Use of Jerome Model 431-X Mercury Analyzer for Measuring Low Levels of Mercury in Process Gas Streams

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Outline:
A. Typical levels of mercury in natural gas and other process streams
B. Why mercury needs to be removed
C. Available mercury analyzers
D. Attractive features of the Jerome 431-X mercury analyzer
E. Absent information in the Jerome 431-X operating manual
F. Proper set-up of sampling system in process plants
G. Proper use of analytical traps
H. Important tips in the use of Jerome 431-X
I. Use of Jerome 431-X for mercury analysis of liquid samples
J. Available mercury analytical assistance

A. Typical levels of mercury in process gas streams
Mercury being one of the elements of the universe is present in nature. Thus, mercury can be present in many natural gas streams and other gas streams such as the cracked gas stream in ethylene plants, and in synthesis gas produced from mercury containing feed stocks such as naphtha or coal. Mercury concentrations in gas streams are usually expressed as micrograms of mercury per normal cubic meter (ug/Nm3). The mercury levels in process streams can range from non detectable to levels above 1,000 ug/Nm3. As a point of reference, the OSHA limit for workers exposed to mercury containing air is 25 ug/Nm3 for an 8 hour exposure. As a further point of reference, mercury containing amalgams are used in dentistry. Thus, anybody with amalgam filling out gases some mercury. Having amalgam fillings I tested my own breath and found it to contain some 10 ug/Nm3 of mercury.
B. Why remove mercury?
Mercury removal may be necessitated by environmental concerns and by process requirements. Even at low concentrations, if a large volume of gas flow is handled, the amount of mercury per year can become significant. In process operations, even extremely low levels of mercury can damage process equipment and deactivate catalysts. Aluminum heat exchangers used in LNG plants, in cryogenic operations such as hydrocarbon recovery natural gas plants, and in ethylene plants are damaged by mercury resulting in unscheduled plant shut downs and costly repairs. Any mercury present can deactivate catalysts used in ethylene plants and in synthesis gas production plants.

To protect the heat exchangers and the downstream catalysts, mercury needs to be removed. Removal is done by passing the gas through a fixed bed of mercury removal adsorbent. Everyone wants to reduce the mercury to the lowest level practical. In process plants, the lowest level of mercury that can be practically measured is about $0.01 \text{ ug/Nm}^3$ (this is 10 nanograms/Nm3). This corresponds to needing to measure levels as low as one part per trillion by volume.

C. Available mercury analyzers
There are numerous mercury analyzers available. They use a variety of mercury detection mechanisms. Cold vapor atomic fluorescence detectors are very sensitive to mercury and they can detect and quantify very low levels of mercury. Analyzers made by PS Analytical, Tekran, and other manufacturers use this detection mechanism. Cold vapor atomic absorbance is also a popular detector mechanism and it is used in many mercury analyzers including analyzers made by Nippon Instruments.

Arizona Instruments sell an analyzer called Jerome 431-X. This mercury analyzer operates on a different detection mechanism. It used the basic electrical principle of Wheatstone bridge. One leg of the Wheatstone bridge is made of gold film. The mercury from the sample gas is passed over the gold film where the mercury amalgamates with the gold and changes the resistance of the gold film. The amount of change in the resistance of that leg of the Wheatstone bridge is proportional to the amount of mercury amalgamating with the gold.

D. Attractive features of the Jerome 431-X mercury analyzer
The Jerome 431-X is light, simple to use, and very portable. The only utility it needs is either 110, or 220 volt power. The set-up consists of plugging in the power into the analyzer and waiting a few minutes for the analyzer to warm-up. By contrast, the atomic fluorescence detector analyzers are lot heavier, more complicated to operate, need lot more set-up effort, and require a source of argon for use as a carrier gas in the instrument. The cold vapor atomic absorbance analyzers are similar in difficulty to the electron fluorescence based analyzers. Another attractive feature of the Jerome 431-X is the cost of the analyzer. The Jerome 431-X is significantly lower priced.
E. Absent information in the Jerome 431-X operating manual

The operating manual of the 431-X teaches how to conduct mercury measurements associated with environmental issues. That is, how to measure ambient air for mercury content. It does not teach how to determine the mercury content of a gas in a process line. The manual also advises that the lowest level of mercury that the instrument can measure is 3 ug/Nm3. This sensitivity is not good enough for process applications. Thus, one can easily conclude that the Jerome 431-X is not applicable for the low level mercury measurement required in process plants. However, this would be an erroneous conclusion. I have successfully used this analyzer for low level measurements in numerous plants around the world. The key is to use proper procedure. Mercury levels below 0.01 ug/Nm3 can be measured with this analyzer.

No mercury analyzer can directly measure the low levels of mercury present in process plants. Not even analyzers using the very sensitive atomic fluorescence detectors. Every analyzer requires the use of an analytical trap. Small amount of process gas is taken from the process line at controlled conditions and passed through the trap. The mercury from the sample gas is trapped in the trap. After a period of time, the sample gas flow is stopped. The trap is then connected to the analyzer and heated. The heat releases the mercury from the trap and the released mercury is passed into the analyzer. The detector in the analyzer detects and quantifies the amount of mercury it sees. The concentration of mercury in the process gas is then calculated from the amount of mercury the detector has quantified and the volume of gas that has been passed through the analytical trap. The predominant trapping surface in the analytical traps is gold.

Arizona Instruments does sell mercury traps in conjunction with the Jerome 431-X. They call these traps “dosimeters”. These are intended for use in monitoring ambient air for mercury. A worker would carry around on his or her person the trap. During the course of the day, a measured amount of air is continuously drawn through the trap. After a period of time, like the end of the day, the trap is connected to the analyzer and heated. The desorbed mercury is swept into the analyzer and the average mercury concentration that the worker has breathed can be calculated. These “dosimeters” can also function as analytical traps for measuring mercury in process gas streams.

Some manufacturers of mercury analyzers proclaim that their analyzer is the best since they use the most sensitive mercury detector. However, if the analyzer can not see the mercury directly and it still requires the use of an analytical trap, it is a mute argument. In all cases, one has to balance the amount of mercury put into the trap with the detectors sensitivity and the trap’s capacity for mercury. With a less sensitive detector all one needs to do is to put more mercury into the trap. This may mean running the sample gas through the analytical trap for a longer period of time, but that usually is no problem.
F. Proper set-up of sampling system in process plants
Regardless of what type of mercury analyzer is used, the key is to get a representative sample from the process line to the mercury analytical trap and eventually to the detector in the analyzer. This is not an easy thing to accomplish. Mercury can be gained, or lost, in the lines between the inside of the process line and the mercury analytical trap. Mercury analysis is analogous to water analysis. Mercury, like water, is quite “sticky”. You can not move it from point A to point B without equilibrating the line in between.

The first requirement is a **proper sample tap** on the process line. The usual ¾” carbon steel sampling connection commonly found in process plants will not do. Even if the sampling connection is located on the top of a horizontal pipe, or on the side of a vertical pipe, this connection will not do. This type of connection is prone to have some solids present. This can be rust, iron sulfide particles, etc, as well as some mercury containing solids. These act as a sponge for mercury. They can collect mercury (reduce the mercury level in the sample), or release mercury usually with even slight changes in temperature. Also, often there is a possibility of some liquids being present in the process pipe. Any liquids present will have the tendency to run along the inside wall of the pipe, so if the sample is drawn off the side of the pipe, there may be some liquids in the sample gas drawn off the process pipe. The presence of liquids will seldom be obvious since the pressure is reduced before the analytical trap and the liquids will flash. The presence of even a small amount of liquid can dramatically alter the mercury readings.

An existing sample connection can be modified for use in mercury analysis. One version of modification is shown in **Figure 1**. This was first shown in the paper by Markovs and Corvini given at the 1995 Laurence Reed Gas Conditioning Conference. The gas sample is taken through a ¼” ss tube that has been installed into the existing sample connection. The tube extends away from the pipe inside wall. In new plants where the need for accurate mercury measurements is expected, the proper sampling taps should be installed during plant construction.

A second requirement is **proper layout of the sampling system**. A recommended layout is shown in **Figure 2**. The analytical traps operate at essentially atmospheric pressure. The process gas lines are always at elevated pressure, sometimes in excess of 1,000 psig. A pressure regulator is nearly always required. The regulator should be of stainless steel with minimum internal area. If there is any possibility of condensing any gas components due to the expansion and adiabatic cooling, the regulator needs to be heated. The mercury analytical traps need to be located in an accessible area such as ground level or on an elevated platform. The sampling taps are seldom nearby so a sampling line is required. The line needs to be stainless steel and of the smallest diameter practical. For permanent lines ¼” o. d. tubing is good. For temporary evaluations, I prefer to use ⅛” tubing. A key feature of the sampling system is the use of the sample gas by-pass line. Most of the gas taken out of the sample
tap and passed through the regulator does not go through the analytical trap but is either vented in a safe area, sent to fuel, or directed to a low pressure area in the process. By having huge gas flow through most of the sampling system, the sampling system gets equilibrated faster.

G. Proper use of analytical traps

The Jerome 431-X analytical traps (“dosimeters”) consist of gold coated resistance wire that is inside a glass tube with an internal volume of about 4.5 cc. The glass tube is enclosed inside a larger nylon tube that is ¾” in diameter and about 5” long. The ends of the tube are sealed. Inlet and outlet flow connections are at the ends of the tube as well as the ends of the gold coated resistance wire. A key requirement is to keep the traps clean. This means do not get any solids or liquids into the trap. Try to make sure that the sample gas is free of any solids or liquids. If you will be measuring two different streams that is expected to have high and low mercury levels (like measuring mercury removal adsorbent bed inlet and outlet gas), use dedicated dosimeters. The dosimeters come with serial numbers attached to them, so as long you record the numbers you will be sure to use always one dosimeter on the inlet gas and the other one on the treated gas. If dosimeters do get contaminated, wash them out with a mercury free solvent like a hexane and dry them out using nitrogen or some other mercury free gas. It should be noted that cp pure solvents are not necessarily mercury free. You may have to make the hexane Hg free by passing it through a small bed of mercury adsorbent.

For critical measurements, always make sure that the dosimeter is clean. A good way to confirm that the dosimeter is clean is to desorb the dosimeter and cap it (caps are provided with the dosimeters, or you can make your own). Leave the dosimeter capped for at least 24 hours. Take the dosimeter, plug it into the analyzer, and desorb it. The reading should still be zero (a reading of 0.000). If any reading is obtained, repeat the process. The dosimeters that give zero readings after being capped for at least 24 hours are clean. The dosimeters that give a slight reading can be used for less critical measurements like analyzing high mercury content gases where the dosimeter is used for a shorter period of time. The dosimeters that give a high reading need to be cleaned.

The sample gas is flowed through the dosimeter at a controlled rate. There are a number of ways to do this. Two of them are shown in Figure 3. In the first, the gas is flowed first through a rotometer and then through the dosimeter. Before putting the dosimeter into service, the gas flow rate from the rotometer is measured with a volumetric measuring device such as a bubble meter. I have found that in most cases a gas flow rate of 100 cc/min is a good rate to operate at. The rotometer gives a visual confirmation of the sample gas flow. Should the rotometer indicated flow change during the sampling period, the sample gas flow rate through the dosimeter can be checked by hooking up a volumetric gas flow measuring device (such as a bubble meter) on the dosimeter exit. Tygon tubing
can be used for connection lines. The collection time will vary from minutes to over 24 hours depending on the mercury level in the sample gas.

In the second method, a flow totalizing device is used. The dosimeter exit flow goes through a dry test meter or similar device. The advantage of this method is that the total volume of gas flow through the dosimeter is accurately summarized. The downside is that the test meter is a bulky item to transport. Operating with the meter after the dosimeter also makes the dosimeter to operate at above ambient pressure. This is not a problem as long as there are no leaks in the system which may affect the calculations.

The dosimeters can be used in series to confirm that the first dosimeter is catching all of the mercury at the 100 cc/min flow rate. If any mercury is found in the second dosimeter, that mercury is included in calculating the mercury concentration in the sample gas. The sampling rate is not critical. A low rate means it takes more time to equilibrate the sampling line and to collect the needed amount of mercury in the dosimeter. A high sampling rate may not provide enough residence time in the dosimeter to catch all of the mercury on the gold coated wire.

It is a good idea to confirm that there is no mercury vapors in the sampling area which could add to the sampling value. One way to confirm this is to take a clean dosimeter and leave it opened in the sampling area for the same duration and then check its mercury content. If any mercury is found on this dosimeter, that mercury originated from the atmosphere and this amount of mercury should be subtracted from the mercury found on the sample gas dosimeter. Alternatively, a spare clean dosimeter can be added to the end of the sample dosimeter. Any ambient mercury diffusing into the sampling system will be collected on this dosimeter.

**H. Important tips in the use of Jerome 431-X for low level Hg measurements**

As stated earlier, the main application for the Jerome 431-X has been the environmental market where extremely low readings are not required. Thus, the operating manual is directed for use of the Jerome 431-X in that application. However, this instrument will serve you well for low level Hg measurements when proper care is exercised.

Keep the analyzer clean. Use the analyzer only with the dosimeters. Do not use the analyzer for direct sampling of any gas stream that is not sure to be clean of solids and liquids and chemical vapors.

During testing sometimes people want to frequently check the accuracy of the analyzer by injecting a small amount of mercury saturated air into the analyzer.
Mercury has high vapor pressure and the air mercury saturation levels are well established. For instance, at 25°C and at atmospheric pressure one cc of air contains some 19.8 nanograms of mercury. Actually, there is no need to do this. The analyzer has been calibrated at the factory and the calibration has shown to be very steady. If you do want to confirm the response of the analyzer, inject a small amount of mercury saturated air (like 0.1 to 0.5 cc) into the dosimeter. Do not inject any mercury saturated air into the analyzer as frequent injections may overload the piping inside the analyzer and some time may be required before 0.000 readings can be achieved with clean dosimeters. Cap one end of the dosimeter and through the other end using a long needled micro syringe inject the Hg saturated air slowly into the dosimeter. Withdraw the needle and cap the end. Let the dosimeter sit capped for 5 minutes, then place it into the analyzer and desorb the contents. The reading on the analyzer should be comparable to the expected value.

In injecting measured volumes of Hg saturated air you need to remember that you are working with saturated air. If your syringe would happen to be just a bit colder than the mercury saturator, you will get some Hg condensation in the syringe which can lead to some unexpected fluctuations in the obtained results. It is always best if the mercury saturator can be a bit colder than room air.

If you need to sample a gas stream that contains H2S, or some other reactive components, this can be done. The 431-X analyzer has internal chemical filters to handle most interfering compounds. However, you do not need to worry about any interfering compounds these since you do not need to put any of them into your analyzer. After the desired amount of sample gas has been passed through the dosimeter, take the dosimeter to the laboratory and purge the dosimeter with Hg free gas like nitrogen or air. You do not need to worry about losing any of the mercury by purging with gas. You could purge the dosimeter all day and all the mercury will still be there. The only thing that liberates the mercury from the gold surface is heat. By purging the dosimeter before placing it in the analyzer only clean gas and mercury enters the analyzer.

Occasionally you may need to analyze gas streams that contain high levels of mercury. The normal sampling techniques shown in Figure 3 are no longer applicable. With high levels of Hg in the gas stream the dosimeter will get overloaded with mercury very quickly. Even if the Hg concentrations are high enough where you could use the analyzer directly without the use of dosimeters, do not do direct analyses. Use the dosimeters. This will avoid the possibility of contaminating your analyzer. There is a simple and accurate method to use the dosimeters when analyzing gas streams containing high level of mercury. A small and precise volume of sample gas can be drawn through the dosimeter by use of a sampling pump commonly supplied with detector tubes. Detector tubes are glass tubes about ¼” in diameter that contain a reagent. A precisely measured amount of gas is drawn through a glass tube containing a color changing reagent. The length of discoloration is proportional to amount of contaminant.
detector tubes are available from a number of companies and they all come with
an accurate volumetric pump. The connections on the dosimeter are about \( \frac{1}{4} \)“ in
diameter – about the same as the detector tubes. So the detector tube sampling
pump can be used to accurately measure the volume of sample gas drawn through
the dosimeter.

It is also a good idea to confirm that the air in the area where the Jerome 431-X
has been set up is free of mercury. A simple and quick way to do this is to install
a clean dosimeter into the analyzer, do not hook up the electric leads to the ends
of the gold coated resistance wire, and energize the analyzer (this pulls the room
air through the dosimeter). Any mercury present in the room air will then be
collected on the cold gold coated wire. After the analyzer has stopped, hook up
the electrical connections, and start the analyzer. If you have any reading, then
there is mercury in the air. If mercury is detected in the room air, try to find a
mercury clean room to set up the analyzer. If relocating to a Hg free room is not
an option, use extra care to minimize exposure of traps to room air. The sensor
gold film eventually gets saturated with mercury and needs to be regenerated
(heated). This is done automatically. The exhaust is scrubbed through a mercury
filter, so there are no local mercury releases. Thus, the Jerome 431-X mercury
analyzer does not need to be set-up in a ventilated lab. It can be set-up even in an
office.

I. Use of Jerome 431-X for mercury analysis of liquid samples

The Jerome 431-X is marketed as a gas analyzer. However, it can also be used to
analyze for mercury in some liquids. The gold film in the analyzer does not care
where the mercury originates. Thus, if one can trap the mercury out of the liquid
sample and get the mercury from the trap into the analyzer without getting
anything else into the analyzer that will affect the resistance reading, an accurate
and dependable analytical technique can be developed. I have developed and
used such a technique to measure mercury from light hydrocarbon stream such as
stabilized natural gas condensate. This stream is still low in viscosity where the
mercury diffusion rate in the liquid is still adequate allowing for reasonable
contact times in the mercury traps. In general, the procedure involves filling the
dosimeter with the sample liquid, allowing sufficient time for the mercury from
the liquid to diffuse and be adsorbed on the gold surface, draining the dosimeter
of the sample liquid, washing the dosimeter with Hg free solvent, drying the
dosimeter, and desorbing the mercury into the analyzer. Mercury levels as low as
0.5 ppbw have been measured.

Mercury analyses of liquids does have its unique challenges. Just like in gas
analyses, unless the mercury detector is broken, the analyzer will give a result.
Just how accurate representation this is of the process fluid depends on many
things. Wrong information at best results in confusion, and at worst to costly
wrong decisions. Some of the critical considerations in dealing with liquid
analyses include: potential presence of mercury containing solids, sample taking procedure, choice of sample containers, handling of sample containers, and the procedure of getting the sample from the sample container into the analyzer.

J. Available mercury analytical assistance

Analyzing mercury in process plants is different from analyzing mercury in air. Proper procedures need to be used to insure that the analyzer’s response accurately represents the mercury content of the fluid in the process pipe. The required techniques are plant specific. What works best at one plant may not be the best at another plant.

Service is available from Adsorption Solutions LLC to help you get accurate information. This service includes such items as:

- Design of the in-plant sampling system for new plants.
- Review and optimization of your existing in-plant sampling system.
- Review and interpretation of in-plant generated mercury analytical information including mercury breakthrough data generated at sampling probes located in mercury removal adsorbent beds.
- Plant visit to examine the sampling system and review your over-all mercury analytical protocol.
- In-plant mercury analyses can be arranged.
Figure 1

Configuration of Sample Point for Measuring Hg in Process Plants

- $\frac{1}{4}$" SS Tubing Valve
- Bored through Swagelock, or similar, Tubing Connector
- Existing Gate Valve
- Typical $\frac{3}{8}$" sampling connection
- Process Pipe
- $\frac{1}{4}$" SS Tube extending away from the wall

Scale: None
Figure 2

Layout of Sampling System for Measuring Mercury in Gas Streams in Process Plants

Vent, send to fuel, or to some low pressure line in plant

Regulator (may require heat source)

Hg Trap

Local vent

Process Pipe
Figure 3

Possible Hg Analytical Trap Set-ups

A) 

B) 

Rotometer for visual indication of flow

Volumetric measuring device such as a bubble meter or similar device

Hg Trap

Flow totalizing device such as a dry gas flow meter

Vent to atmosphere