A CONTINUOUS EMISSIONS MONITOR FOR TOTAL, ELEMENTAL, AND TOTAL SPECIATED MERCURY

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ABSTRACT

ADA Technologies, Inc., is developing a continuous emissions monitoring system that measures the concentrations of mercury and volatile mercury compounds in flue gas. These pollutant species are emitted from a number of industrial processes. The largest contributors of these emissions are coal and oil combustion, municipal waste combustion, medical waste combustion, and the thermal treatment of hazardous materials. It is difficult, time consuming, and expensive to measure mercury emissions using current, manual sampling test methods. Part of this difficulty lies in the fact that mercury is emitted from sources in several different forms, such as elemental mercury and mercuric chloride. The ADA analyzer measures these emissions in real time, thus providing a number of advantages over existing test methods: 1) it will provide a real-time measure of emission rates, 2) it will assure facility operators, regulators, and the public that emissions control systems are working at peak efficiency, and 3) it will provide information as to the nature of the emitted mercury (elemental mercury or speciated compounds). This paper presents an overview of the CEM and describes features of key components of the monitoring system--the mercury detector, a mercury species converter, and the analyzer calibration system.

THE NEED FOR A MERCURY CEM

Future strategies for controlling hazardous air pollutants will involve the use of continuous emissions monitoring systems. These systems provide a real-time measure of pollutants being emitted from sources and are needed in terms of assuring compliance with emissions regulations. They can also be used to help facilities operate pollution control equipment at peak efficiencies.

Mercury is a pollutant that has been receiving much attention in terms of monitoring and control strategies. The toxicity of mercury has prompted industry and regulators to develop methods to minimize its release to the environment. Continuous monitoring systems will play a key role in assuring that emissions of this hazardous material are minimized.

Mercury is emitted from industrial sources in a variety of chemical forms depending on the specific process and flue gas conditions. For example, mercury is known to exist as elemental mercury [Hg^0] and as mercuric chloride [$HgCl_2$] in most industrial flue gases that contain mercury.[1] A knowledge of the relative concentrations of the various forms of mercury will be required for air pollution control devices to operate effectively. An example of this principle is given in Table 1 for a coal-fired power plant.[2]

Current standard testing techniques rely on manual "grab samples" where flue gas is drawn through a series of impinger solutions to collect elemental and speciated forms of mercury.[3] The collected samples are analyzed in an analytical chemistry laboratory using complex techniques and instrumentation. These field sampling and analytical techniques are cumbersome, labor intensive, and expensive. A 1-week comprehensive sampling program can cost in the range of $25,000-$50,000.

A continuous mercury monitoring system should address the following needs:

- Since the optimum control device depends on the specific chemical form of the mercury, an analyzer that can distinguish between the chemical forms is needed to assure effective operation of the APCD.
- An analyzer is needed that will assure the APCD is working properly.
- An analyzer is needed that can be used to control the feed rate of a process generating the mercury emission.
- An analyzer is needed that will help assure the public and regulatory agencies that facilities which produce mercury emissions are in compliance with regulatory limits.

DESCRIPTION OF CEM

In response to the need for monitoring mercury emissions in real-time, ADA Technologies has developed a continuous emissions monitoring system that is capable of measuring total mercury, elemental mercury, and (by difference) total speciated mercury. The system features a sensitive mercury detector, a mercury species converter, and a calibration system. Figure 1 shows the components in a typical CEM arrangement.

The "converter" is used to change speciated mercury compounds to elemental mercury. When the sample gas is placed through the converter, a measure of the total mercury content of the flue gas is obtained. When the converter is bypassed, only elemental mercury is measured in the gas sample. The difference between the two measurements is the concentration of total speciated mercury content.

A heated, non-reactive sample transport line is used to convey the gas sample to the analyzer. Calibration gas is introduced to the end of the sample line in order to assure that the entire sampling system and the analyzer are calibrated as a single unit.

DESCRIPTION OF COMPONENTS

Mercury Detector

The analyzer uses a unique ultraviolet absorption technique to quantify the mercury. Proprietary optical components are incorporated that provide a measurement sensitivity below 1 $\mu g/m^3$ (less than approximately 150 ppt v/v). The analyzer has a linear response to a concentration of greater than 100 $\mu g/m^3$. The optical design also eliminates the effects of interfering gases such as sulfur dioxide.

Figure 2 shows the analyzer response when elemental mercury was introduced at a concentration of 2.6 $\mu g/m^3$ (390 ppt v/v). Also shown in the figure is the signal when zero gas was introduced into the analyzer. Based on the peak-to-peak noise level observed, a minimum level of detection (defined as 2x noise level) of 0.39 $\mu g/m^3$ (58 ppt v/v) is calculated. Operation with detection limits as low as 45 ppt have been observed under ideal conditions.

The ADA analyzer incorporates a unique optical design that eliminates the effects of interfering gases such as sulfur dioxide. Figure 3 shows the response of the detection system when measuring mercury at a concentration of 8.1 $\mu g/m^3$ (1.2 ppb v/v) in the presence of sulfur dioxide at a concentration of 1000 ppm. Within the uncertainty of the measurement, the analyzer corrects for the SO_2 absorption perfectly.

Figure 4 shows the response of the analyzer over a concentration range of 0 to 6 ppb (v/v). This range is expected to cover most concentrations expected in coal-fired and municipal solid waste generated flue gases. A dilution probe is used on the analyzer for situations in which high concentrations of mercury are present, such as when monitoring uncontrolled emissions ahead of an APCD.

Converter

A mercury species converter is another key component of the CEM system. The converter is used to distinguish between concentrations of elemental and "total" mercury found in the flue gas. Since the mercury detector measures only elemental mercury, the converter is needed to change speciated forms of mercury present in the flue gas to elemental mercury. Total mercury is, therefore, measured by passing the flue gas sample through the converter. Elemental mercury concentrations are measured by the CEM when the flue gas sample bypasses the converter. Total speciated mercury is then determined as the difference between the measured total mercury concentration and the elemental mercury concentration.

The converter uses a unique design that eliminates the need for expendable chemicals to reduce the speciated forms of mercury. Figures 5 and 6 show the response of the analyzer to two surrogate speciated mercury compounds--mercuric chloride and dimethyl mercury. The test sequence repeatedly injected the mercury species through the converter to allow measurement of the resulting elemental mercury and then bypassed the converter to demonstrate the converter effectiveness. Note the slower response time of the analyzer for the speciated forms relative to elemental mercury. This is due to adsorption of the "sticky" speciated forms of mercury on the walls of the tubing and gas cells. Heat tracing of the gas handling system mitigates this problem to some extent. This becomes important in the final analyzer system as it will limit how quickly one can calibrate the analyzer for speciated forms of mercury and therefore how often this procedure can be done.

Calibrator

ADA Technologies developed a calibrator for use with the mercury CEM. The calibrator is based on the use of permeation tubes to provide known and accurate concentrations of elemental mercury and mercuric chloride. These devices are considered primary standards for calibrating continuous monitors and they are used to calibrate ambient air analyzers. ADA has developed a two-channel calibrator--one channel is used to calibrate the elemental mercury detector and the other is used to calibrate the converter.

REFERENCES

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2. McIlvaine Company (1992). "Mercury Speciation is Important and Doable," Air Pollution Monitoring and Sampling Newsletter, No. 147, January.
3. Toney, M.L. (1993). "Update on EPA's Experience with Method 301: Field Validation of Emission Concentrations," Paper No. 93-RP-145.01, presented at the 86th Annual Meeting of the Air & Waste Management Association, Denver, CO, June 13-18.

TABLES

Table I. Mercury Removal Under Different Process Conditions

Plant	Ash Loading to Spray Dryer	Coal Cl	% Mercury Removed
A	High	Low	14
B	High	Low	23
C	High	Low	6
G	High	Low	16
E	Low	High	55
H	Low	High	44
F	Medium	High	89
D	High	High	96

FIGURES

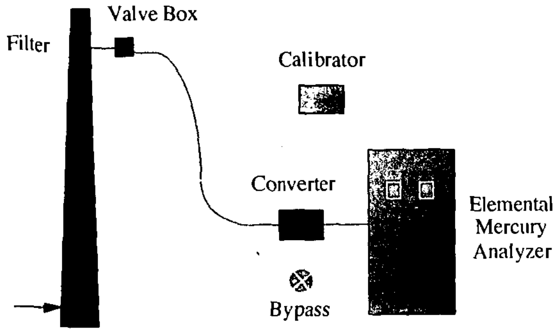

Figure 1. Mercury CEM arrangement.

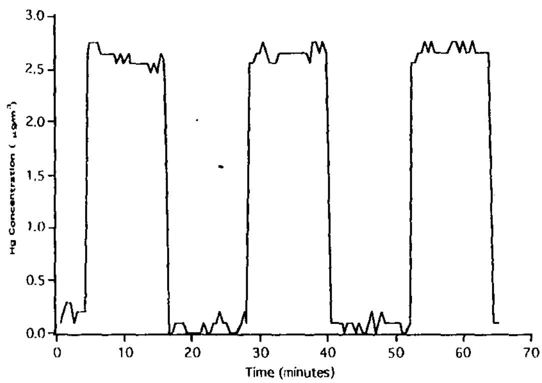

Figure 2. Response of the analyzer to 2.6 $\mu g/m^3$ of mercury.

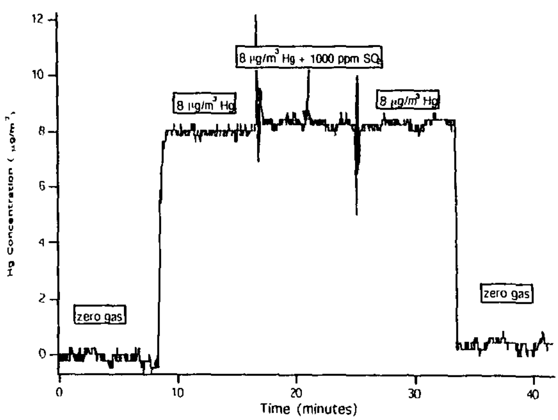

Figure 3. Mercury detector response when measuring mercury in the presence of sulfur dioxide.

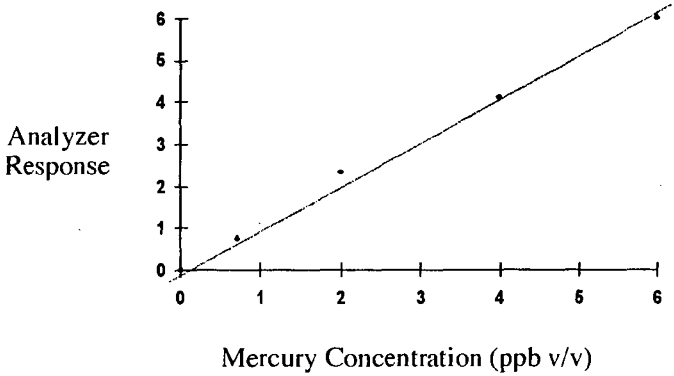

Figure 4. Linearity of the mercury detector.

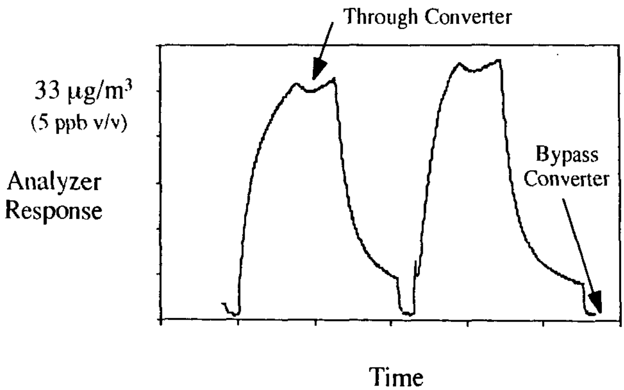

Figure 5. Mercuric chloride being converted to elemental mercury.

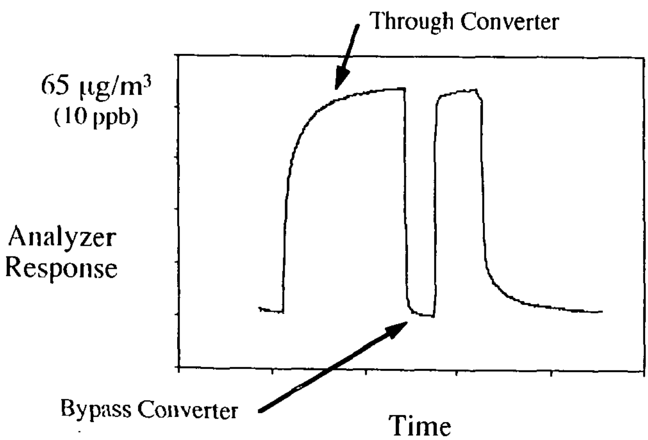

Figure 6. Dimethyl mercury being converted to elemental mercury.