission rate from the source.

Permeable Wall

Permeant Gas (pure vapor phase)
Permeant Gas (pure liquid phase)

Permeating Gas (rate is function of temperature, permeable wall and gas type)

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Figure 11. Schematic of Permeation-Tube Calibrator

Figure 12 shows a diffusion cell. A few crystals of volatile material sit in a small vial having a long, thin capillary as the only means of egress for the contaminant vapor. The rate at which the contaminant enters the calibration-gas flow is a function of the rate of diffusion along
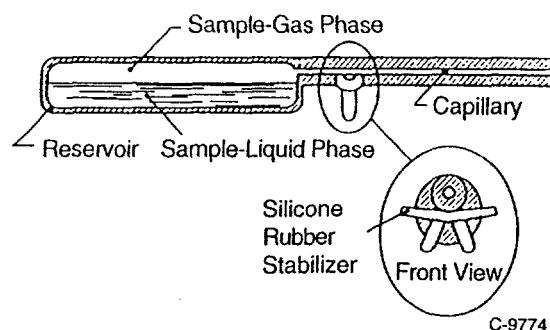
Figure 12. Schematic of Capillary Diffusion
Tube Calibrator

and out of the capillary. This rate depends on
the capillary's length and diameter, as well as
the temperature and physical characteristics of
the gas through which the contaminant is
diffusing.

Permeation tubes and diffusion cells can
be calibrated gravimetrically. That is, the cells
can be weighed periodically on a microbalance,
and over time the weight loss of material from
the cell can be quantified. This approach
generally works well only for sources having
emission rates greater than about 10 ng min^{-1}.
Sources with emission rates slower than this
level take too long to calibrate accurately using
a gravimetric approach and are usually better
calibrated against some form of bench-top
analyzer.

Data acquisition and control system.
The data acquisition and control system
regulates all components of the mercury
monitor, collects data from each component,
runs automatic system calibrations, converts
collected data into mercury or mercuric chloride
concentrations, and displays measurement
results in real time as well as stores them for
later retrieval and archiving. For the current
program prototype, we will use a portable
computer for this purpose. A commercial
instrument would undoubtedly incorporate a

single-board computer with operations program-
med into EEPROM memory.

We plan to use an IBM-compatible port-
able PC with Windows-based software. Several
data acquisition and control boards would be
installed inside the console. Software to
monitor and control the boards will most likely
be developed using the National Instruments
LabWindows package.

Design Engineering Tasks

The purpose of these tasks will be the
design of a prototype hazardous waste monitor.
This design will balance a number of consider-
ations including power management and
portability. The location of each component in
relation to the others will be studied to identify
configurations that promote simple operation
and servicing while retaining compactness in the
whole instrument. We will develop our system
using AUTOCAD, the industry standard
computer-aided design system (CAD) for IBM
PC compatibles. This will also allow us to
produce standard engineering drawings of the
system we shall fabricate in the Phase C
program.

A second part of this task is to identify
and specify each of the components in the
instrument design. In addition, where necessary,
commercial suppliers of each component will be
identified. We will also investigate the efficacy
of in-house construction of some components
versus their purchase from commercial OEM
suppliers. For example, the major parts of the
optical detection system will almost surely be
more cost effectively obtained from an OEM
supplier. The final component suppliers will be
determined by balancing various factors,
including adaptability, quality, size, weight, and
cost.

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Throughout the design phase of the program we will interact extensively with our subsidiary company Spectrum Diagnostix (SDx). They provide instrumentation to the power generation industry for monitoring and controling combustor temperatures and to measure concentrations of ammonia in gas streams. Both of these diagnostics are important in the control of NO_x emissions from combustors.

Technology Extension Tasks

Activities on this task will follow procedures developed during the first phase of the program. The main purpose of this task will be to establish sensitivities for detecting additional hazardous species that were not addressed in the first phase of the program. The list of species includes the heavy metals, Sb, Be, Cd, Cr, Pb, and Hg, and the radionuclides, Tc, U, and Th. Initially, to develop our diagnostic technique, we plan to work with volatile compounds of these species. In later stages of the program we will address explicitly their detection as fine aerosols.

Compounds of the element Tc are very strictly regulated and cannot be handled except in rigorously licensed locations. Because our obtaining such licensing in a timely and cost effective manner is highly improbable, we shall do our work on this species in two stages. The first is to develop a portable experimental system at PSI and test it out on Tc-surrogate compounds such as those containing Mn or Re. Then the facility will be transported off site to a location properly licensed for Tc handling and we will develop Tc detection procedures there.

Conclusions

Our Phase A program indicated that ANET is a very sensitive technique for monitoring heavy metals and chlorinated hydrocarbons. Our approach requires no special sample preparation and can operate continuously. In spite of the fluorescence quenching we have observed, the overall sensitivity is at or below ppb levels, even under less than ideal conditions.

We are now beginning to develop techniques, plans and procedures needed to develop our concept into a real-time monitor of toxic heavy metals and radionuclides at building sites, hazardous waste land fills

Future Activities

The third, and final phase of the program will be to build and field test an alpha-prototype hazardous waste monitor. The fabrication will follow closely the designs developed in the current phase of the program. The alpha-prototype development will be followed by several months of testing and refinement in our laboratories. Finally, the program will conclude with an extensive series of field tests of the instrument.

At the program's conclusion, we will transfer the technology we have developed to Spectrum Diagnostix (SDx), a subsidiary of Physical Sciences Inc. They have commercialized several instruments initially developed at PSI on SBIR programs. Their primary product line currently consists of instrumentation used by the power generation industry but their long-term strategy is to expand into other environmental monitoring and management areas.

Acknowledgements

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