



*Kevin C. Galbreath  
Principal Investigator*

# DEVELOPMENT OF AN OXIDIZED MERCURY SPIKING SYSTEM

**Key Personnel:** Kevin Galbreath (EERC), Blaise Mibeck (EERC), Steven Wilmoth (EERC)

## ***Project Description***

Liquid chemistry conditioning/conversion systems can become sinks (cold spots, absorbing residues) or sources (condensation, desorbing residues) of gaseous mercury and drastically affect continuous mercury monitor (CMM) results (1). Dry reduction catalyst conversion systems can also be compromised by flue gas chemistry. Essential to the operation of any continuous emission monitor (CEM) is a reliable calibration source for characterizing the entire measurement system. In the case of CMMs, it is not enough to simply test the installed system with elemental mercury; a significant portion of mercury in coal-fired utilities is oxidized ( $\text{Hg}^{2+}$ ).

The EERC recently developed an oxidized mercury-spiking system for determining conditioning/conversion system biases. This system allows CMM operators to detect and troubleshoot biases and provides researchers with an indication of CMM performance. This report will summarize the work accomplished so far and how current and future research will benefit from this new tool.

## ***Goal***

The goal of this project is to design a  $\text{Hg}^{2+}$ -spiking system that can be used in field CMM installations. This system will be based on gold catalysis of elemental mercury and chlorine to form a reactive gaseous  $\text{HgCl}_2$ . For this system to be useful, it must be able to generate a stable concentration of oxidized mercury at concentrations around  $20 \mu\text{g}/\text{m}^3$  at flow rates of 12 L/min.

## ***Rationale***

While calibrations can be performed on instruments and elemental mercury ( $\text{Hg}^0$ ) added to the sample stream (or in its place), the ability for a continuous emission monitor to measure reactive gaseous mercury (RGM) is of great concern (2). Site-specific flue gas composition and other conditions can lead to performance differences in CMM installations.

Calibration gas cylinders for various RGM compounds exist but appear to drift in concentration because of low vapor pressure and reactions with stainless steel, making transport to a CMM system

difficult. Permeation sources of solid mercury compounds have similar issues, with the added difficulty of containing several grams of hazardous material. Using either a calibration gas or permeation source requires a modified EPA Method 101A measurement to determine the concentration being emitted. One study has observed a significant portion of the mercury from  $\text{HgCl}_2$  permeation sources is emitted as elemental mercury.

$\text{Hg}^0$  and chlorine sources are readily available and simple to use. It is desirable, because of the inherent difficulty of working with  $\text{HgCl}_2$  sources, to develop a method for generating only the specific quantity needed to test a CEM system. This has prompted investigations ranging from the use of photocatalytic reactors and dry catalysts such as spent activated carbons to generate a stream of  $\text{HgCl}_2$  using such precursors as  $\text{HCl}$  and  $\text{Cl}_2$ .

An oxidized mercury-spiking system based on gold catalysis has been demonstrated, based on reacting  $\text{Hg}^0$  from the permeation source with a precursor gas. The amount of  $\text{Hg}^0$  entering the oxidation reactor can be directly measured with the instrument within the CMM. This allows a known amount of gaseous RGM to be formed on demand. Similarly, during use, the precursor gas can be added and subtracted, in essence, switching the spiking gas between RGM and  $\text{Hg}^0$ .

A difference in total mercury between these two states is an indication of how well the CMM can measure RGM, i.e., allowing the quantification of captured or released RGM in the CMM system. Another advantage to this system is that the reactor is small enough to mount to the probe injecting directly to the probe inlet. This further reduces problems associated with transporting RGM to the CMM system. This system can allow biases to be determined and quantified daily in a CMM installation and provide a troubleshooting tool for CMM operators and a quality assurance/quality control (QA/QC) test for researchers and plant engineers.

All parameters and measurements involved in generating a  $\text{HgCl}_2$  stream using this method can be National Institute for Standards and Technology (NIST)-traceable.

### ***Approach***

The reactions considered during this project that are responsible for the catalytic effects between gold, mercury, and chlorine are illustrated in Figure 1. Note that compounds of  $\text{AuHgCl}_2$  are highly unstable at temperatures above 250°F. The formation of  $\text{AuHgCl}_2$  quickly results in the formation of  $\text{HgCl}_2$ . A cursory examination of these reactions, using Density Functional Theory (DFT), was performed but limited to the reactions between a gold atom, mercury atom, and chlorine molecule.

Literature and previous experience with gold catalysts mercury and flue gas indicate four parameters need to be considered to accomplish the goal of this project: gold thickness, temperature, residence time, and precursor concentrations (3–5). The effect of these parameters on the ability of the gold reactor to transform all elemental mercury into  $\text{HgCl}_2$  has been measured using the experimental apparatus described below.

### ***Experimental Apparatus***

The apparatus comprises three parts: precursor sources, reactor, and speciating mercury emission monitor. Chlorine and mercury from permeation sources are metered, preheated, and mixed before the

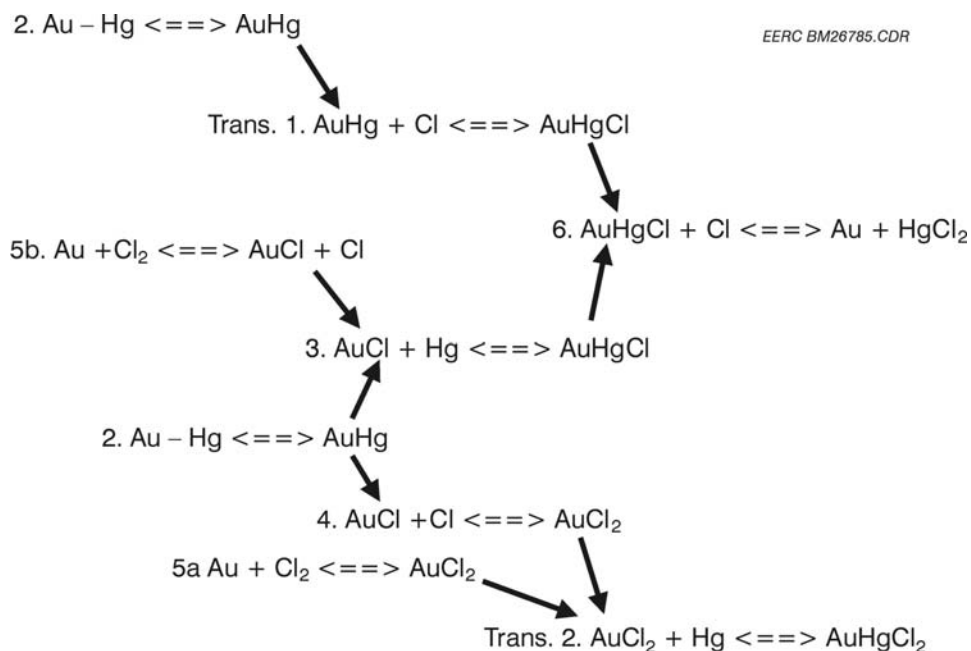


Figure 1. Reactions involved in a model describing the interactions between single atoms of mercury and gold and a molecular and atomic chlorine.

reactor. The reactor is composed of a filter holder, support, and gold-coated quartz filter. The product gas is diluted after the reactor and carried to a conversion/conditioning unit through heated Teflon lines. The Hg CEM pulls a slipstream off the product gas and analyzes the concentrations of elemental and total mercury (Figure 2).

Permeation ovens and sources for chlorine and mercury are from VICI Metronics and are being used to control the concentrations of the precursors. Rotometer flow controllers and pressure gauges are used in this test apparatus, all traceable to NIST standards using Gilibrator calibrations.

### Approach

This investigation has been carried out by testing parameters known to control the reactions leading to the generation of HgCl<sub>2</sub>. Initial tests were used to understand the ranges and resolutions necessary to elucidate the behavior of particular catalysts and configurations. Because the goal of this project is so focused on the development of a working product for generating a calibration gas, our understanding of the reaction mechanisms involved is not as clear as it could be. Nonetheless, a qualitative understanding of these mechanisms has been included.

### Progress

Parametric testing has allowed the design of a system capable of producing a stream of nearly 100% oxidized mercury. More than 95% of the mercury entering the reactor is oxidized to a form that is transportable (i.e., HgCl<sub>2</sub>) (Figure 3). The experimental system was evaluated, and a design for a portable

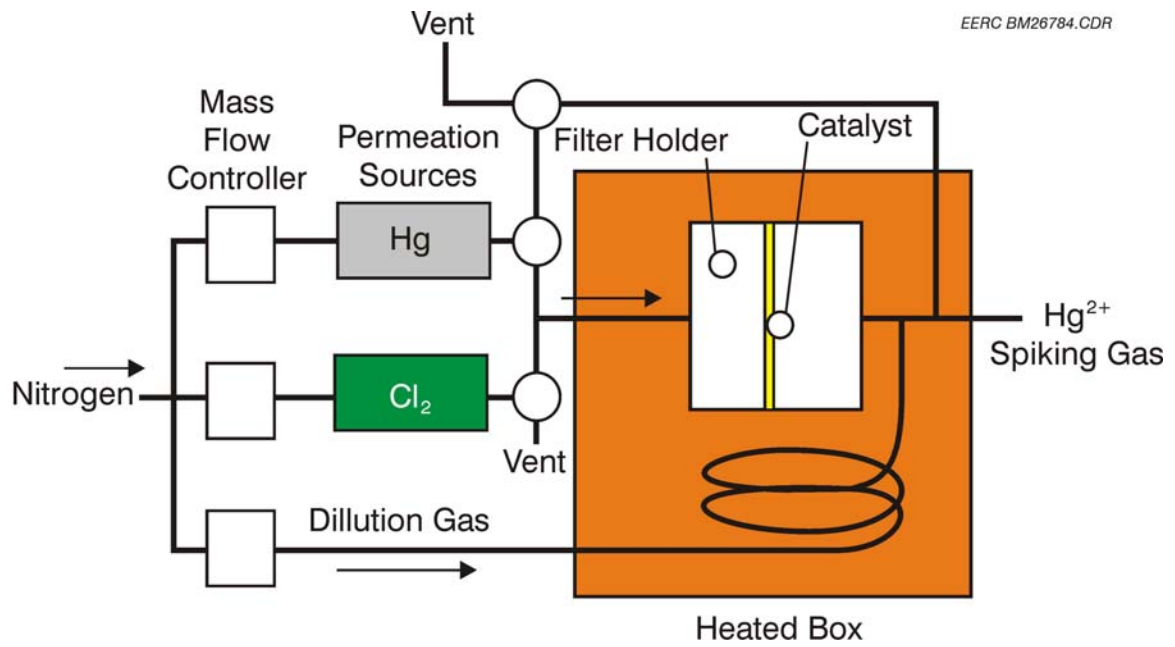


Figure 2. Schematic diagram of oxidized mercury-spiking system experiment.

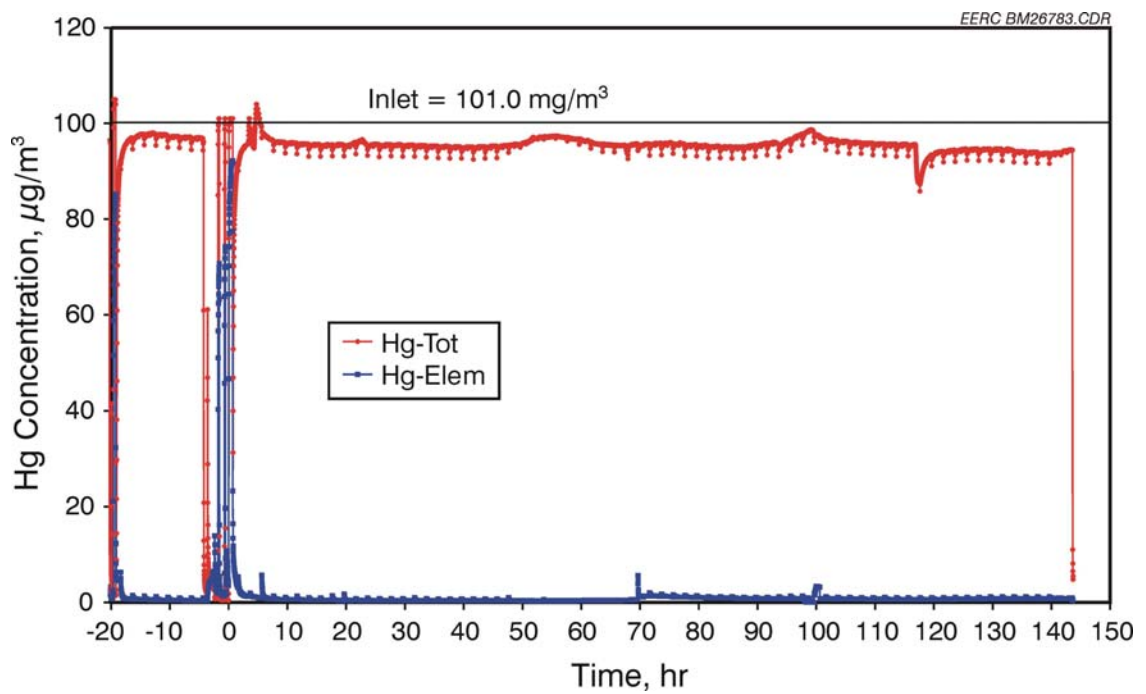


Figure 3. Long-duration test of oxidized mercury-spiking system.

system has been assembled for laboratory- and pilot-scale work. This system has a valve arrangement that prevents the user from damaging the catalyst by incorrectly exposing the catalyst to the precursors. It also allows the user to switch the gas stream being sent to the reactor to one of the following states: zero gas,  $\text{Hg}^0$ , or  $\text{Hg}^{2+}$ .

Many catalysts were made with gold thicknesses that varied between  $30 \mu\text{g}/\text{m}^2$  and  $600 \mu\text{g}/\text{m}^2$ . This parameter affected the reaction in the following ways. Below  $100 \mu\text{g}/\text{m}^2$ , significant amounts of elemental mercury pass through the catalyst without reacting. Above  $200 \mu\text{g}/\text{m}^2$ , the gold density approaches that of bulk gold and causes significant portions of mercury to amalgam. If this mercury does become oxidized, it is strongly bound to the gold and, therefore, requires higher temperatures to break free.

Parametric testing results for several catalysts shows that reactor temperatures in the range of  $300^\circ$  to  $450^\circ\text{F}$  do not play a significant role in the reactions taking place. In tests where the temperature was increased by  $25^\circ\text{F}$ , from  $200^\circ$  to  $500^\circ\text{F}$ , the effect of increasing temperature was to drive off some of the captured mercury. As the temperature stabilized, this capture of mercury would return. At excessively high temperature (above  $450^\circ\text{F}$ ), the reaction appeared to be less complete, i.e., resulted in less oxidation. This may be due to oxidized mercury that is strongly bound to the gold by amalgamation and is reduced to elemental mercury. At lower temperature (below  $300^\circ\text{F}$ ), the amount of mercury being transported through the reactor begins to decrease, i.e., the catalyst becomes an absorber.

### ***Quality Assurance/Quality Control***

QA/QC design for this project recognizes that the ability to measure the ratios of elemental, RGM, and trapped mercury are more critical than the measurement of absolute mercury concentrations. Nevertheless, permeation sources will be certified using EPA Method 101A to quantify the permeation rates for elemental mercury sources. VICI Metronics, Inc., has been instructed to certify the chlorine permeation device at two separate temperatures in order, allowing the ability to adjust this sources output. Rotometer flow controllers will be used for flow regulation throughout, and all flows will be calibrated using the NIST-traceable Gilibrator primary flow standard.

### ***Status***

Several Ontario Hydro tests are planned and should be completed in the next month. Some further parametric testing of the kinetics of the reaction (face velocity of the precursors across the catalyst) are also planned. This project is nearly complete.

### ***Potential Users/Technology Transfer***

CMM manufacturers, researchers, and power plants can benefit from such a QA/QC tool.

### ***References***

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