

**DEVELOPMENT OF A REAL-TIME MONITOR OF MERCURY IN COMBUSTOR FLUES  
BASED ON ACTIVE NITROGEN ENERGY TRANSFER (ANET)**

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IN-HOUSE COVER

AUGUST 1996

# DEVELOPMENT OF A REAL-TIME MONITOR OF MERCURY IN COMBUSTOR FLUES

## BASED ON ACTIVE NITROGEN ENERGY TRANSFER (ANET)

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### 1. Introduction

Physical Sciences Inc. (PSI) is developing a compact, portable instrument for real-time monitoring of mercury levels in combustor flues. The instrument will be able to monitor mercury levels in power plant effluents, and can provide feedback to control mercury scrubbing operations. In the event mercury emission levels become regulated by the EPA, the instrument will be able to provide real-time compliance verification. This technique involves exciting mercury ~~fluores~~ at 254 nm by active nitrogen energy transfer (ANET)<sup>3,4</sup>. The active nitrogen is made in a dielectric-barrier (D-B) discharge operating in nitrogen at atmospheric pressure<sup>5,7</sup>. ANET excites only the one mercury emission line, so spectral resolution requirements are modest. In addition, the technique provides a unique identification of oxidized that molecular emission from HgCl is observed when HgCl present in the discharge. The instrument is compact, low power, and mechanically simple. This system detects mercury at sub parts-per-billion levels and has a high tolerance for particulate

**PSI's instrument has five essential components:**

1. **A sampling system to withdraw gas from the stack and dilute it with nitrogen;**
2. **A discharge system to create the active nitrogen which excites Hg and HgCl fluorescence;**
3. **A detection system to measure Hg and HgCl fluorescence intensities;**
4. **An *in-situ* calibration system for both Hg and HgCl to ensure the accuracy of the flue-gas measurements; and**
5. **A data processing system to manage instrument components and report results.**

During the developmental work, each of these issues was considered in some detail before beginning instrument design and fabrication. Much of the design detail has been presented previously.<sup>1,2</sup> We will focus here on preliminary bench-scale test results.

### 2. Instrument Description

Before describing preliminary test results, we shall describe the basic principles of instrument operation. Figure 1 shows a component schematic of the instrument where the component subsystems are identified. The sample gas is withdrawn from the stack through a heated sample probe. It then passes through heated chambers containing a particulate filter and a two-stage gas ejector pumping system. The ejector pumping system provides both the force needed to withdraw the sample from the stack, and in addition, it dilutes the sample to minimize quenching effects in the discharge. The diluted sample then flows into the main instrument box where it is processed.

The main instrument box contains the discharge, detection, and calibration systems. In the discharge chamber,  $N_2$  metastables, and subsequently, Hg fluorescence, are excited. Light from the discharge is dispersed by a small monochromator and detected with a photomultiplier. The photomultiplier signals are read and processed by a computer system, and results are displayed and stored. The computer system can also provide feedback signals to the power plant control room for active control of flue-gas cleanup processes. A calibration system is included so that known quantities of mercury or mercuric chloride can be injected into the diluted sample flow prior to its entry into the discharge cell. In addition, an on-line oxygen monitor is included with the alpha prototype so that oxygen levels in the discharge cell can be accurately known. This allows the fluorescence data to be corrected for quenching. A more direct monitor of quenching is being developed that should allow eliminating the oxygen monitor from subsequent versions of the instrument.

Our initial system performance and design goals are as follows:

- Ability to detect both Hg and HgCl<sub>2</sub> gas phase and, ultimately, on particulate;
- Sensitivity range for both species 0.1 to  $10 \mu\text{g m}^{-3}$  (0.1-10 ppbw);
- Automatic, *in situ* calibration of Hg and HgCl<sub>2</sub>
- Unattended operation for at least six months between repair and maintenance operations;
- Analysis and display of results in less than 1 minute;
- Size, <5 ft<sup>3</sup>, excluding sample probe and gas supply;
- Weight <25 kg; and
- Power <500 watts.

## 2.1 Sampling System

The primary constraint on the sampling system design is that this 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 mercury, 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. In our alpha-unit design we focussed only on gaseous sampling. We will defer the issue of particulate sampling until a later phase of the program.

Gas-driven ejector pumps provide the necessary vacuum to draw the sample from the stack 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 allows for larger orifices ( $100 \mu\text{m}$ ) which reduces the chance of orifice clogging.

Flue gas contains substantial quantities of water so the sampling system temperature must remain above the dew point of the stack gas. After dilution, the dew point of the sample is low enough to allow subsequent gas handling lines to be at ambient temperatures. The probe, particle filter and first pumping stage, however, must be maintained at temperatures around 150 to 200. The system is designed so that the probe, particle filter, and ejector pumping system can all be heated independently.

To maintain materials compatibility with mercury, the probe has a quartz sleeve, sapphire critical orifices, Teflon PFA tubing and fittings for the plumbing, Teflon-coated thermoprobe probes, and the ejector pumps have been coated with Teflon-PFA.

Two series of tests were performed on the pumping system. The first was to determine the flow rate of gas pulled into the pump through the critical orifice as a function of ejector-gas flow rate. These tests determined the dilution ratios one can achieve with this system. The second series of tests was to monitor the dilution ratio separately by pumping pure oxygen into the system and measuring the oxygen mixing ratio at the pumps outlet. The system mixing ratios derived from these two independent methods agreed excellently.

Figure 2 shows the correlation between the directly measured oxygen concentration after the first dilution stage and that calculated based upon the flow rate of air aspirated into the first-stage ejector pump. Clearly the correlation is excellent. Under typical operating conditions, the oxygen mole fraction in the first-stage plenum is between 2000 and 3000 ppm. The second dilution stage will result in a little over two orders of magnitude of additional dilution. This will give a final oxygen mole fraction in the discharge region of about 20 to 30 ppm, well below the level leading to significant quenching of the metastables as determined from our metastable quenching measurements.

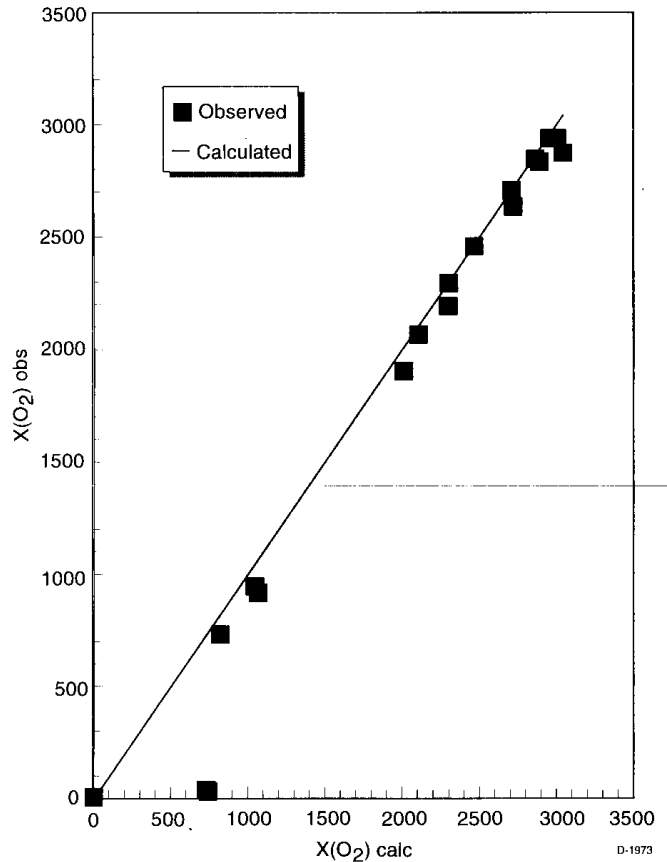
## 2.2 Detection System

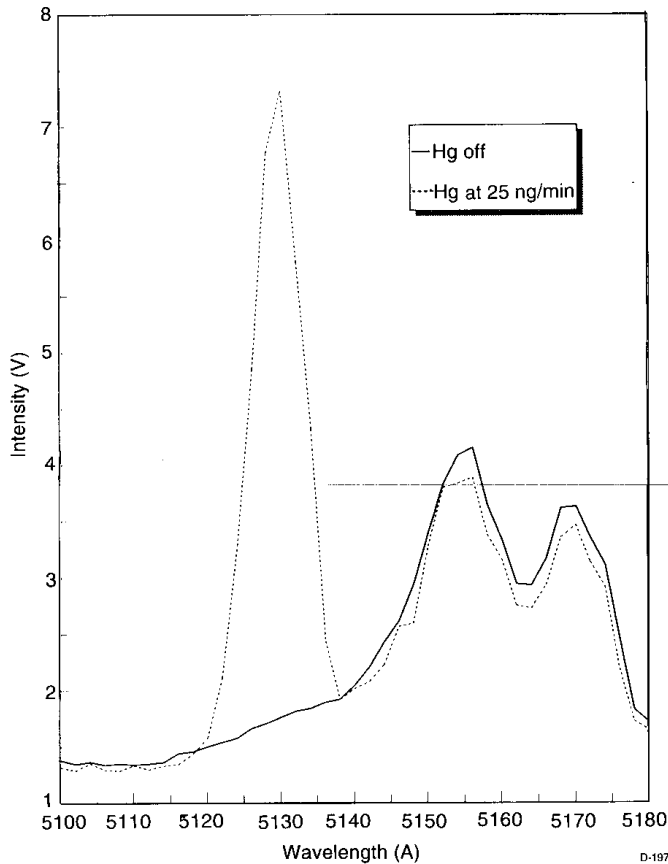
The detection system monitors mercury fluorescence at 254 nm, HgCl fluorescence between 500 and 560 nm, and Herman infrared (HIR) fluorescence between 695 and 710 nm. In the Phase I program, it was demonstrated that the HIR fluorescence can be related directly to the concentration of metastables produced in the discharge. Monitoring the HIR emission, therefore, provides a means of compensating for variations in metastable concentrations that might occur with variations in oxygen levels in the sample.

The spectral resolution necessary to separate the atomic mercury fluorescence from neighboring nitric oxide emissions is about 0.4 nm. Commercial interference filters with this level of spectral isolation are still in developmental stages and are too expensive to be considered seriously. Spectral resolution requirements at the other two wavelengths are less stringent, so using interference filters at 540 and 700 nm could be a viable option. A spectrometer is necessary to obtain adequate spectral resolution at 254 nm, however, and works well to isolate the other two wavelengths.

Our system is comprised of a 110 mm focal length monochromator with a  $1800 \text{ g mm}^{-1}$  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 collects data from a few discrete wavelengths in each spectral region, then slews to the next and repeats the procedure. We monitor the mercury line in second order, at a grating position equivalent to first-order wavelengths around 508 nm (see Figure 3). The grating can then be slewed to 540 nm to measure mercuric chloride concentrations (see Figure 4) and to 705 nm to monitor the HIR system. A UG-5 glass filter transmits the 254 nm radiation while completely blocking that at 508 nm. At the other two wavelengths, a long-pass colored glass filter effectively blocks second-order UV radiation while transmitting that at wavelengths longer than 475 nm.

A compact photomultiplier assembly detects fluorescence. Emissions from the discharge extend for periods of tens of nanoseconds after the initiation of the discharge pulse if they are excited directly in the discharge, but can extend up to 100 to 200 ns if excited by metastable transfer. To enhance discharge





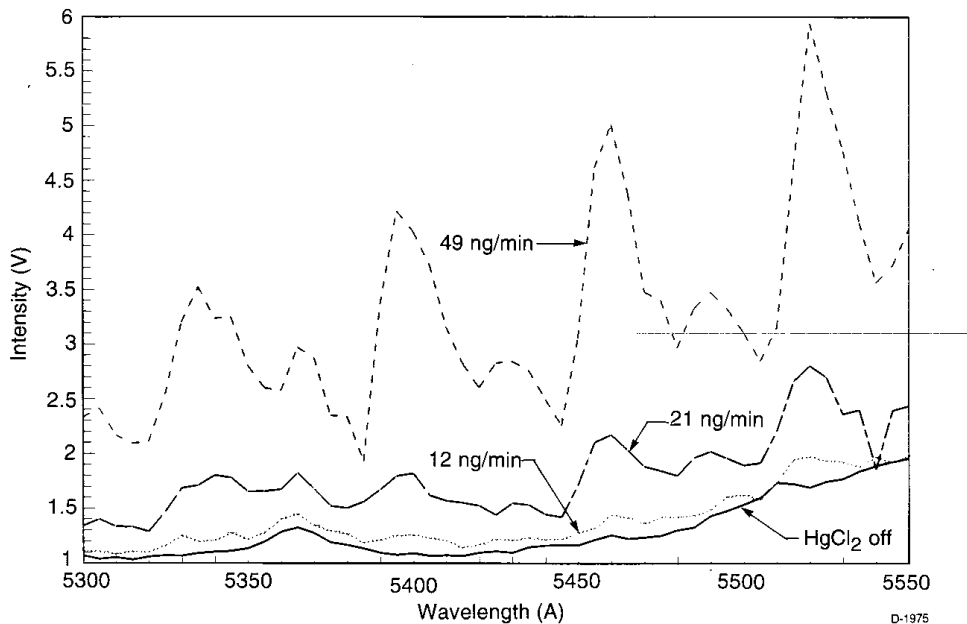
emission relative to dark current, the photomultiplier's output is integrated for a period of 150 $\mu$ s after the discharge pulse. The data acquisition system then reads the voltage output of the integrator and averages the result with those of several previous pulses.

### 2.3 Discharge System

The discharge system is similar to that used previously.<sup>2</sup> It is powered by applying 15 V pulses to a automobile ignition 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.

### 2.4 Calibration System

The calibration system is comprised of two elements: accurately metered sources of Hg and HgCl<sub>2</sub> vapor, and a sensor for O<sub>2</sub> in the sample gas. The Hg and HgCl<sub>2</sub> sources allow *in situ* calibration of the monitor, while the O<sub>2</sub> sensor provides a means of



compensating for quenching effects. Monitoring the HIR bands should suffice for determining the quenching correction. In the alpha prototype, however, it seemed prudent to have an additional support. Our test plans

call for extensive correlation between Hg intensities, HIR levels, and concentrations. It is not anticipated that the commercial instrument will need the added expense and complexity of a sensor.

The calibration system is comprised of sources of Hg and HgCl<sub>2</sub> used in separate sample cells. The temperature of each cell can be controlled independently and precisely by a PID loop governed by the instrument's computer software. The gas flowing through the calibration system is diverted to one of three pathways: through the Hg permeation-tube cell, through the HgCl<sub>2</sub> diffusion-tube cell, or through a blank cell.

This last option provides the ability to make a blank determination to ensure that the addition of pure calibration gas to the sample flow does not affect the readings of our Hg monitor. The calibration gas then joins the main sample gas flow downstream from the second ejector-pump stage, but upstream from the discharge cell. This allows a calibration to be made under conditions identical to those of the stack-gas measurements in terms of concentrations of quenching species such as SO<sub>2</sub> in the sample flow. This approach provides additional confidence in the correctness of the quenching compensations built into the data analysis.

The mercury source is a permeation device, consisting of a drop of mercury sealed inside a permeable tube (available commercially from VICI Metronics). The rate of permeation out of the tube is a function of the material from which the device is made, generally Teflon, and the temperature at which the device is held. Permeation tubes are conventionally calibrated gravimetrically. For very low-permeation-rate tubes (<10 ng min<sup>-1</sup>), the gravimetric process is too time consuming for most practical purposes. Such devices can, however, be calibrated using conventional bench-top Hg detectors that allow integrative sampling.

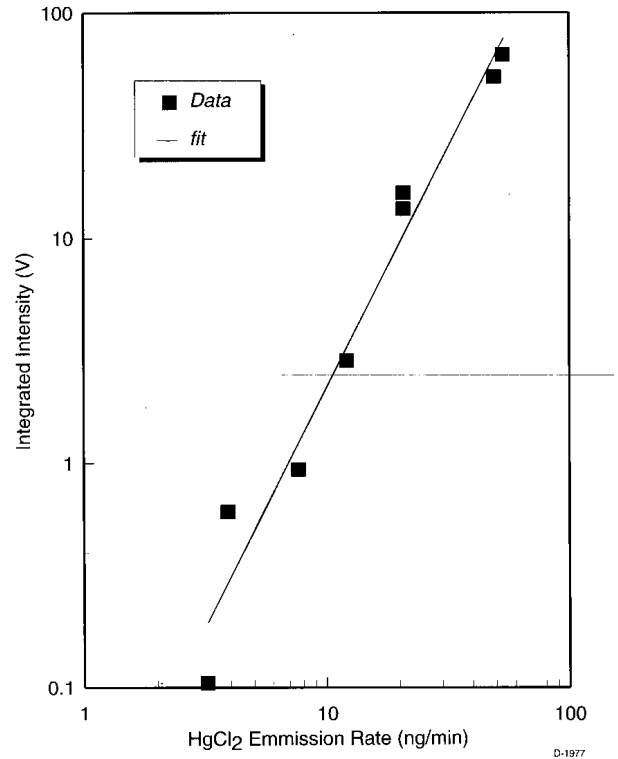
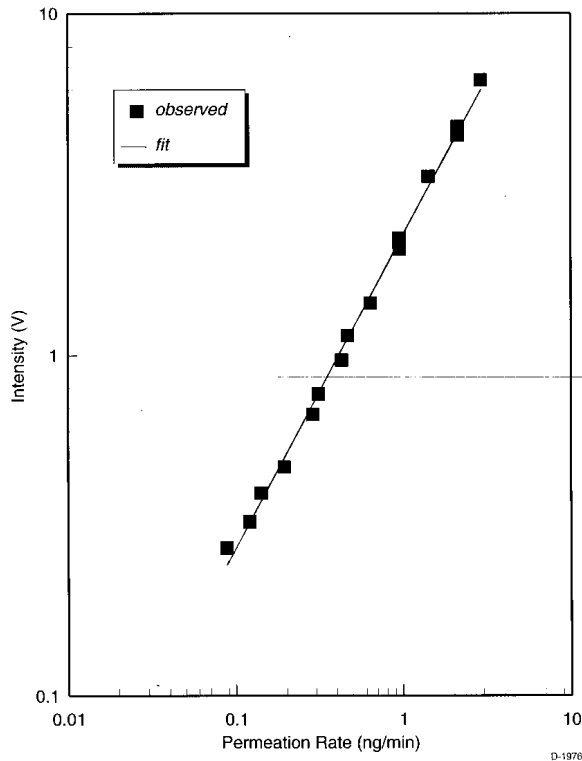
Mercuric chloride is not available commercially in permeation tubes. Instead a capillary diffusion tube is used to meter known amounts of HgCl<sub>2</sub> into the calibration gas flow. This is a small vial with a long, thin capillary providing the only means of egress for the HgCl<sub>2</sub> vapor. The rate at which HgCl<sub>2</sub> enters the calibration-gas flow, then, is related to the rate of diffusion along the capillary. This rate is a function of the capillary's length and diameter, as well as its temperature and the properties of the two diffusing gases. In theory, such a system can also be calibrated gravimetrically, but because of the high level of toxicity, other methods which allow better containment of the HgCl<sub>2</sub> are preferable. The HgCl<sub>2</sub> diffusion vial was calibrated by reducing the gaseous mercuric chloride to mercury in an aqueous solution of stannous chloride followed by mercury analysis with a bench-top Hg analyzer.

Figures 5 and 6 illustrate the operation of the calibration system. They show the correlation between the rates of Hg and HgCl<sub>2</sub> emission from their sources and the intensity of the 254 nm Hg line or the 404 nm HgCl band excited by the ANET process. The Hg and HgCl<sub>2</sub> emission rates were varied by varying the temperature of the cell holding the sources. The system is quite linear over several orders of magnitude.

## 2.5 Data Acquisition and Control System

The data acquisition and control system manages all components of the mercury monitor. It collects data from the instrumentation, sets, monitors and adjusts operating parameters such as flow rates and temperatures, runs automatic calibrations of the system, converts collected data into mercury or mercuric chloride concentrations, and displays the measurement results in real time. In addition, measurements are stored for later retrieval and archiving.

The system includes an IBM-PC compatible computer with a 486 microprocessor, two data acquisition and control boards from National Instruments, and uses the National Instruments LabWindows software. This provides a Windows-like operator interface. The system has 64 single-ended or 32 differential analog-to-digital (A/D) data channels each with 12-bit resolution (0.025%), 12 digital-to-analog (D/A) output channels, 16 digital input/output (DI/O) channels, and three counter-timer channels.



### 3. Summary of Hg Monitor Development

This paper described the basis upon which the ANET monitoring technique rests and how the results of a Phase I program impact the design of a prototype instrument. This instrument is comprised of five major systems: sampling, discharge, detection, calibration, and data acquisition and control. Physically, the prototype consists of three parts: (1) heated sampling system, (2) primary instrument box, and (3) acquisition and control system (see Figure 1).

Initial instrument testing in the laboratory, as described above, is used to verify design choices. Further laboratory testing will involve sampling from a drop-tube furnace, entrained-flow coal combustor. This system burns pulverized coal at rates on the order of 1 to 3 grams per minute. The laboratory sampling will provide a better test bed for component and system verification than bench-top testing of isolated components because the sample will present many of the same difficulties encountered at a power plant, e.g. high humidity and significant particle loading. Following laboratory testing, the unit will be transported to a power plant in the Boston area for direct flue-gas sampling. We hope to complete this testing by the end of 1996.

A completed commercial system is expected to contain all essential instrumentation in a single enclosure connected to the sample probe with the instrument control system located some distance from the sampling site, down inside the power plant control room. The design and preliminary test results, outlined here, should lead to the development of a compact, sensitive instrument for air toxics monitoring in combustor flues that will be available near to the time the Hg-emission regulations are implemented. It should prove a cost effective aid to compliance.

### 4. Acknowledgements

We appreciate financial support from the Department of Energy under Grant No. DE-FG02-93-ER81528.

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