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Evaluation of Portable Mercury Vapor Monitors and Their Response to a Range of Simulated Oil Processing Environments

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Abstract

Portable mercury vapor monitors are relied on for quick decision making to determine safe work practice requirements. There is little specific information regarding their use limitations and/or potential interference data, especially in environments of high temperature/humidity and various concentrations of hydrocarbons (HC) and inorganic gases, as are commonly found in oil processing environments. This work was undertaken to objectively assess the accuracy of each monitor under ideal conditions and then assess the effects of potentially interfering conditions or substances on monitor accuracy. This data was used to highlight specific limitations and create field user guides. A secondary objective was to compare the overall usability and user-friendliness of the monitors evaluated. The paper describes the experimental method used and results provided by several mercury vapor monitors exposed to known concentrations of mercury vapor while other variables such as temperature, relative humidity and the concentration of potentially interfering compounds were varied to simulate field measurement conditions. Two types of detection technology were assessed, Gold Film resistance and Cold Vapor Atomic Absorption, (CVAAS). All monitors were tested against a variety of potential interference compounds, e.g., organics, benzene, toluene, and inorganics, ammonia, sulfur dioxide, nitrogen dioxide and hydrogen sulfide. The testing revealed several strengths and weaknesses for each monitor. Negative interference was found with the Gold Film unit in high relative humidity (RH). All CVAA units showed positive interference with high organic concentrations. Poor repeatability across the entire exposure range is common. Survey technicians need to become familiar with the specific limitations of the survey meter used to accurately assess the work environment where mercury (Hg) vapors are present.

Introduction

The presence of elemental mercury (Hg) and mercuric salt deposits in oil processing equipment has been known for a number of years¹. This has created the need to test atmospheres in these environments using portable monitoring equipment to assess the presence of Hg vapor to designate appropriate safe work practices and personal protective equipment. Oil Processing environments may contain a range of materials that could potentially interfere with the accuracy of the readings of the portable monitors. For example, practices such as the steaming out of vessels may result in elevated levels of hydrocarbons and high residual RH to be present in the test atmosphere. In addition, these typical test atmospheres may also contain inorganic compounds such as ammonia (NH₃), hydrogen sulfide (H₂S), nitrogen dioxide (NO₂), and sulfur dioxide (SO₂) that could act as interferences. The literature and manufacturers' specifications^{2, 3, 4, 5, 6} contain little specific information regarding use limitations and/or potential interference data. This paucity of data is one of the reasons this work was undertaken. We wanted to objectively assess the accuracy of several manufacturers' monitors under ideal conditions and then assess the effects of potential interferences on monitor accuracy. Included in our experiment was a qualitative analysis of each monitor's usability to highlight any issues that a specific monitor's user guide would need to address.

Description and Application of Equipment and Experimental Processes

The monitors selected for testing purposes were a combination of instruments that are currently used in several of Chevron's field operations based on the long established "gold film" resistance technology and four other units that make use of CVAAS. These two measurement technologies represent the current field of existing portable Hg vapor testing equipment. However, our testing did not include all of the Hg monitors currently available on the market. After a review of monitor specifications (e.g., detection ranges, weight, size, ruggedness, etc.) the following portable monitors were selected for testing:

- “Jerome® 431-X” (Arizona Instruments, Tempe, AZ), (Gold Film);
- “Jerome® 471” (Arizona Instruments, Tempe, AZ), (CVAAS);
- “Genesis Hg 253” (Genesis Laboratory Systems, Inc., Grand Junction, CO), (CVAAS);
- “Nippon EMP-1A” (Nippon Instruments Corporation, Tokyo, Japan), (CVAAS);
- “Mercury Tracker 3000” (Mercury Instruments, GmbH, Karlsfeld, Germany), (CVAAS).

The Jerome® 431-X is the updated version of the Jerome® Model 411 Gold Film mercury vapor analyzer that has been and still is in common use throughout the industry. It was anticipated that comparison of this monitor with the others based on CVAAS technology would provide good comparative data for analysis in our experimental design.

Two rounds of experiments were run during our testing process. During the first round of experiments the Jerome® 431-X & 471, Genesis Hg 253, and Nippon EMP -1A were tested. Upon completion of the testing it was determined that the Genesis Hg 253 may have been experiencing some computer software problems. A second Genesis unit and the Tracker 3000 were tested in a second round of experiments that duplicated the first round testing. The Genesis units have been designated as Genesis 1 and Genesis 2 respectively, and monitor response curves were generated for both units.

Test and Exposure Methodology

Our desired outcome was to determine the impact that interferences may or may not have on the Hg vapor reading of the selected monitors in some realistic oil processing environments. In many situations these portable monitors are used to monitor inside of process vessels prior to entry. One of the common practices to clean vessels prior to entry is known as “Steaming”. During this process, steam is used to help rapidly clean the process vessel of residual hydrocarbons and hydrocarbon vapor. It is common for the high humidity to persist upon initial entry; therefore, a high humidity environment is assured as one of the challenge atmospheres. In addition, small amounts of HC remain in the vessel as well as other inorganics such as H₂S, NO₂, SO₂, and NH₃. Our experimental design was developed to cover a range of exposures to include realistic and “worst case” atmospheric conditions from an occupational health perspective. We also wanted to test the response of the monitors when they are exposed to high Hg vapor concentrations (above 600 µg/m³) – in one case well above the upper reading range of the monitor – to determine how quickly the monitors would zero upon exposure to clean air.

To gather this data a mercury exposure chamber was constructed to facilitate the generation of test atmospheres to which the various monitors would be exposed. This chamber allowed for the control of the all four measured variables, temperature, relative humidity, Hg vapor, and interferent compounds. The specific concentrations of Hg vapor of interest were 5, 125, and 250 µg/m³. This range of concentrations was close to the lower limit of detection ($\leq 1 \mu\text{g}/\text{m}^3$) of all the monitors and included the upper limit that is ten times the acceptable occupational exposure limit (25 µg/m³). For our purposes the accuracy of the monitors above this level is not as critical since appropriate PPE selection and work practice controls are determined based on monitor readings in this exposure range. The center point (125 µg/m³) is included to verify reproducibility of the input variables and the monitor response, as well as to provide an indication if the response to individual factors or interactions have significant curvature over the range being studied.

For each set of specified test conditions, each monitor was subjected to the conditions for 10 minutes. Monitor responses were collected at 0.5, 1, 2, 5, and 10 minutes. The average of these responses is what is indicated in the tables and graphs throughout this paper.

A table of contrast coefficients⁷ was generated and then randomized to determine the order in which the test chamber conditions would be presented to the monitors. The results of the blocked experiments were analyzed by the Yates algorithm⁷ which compare successive pairs of experiments to extract an overall average response, the main effects from single variables, and the interaction effects amongst the variables. The Yates algorithm is easily implemented in a spreadsheet since it involves only addition and subtraction of data pairs to obtain the final results.

To estimate the variability of the instruments, a series of “center points” using constant conditions of an intermediate mercury concentration (125 µg/m³), temperature (30°C) and relative humidity (50%) were performed over the course of the testing.

The data on the replicated center points of the design can be used to estimate the variability of the individual instruments within these experiments. From that variability, we can then evaluate whether the instrument response coefficients determined during the factorial experiment are real effects, or simply the result of the instrument variation. Generally instrument response coefficients determined in the factorial design that are less than two relative standard deviations of the replicated center points can be considered insignificant.

The factorial designed experiment evaluated the response of the individual instruments over a broad range of mercury concentration (5 - 250 $\mu\text{g}/\text{m}^3$), temperature (20-40°C), and relative humidity (10 – 90 %) which represent expected ranges found in actual oil processing operations. Further details on the experimental design are provided in Appendix A.

Figure 1 provides a diagram of the test chamber set up. The use and operation of the test chamber are described in the paragraphs that follow.

Generating Controlled Mercury Vapor Atmospheres

A mercury diffusion source was devised consisting of a glass Diffusion Vial (VICI Metronics, Poulsbo WA, and Item No. 19 D) containing elemental mercury placed in a temperature-controlled oven swept with a precisely controlled flow of clean air (Kin-Tek 570 Gas Standards Generator). This method has been described in *Gas Mixtures: Preparation and Control*⁸.

The mercury generator oven was operated nominally at 90°C with a tolerance of +0.1°C while the oven was swept at a flow rate of > 1 L/min. The Diffusion Vial, having a diffusion diameter of 5.0 millimeter (mm) and a diffusion length of 75 mm was modified to a diffusion length of 25 mm to attain the desired delivery rate of mercury vapor at 90°C. The mercury delivery rate was determined by sequentially weighing the diffusion vial periodically and dividing the weight loss of mercury by the elapsed time. The mercury delivery rate determined after two weeks was found to be 0.94 mg/day and this value stayed constant over the four weeks of the study.

Known Hg concentrations of 5, 125, and 250 $\mu\text{g}/\text{m}^3$ were generated by passing flows of 131, 5.25, and 2.62 L/min of clean air, respectively, through the oven and over the mercury diffusion vial.

Present Known Mercury Concentrations to Monitors

Mercury concentrations from the Kin-Tek oven generator were presented via non-contaminating PTFE or polypropylene tubing, and then blended with make-up air provided by the Miller-Nelson HCS-401 (temperature, humidity, and flow controller) to obtain the desired humidity. Combined flow rates at 2.62 and 5.25 L/min were confirmed by an absolute method using a soap film air burette. For the highest flow rate (131 L/min), we relied on a mass flow controller which had been calibrated against a dry gas meter. The final mercury concentration was directed into an inert plastic enclosure having two open ports so that each monitor could draw a sample, at its own flow rate, without developing any significant back-pressure or vacuum.

Present Known Hg Concentrations at Controlled Temperature and Humidity

The monitor under test was placed in a temperature-controlled incubator near the fume hood having a small hole allowing the passage of tubing connected to the monitor's sampling probe. The sampling probe, in turn, was connected to the plastic enclosure containing the known mercury concentration.

Present Hg with Known Concentrations of Potentially Interfering Substances

In the case of potentially interfering substances that were organic liquids (benzene, toluene, naphtha), vapor was generated by introducing liquid at a metered rate from a syringe pump through a micro-needle and septum installed in the tubing carrying the mercury concentration in air. Heating was applied to the organic liquid as needed to accomplish vaporization. These tests were carried out at < 10 %RH and 25°C.

In the case of potentially interfering substances that were inorganic gases (ammonia, sulfur dioxide, nitrogen dioxide, and hydrogen sulfide), vapor was generated by introducing gas from a certified cylinder, metered by a mass flow controller, into the tubing carrying the mercury concentration via a "T" joint. These tests were carried out at 25°C and either 10% or 90%RH.

Determine Recovery from high Hg vapor concentration, "Saturation"

Each monitor was exposed to an Hg vapor concentration of 600 $\mu\text{g}/\text{m}^3$ for 10 minutes. Clean air was then introduced to the monitor and its response was recorded as a function of time.

Evaluate Overall User-Friendliness

The size, weight, convenience, start-up time, control panels, durability, convenience, and other practical factors were compared to determine the user-friendliness of each monitor under evaluation.

Presentation of Data and Results

The series of experimental runs were performed as designed and the results entered into Tables 1 through 10. Yates analysis was performed on the results to generate the response curves for each monitor. Figures 2 through 7. The response curves for each of the monitors are compared to the reference concentration in Figure 8.

Experiments to Determine Sensitivity to Temperature & Humidity Variation

All analyzers (except the AZ 431-X) use CVAAS to determine Hg concentration. None of the CVAAS monitors appeared to show sensitivity either to temperature or humidity variations. The AZ 431-X seemed to lose its ability to detect the $5 \mu\text{g}/\text{m}^3$ level at very high humidity, although this response was not significant ($>2 \times \text{RSD}$) based on the Yates analysis. The AZ 431-X may also be temperature sensitive, but data are insufficient to reach a definite conclusion. These data are presented and summarized in Table 1.

Table 2 data show that only the one main effect, changing mercury concentration from $5 \mu\text{g}/\text{m}^3$ to $250 \mu\text{g}/\text{m}^3$ impact the instrument response over the averaging period: neither temperature in the range 20-40 C, nor relative humidity in the range 10-90% affect the monitors response in a significant ($>2 \times \text{RSD}$) way.

The factorial design allows us to estimate the three second-order (Hg-T, Hg-RH, T-RH) and single third-order (Hg-T-RH) interactions. The data in Table 2 also show that none of the interaction effects are significant by the same criteria.

The mean, standard deviation and RSD for the center points are shown in Table 3. Since only the mercury concentration impacts the monitor response in these tests, then all the other variation can be collectively used to obtain a better estimate of the monitor variation that was obtained by averaging the center point replicates from Table 3. Both the data from Tables 1 and 3 were then combined to obtain the response curves shown in Figures 2 through 8. These curves contain the data from 12 independent randomly conducted measurements for each monitor (four points at $5 \mu\text{g}/\text{m}^3$, four at the $125 \mu\text{g}/\text{m}^3$ center points and four points at the high concentration $250 \mu\text{g}/\text{m}^3$).

The value of a randomized factorial design is demonstrated in these experiments in that it allows us to estimate both primary effects of each variable and interaction effects between the variables. In this case, all primary and interaction effects except for the mercury concentration are insignificant. Since that is the case, then all of the data can be used to make a more accurate estimate of the overall response of the instruments since more data points are included into the calibration curves for mercury concentration.

The monitor response curve for the AZ 431-X is presented in Figure 2. The response curves for the CVAAS monitors are presented in Figures 3 – 7, and Figure 8 summarizes the response curves for all monitors. All monitor responses are compared to the test chamber Hg concentration.

Experiments to Determine Sensitivity to “Potentially Interfering” Substances

Similar testing using factorial designs were used to evaluate the instrument response to both potential organic and inorganic interferents. The fractional factorial design requires fewer experiments, but confounds some of the main effects that might be selected (Hg, T, RH, interferent concentration, etc) with higher-level interactions (second and third-order interactions in our case). Often we find that the higher level interactions are insignificant, so the reduction in experimental burden is valuable. If significant effects are found, then additional experiments can be performed to resolve the main effects from the higher-order interactions.

Full factorial designs were used to evaluate the impact of the organic interferents. Only two primary variables – mercury concentration and interferent concentration – were considered since neither relative humidity nor temperature are expected to interact with the organic species, and both temperature and RH were previously shown not to have an impact on the analyzer measurements.

Fractional factorials were selected to compare three primary variable effects for the inorganic interferents – mercury concentration, relative humidity, and interferent chemical species. Because of the experimental design, the relative humidity effect and the interferent effects were confounded. Only the interferent effect is reported here. Since we have already established that relative humidity has no impact on the instruments, the confounding issue is reduced in concern.

Primary and interaction effects were determined for the interferent tests again using Yates’s algorithm to reduce the data.

Experiments to Determine Sensitivity to “Potentially Interfering” Organic Substances

The data set from the organic interferent experiments are summarized in Tables 4 and 5. The data show that none of the monitors were subject to interference from benzene at the levels tested. However the CVAAS monitors showed significant impacts from elevated concentrations of toluene and naphtha. Not unsurprisingly, the naphtha impacts were more variable given the broad range of chemical species present compared with the other two pure component interferents. In fact, the interferences seen in the naphtha test could be unrelated to the presence of aromatic compounds which are expected to be interferents due to similar absorption bands to mercury. It is possible that the interferences observed for naphtha could also be related to inorganics that may be present in the naphtha.

Experiments to Determine Sensitivity to “Potentially Interfering” Inorganic Substances

In our evaluation, readings of the AZ 431-X were not significantly affected by any of the concentrations of sulfur dioxide presented, but were significantly elevated by both the high and low concentrations of NH₃, H₂S, and NO₂. Further, exposure to the any of the acid gases (SO₂, NO₂, H₂S) tended to render subsequent readings of the AZ 431-X unstable and variable until a sensor regeneration cycle was conducted.

The CVAAS monitors were not significantly affected by either the high or low concentrations of any of the inorganic gases presented to them based on the same instrument variability criteria used in the previous discussions. These data are summarized in Tables 6 and 7.

Effect of Extended Lengths of Sampling Tubing

The insertion of 5 meter (M) and 10 M lengths of PTFE tubing (approximately 6.4 mm O.D., 3.2 mm I.D.) had minimal affect on the readings of the AZ 431-X, Genesis, Nippon, and Tracker monitors. The insertion of 10M of tubing added a hold-up volume of approx. 16 mL to the sampling train. Since these monitors continue to sample at 200 mL/min, or higher, with the extra tubing in place, the additional hold-up time in reading mercury concentrations was less than 6 seconds in each case.

In the case of the AZ 471, however, the insertion of 5 M and 10 M of tubing reduced the monitor's sampling rate, apparently due to the increased back pressure induced by the extra tubing. The AZ 471 sampled at 2.0 L/min with no tubing added, but sampled only at 0.2 L/min when 5 M of tubing was added to the sampling train. When 10 M of tubing was added, the AZ 471 was unable to sample at all. These data are presented in Table 8.

Experiments to Determine Rate of Recovery of Monitors after High Mercury Concentrations

After exposure to a concentration in excess of 600 µg/m³ for ten minutes the AZ 471 and Nippon monitors recovered and returned to reading zero in less than 0.5 minutes. The AZ 431-X which operates intermittently was subjected to repeated samplings at 600 µg/m³. After 12 samplings the AZ 431-X was saturated and needed to be regenerated. After regeneration, requiring 10 minutes, the AZ 431-X returned to reading zero.

After exposure to a concentration in excess of 600 µg/m³ for ten minutes the Genesis monitors recovered and returned to reading zero within 5 minutes. Under the same treatment regime, the Tracker monitor returned to reading 6.6µg/m³ after 5 minutes and to 4.1µg/m³ after 10 minutes of exposure to clean air. These data are presented in Table 9.

Semi Qualitative Usability Evaluation

This is admittedly a subjective evaluation. In this evaluation, monitors are ranked in descending order of user-friendliness, and our rationale is given. Based on the reasoning, the reader can determine which factors are important to his/her application, and use this information selectively. The monitor specifics are summarized in Table 10.

Nippon EMP-1A

The Nippon is second lightest (7.3 lb.), is the smallest, has the fewest controls, is easy-to-read, and responds the most quickly of all the monitors tested. It is the simplest to use. The handle attached to the monitor makes it convenient to carry it from place-to-place while it is actually being used. This monitor can not be run from AC, and its internal battery cannot be charged while in use. This unit has fewer logging, recording, and output functions than most of the others. The Nippon takes 20 minutes to warm-up.

Jerome® AZ 431-X

The AZ 431-X is the lightest (6.9 lb.). It is not as simple to operate as some of the CVAAS monitors, but the manual is easy to understand. Unlike the other monitors evaluated, which measure continuously, this one makes a discrete measurement taking 12 seconds when you push a button. A continuous mode is available, but the manufacturer acknowledges that in that mode the 431-X is less accurate and less sensitive. The handle attached to the monitor makes it convenient to carry it from place to place while it is actually being used. This monitor has been on the market for many years; it has been used in a number of different industries, and has been refined for ease of use over the years. The AZ 431-X warms up and is ready to use in 1 minute.

Mercury Tracker 3000

While the Tracker is twice as heavy (14.0 lb.) and has a much larger footprint (170 in²) than the Nippon and AZ 431-X, it is equally simple to operate and has the most easily read display of any of the monitors tested. The Tracker is built into a metal case. One side of the case needs to be removed in order to read the display. Despite its size, it is narrow, so it is easy to carry the Tracker around with its shoulder strap and wand. The Tracker warms up in 3 minutes, by far the most rapid of the UV spectrometers.

Genesis Hg 253

The Genesis is the most complicated to use and makes the most noise. The display is complex, difficult-to-read, especially in bright outdoor light, and provides considerable information not necessary to operate the monitor. The touch screen is also not very sensitive to the touch, so that it can be difficult to actuate the functions. This monitor auto-zeros frequently and takes a long time to perform this function, during this auto-zero it is not making any measurements at all. Although it is not very heavy, the Genesis is almost square which makes it harder to carry around than the other monitors. The Genesis warms up in 20 minutes.

Jerome® AZ 471

The AZ 471 is the heaviest (15.0 lb.) of the group. The manual contains many warnings regarding the fragility of the monitor. It is simple to operate. The unit can run directly from AC and recharges rapidly. The display is complicated, but is easy-to-read. The Jerome® AZ 471 is very sensitive, but since it is heavy, bulky, and fragile, it seems more like a laboratory instrument rather than something to carry around in a plant. The inability of the sampling pump to maintain flow rate through narrow bore tubing is also a difficulty in the field.

Conclusion

All the monitors that use CVAAS technology do not appear to show sensitivity to either temperature or humidity variations. The Gold Film resistance monitor, AZ 431-X, did not accurately detect the 5 $\mu\text{g}/\text{m}^3$ level at high humidity (90%RH). The sensitivity to humidity is documented in the monitor's users manual, which cautions the user to warm up the unit in the ambient environment. This would help avoid any condensation that could be generated in the monitor from a rapid shift in temperature. At higher Hg concentrations (125 & 250 $\mu\text{g}/\text{m}^3$) high humidity appeared to have less of an effect on the accuracy of the device. The AZ 431-X may also be temperature sensitive, but data are insufficient to reach a definite conclusion.

None of the CVAAS monitors appeared to be sensitive to the inorganics tested. However, exposure to the any of the acid gases (SO_2 , NO_2 , H_2S) tended to render subsequent readings of the AZ 431-X (Gold Film) unstable and variable until a sensor regeneration cycle was conducted. This interference is noted in the user manual, but little information on the acid gas filter capacity is provided. Consequently, our user guide recommends frequent sensor regeneration when working in environments where these substances are present. In addition, the acid gas filter change-out schedule may need to be shortened.

A positive interference was observed in the CVAAS monitors when they were exposed to high concentrations of toluene and naphtha. At low Hg concentrations this may cause users to overestimate the true Hg concentration. This effect appears to diminish at higher Hg concentrations. See Table 2.

Nippon had the best agreement (86 – 87%) with the reference concentrations at all levels as well as the best reproducibility ($R^2 = 0.997$) of all the monitors studied. The AZ 431-X and Tracker had the second and third best agreement with the reference concentrations, (71 – 93%) and (76 – 92%) respectively. The AZ 471 and Genesis monitors demonstrated the poorest agreement with reference concentrations, (42 – 73%) and (57 – 88%) respectively. The AZ 471 monitor seems to be optimized at lower concentrations, as its agreement with the reference concentration decreased at the higher reference levels. Both of the Genesis monitors demonstrated the highest variability of all monitors studied. These results are presented as response curves for each monitor in Figures 2 – 7. The solid line on the graphs represents a perfect correlation with the exposure chamber Hg vapor concentration. An overall response curve comparison for all the units is shown in Figure 8.

As these figures demonstrate, all the monitors appear to underreport the Hg vapor reference concentration. The monitors demonstrated a large underreporting of the Hg vapor reference concentration, especially at the highest concentration (250 $\mu\text{g}/\text{m}^3$) where the monitor results varied between 42 – 86% of the reference concentration. These results could reflect some experimental error with the test chamber set up. However, since the vapor concentrations were generated using an established NIST based method and at least one monitor's performance closely matched the test chambers concentration level, we conclude that the reporting deficit present with the other monitors is real. The reporting deficit at the occupational exposure limit (25 $\mu\text{g}/\text{m}^3$) is not large for all the monitors that were tested (see Figures 2 – 8). When these monitors are used to measure higher Hg vapor concentrations the tendency to underreport needs to be factored into their use. Our specific user guides include the monitor's response curve in them to help field users in making their Hg vapor assessments where high Hg vapors may be anticipated. This allows the field operator a semi-quantitative method to adjust the monitor's reading appropriately. Since any adjustment results in a higher Hg vapor reading than what the monitor would normally read we are being conservative with respect to PPE and safe work practice recommendations.

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Appendix A: Experimental Design

Primary input variables

Mercury concentration ([Hg]) in $\mu\text{g}/\text{m}^3$.

Calculated based on mercury vapor pressure and known sweep gas flow rates. Mercury vapor pressure based on correlation recently released by NIST⁹ and assumed ideal gas behavior

$$\ln(p/p_c) = (T_c/T)(a_1\tau + a_2\tau^{1.89} + a_3\tau^2 + a_4\tau^8 + a_5\tau^{8.5} + a_6\tau^9)$$

Where:

$\tau = 1 - (T_c/T)$	$a_1 = -4.57618368$
$T_c = \text{critical temperature} = 1764 \text{ K}$	$a_2 = -1.40726277$
$T = \text{temperature, degK}$	$a_3 = 2.36263541$
$p_c = \text{critical pressure} = 167 \text{ MPa}$	$a_4 = -31.0889985$
$p = \text{pressure,}$	$a_5 = 58.0183959$
	$a_6 = -27.6304546$

Temperature, °C	Vapor pressure of Hg(0), MPa	Concentration, $\mu\text{g}/\text{m}^3$ (ideal gas)
0	2.699×10^{-8}	2384
10	7.028×10^{-8}	5988
20	1.713×10^{-7}	14,090
30	3.931×10^{-7}	31,290
40	8.551×10^{-7}	65,870
50	1.771×10^{-6}	132,200

Relative Humidity

Base on dilution of saturated gas absolute humidity and then calculate final relative humidity.

Interferent concentrations

Seven interferents are included in the design based on process knowledge of the monitors are to be used, and based on known interferences as cited by manufacturers.

Three are organic compounds (benzene, toluene, raw naphtha) that are not expected to react with gaseous Hg(0) and various levels of humidity. The designs used are only the interferent and [Hg] in these cases, and are blocked for the individual interferent.

Four are inorganic gases that could react with Hg(0), most likely via initial reaction with air and/or humidity, to convert the elemental mercury into an inorganic salt. The designs are blocked by interferent to simplify the experiments and include input variables for [Hg], relative humidity and concentration of the interferent.

Primary output variables:**Monitor reading Hg concentrations in $\mu\text{g}/\text{m}^3$**

Measured as a function of time measuring a constant concentration gas stream at a constant temperature and ambient pressure. Data will be analyzed using both the directly measured values and the difference between the measured and inlet mercury concentrations.

Determination of monitor response times and ultimate readings based on varying two factors: mercury concentration and relative humidity

This is the first block of a two-block design using temperature as the blocked factor and varying the two other factors: mercury concentration and relative humidity.

For each experiment, the monitor responses should be recorded at 30 sec, 1 min, 2 min, 5 min, 10 min, and longer if the monitor reading is not stabilized. These data will give response times for the overall system.

If some or all of the primary variables ([Hg], Temp, RH) and interactions between the variables studied in the first two blocks are insignificant, we will use those runs to quantify the variance of the experimental measurements and the monitor responses.

Temperature = 30°C

	Mercury concentration, [Hg], $\mu\text{g}/\text{m}^3$	Relative humidity, RH, %
Center	125	50

Temperature = 20°C

Experiment sequence (time order)	Mercury concentration, [Hg], $\mu\text{g}/\text{m}^3$	Relative humidity, RH, %
2	250 (+)	10 (-)
4	250 (+)	90 (+)
1	5 (-)	10 (-)
3	5 (-)	90 (+)

Temperature = 30°C

	Mercury concentration, [Hg], $\mu\text{g}/\text{m}^3$	Relative humidity, RH, %
Center	125	50

Determination of higher temperature performance using the same factors as described above

This is the second block of a two-block experiment using temperature as the blocking factor, and varying two other factors: mercury concentration and relative humidity. By combining the results of both sections we will be able to estimate the effect of the primary variables ([Hg], temperature, relative humidity) along with quantitative measures for the 2-factor and single 3-factor interactions.

The center points are included to verify reproducibility of the input variables and the monitor response, as well as to provide an indication if the response to individual factors or interactions have significant curvature over the range being studied.

Temperature = 30°C

	Mercury concentration, [Hg], $\mu\text{g}/\text{m}^3$	Relative humidity, RH, %
Center point	125	50

Temperature = 40°C

	Mercury concentration, [Hg], $\mu\text{g}/\text{m}^3$	Relative humidity, RH, %
4	250 (+)	90 (+)
2	250 (+)	10 (-)
3	5 (-)	90 (+)
1	5 (-)	10 (-)

Temperature = 30°C

	Mercury concentration, [Hg], μg/m ³	Relative humidity, RH, %
Center point	125	50
Use no tubing followed by 5 meter and 10 meter tubing lengths to see if readings are impacted.	5	50

Interferences

There are two categories of interferences:

1. Non-reactive interferences (NRI) – benzene, toluene, raw naphtha
2. Reactive interferences (RI) – ammonia, sulfur dioxide, nitrogen dioxide, hydrogen sulfide

The plan separates these two since the NRI likely will not interact with either the mercury or water vapor or other interferences, but the RI may.

Non-reactive interferences

Standard order factorial:

Experiment number	[Hg]	[Interferent], ppm Note: fill in the concentrations using the data below for the low (-) and high (+) levels for each pollutant
1	5	-
2	250	-
3	5	+
4	250	+

Randomized run order for full factorial for each non-reactive interferent:

Temperature = 25°C for all tests

	Low conc. (-) ppm	High conc. (+) ppm	Experiment run order
Benzene	0.1	50	1, 2, 3, 4
Toluene	2	400	2, 3, 4, 1
Raw naphtha	30	500	3, 1, 4, 2

Reactive interferences

This series has one more factor, relative humidity, since that can interact with these gases and may generate species that react with mercury, or it may affect the acid gas adsorption bed in the instrument. Fractional factorials are used to cut the number of experiments for each interferent down from 8 to 4. This gives the same data, but with the slight danger that some multifactor interactions might be confounded with a two-factor interaction.

Standard order full factorial and fractional factorial (highlighted rows):

Experiment	[Hg], μg/m ³	RH, %	Interferent, ppm Note: fill in the concentrations using the data below for the low (-) and high (+) levels for each pollutant
1	5	10	-
2	250	10	-
3	5	90	-
4	250	90	-
5	5	10	+
6	250	10	+
7	5	90	+
8	250	90	+

Randomized run order for fractional factorials for each reactive interferent:
Temperature = 25°C for all tests

	Low conc. (-) ppm	High conc. (+) ppm	Experiment run order
Ammonia	0.5	35	7, 6, 1, 4
Sulfur dioxide	0.2	5	1, 7, 4, 6
Nitrogen dioxide	0.3	5	4, 7, 6, 1
Hydrogen sulfide	0.1	15	1, 6, 7, 4

Table 1 – Experiments to Determine Sensitivity to Temperature & Humidity Variation

Conc'n $\mu\text{g}/\text{m}^3$	Temp $^{\circ}\text{C}$	RH %	AZ 431-X (a)	Genesis (b)	Nippon (a)	AZ 471 (b)	Tracker (b)	Genesis (b)
5	20	10	0.006	5.3	0.004	4.8	4.2	2.8
5	20	90	0.000	5.5	0.005	3.9	5.2	2.2
5	40	10	0.008	4.0	0.005	3.2	4.8	3.9
5	40	90	0.000	2.8	0.004	2.6	4.2	2.9
Ave Reading =			0.004	4.4	0.004	3.6	4.6	3.0
% Reference Conc =			71%	88%	86%	73%	92%	59%
% Rel Std Dev = +/-			118%	28%	6%	26%	11%	24%
125	30	50	0.121	88.9	0.110	63.4	103.2	76.3
125	30	50	0.132	89.9	0.100	66.8	107.5	69.6
125	30	50	0.100	87.2	0.112	59.8	103.6	83.0
125	30	50	0.111	64.8	0.112	56.3	123.9	105.2
Ave Reading =			0.116	82.7	0.108	61.6	109.5	83.5
% Reference Conc =			93%	66%	87%	49%	88%	67%
% Rel Std Dev = +/-			12%	15%	5%	7%	9%	19%
250	20	10	0.216	186.9	0.226	107.6	180.0	129.3
250	20	90	0.215	167.1	0.215	106.6	188.9	129.5
250	40	10	0.184	165.2	0.212	104.3	204.6	172.8
250	40	90	0.188	125.9	0.209	98.1	189.8	138.5
Ave Reading =			0.201	161.3	0.216	104.1	190.8	142.5
% Reference Conc =			80%	65%	86%	42%	76%	57%
% Rel Std Dev = +/-			9%	16%	3%	4%	5%	14%

(a) Read-Out in mg/m^3 (b) Read-out in $\mu\text{g}/\text{m}^3$

Table 2 – Results of factorial – instrument response coefficients based on average response for test period 1-10 minutes after initial exposure

Instrument	Hg*	T	RH	Hg x T	Hg x RH	T x RH	Hg x T x RH
AZ 431-X	197	14	15	3	4	1	2
Genesis 1	157	17	15	15	15	5	4
Nippon EMP-1A	213	-5	-3	-3	-6	2	0
AZ 471	100	-4	-2	-2	-2	-1	-2
Tracker	186	6	6	2	2	6	6
Genesis 2	140	14	13	-9	-8	-9	-9

*All data in $\mu\text{g}/\text{m}^3$

Table 3 – Results of center point replicates

Instrument	1*	2	3	4	Mean	Std dev	RSD, %
AZ 431-X	132	100	111	121	116	13.7	12
Genesis 1	90	87	65	89	83	12	14
Nippon EMP-1A	100	112	112	110	109	6	5
AZ 471	67	60	56	63	62	5	7
Tracker	108	104	124	103	110	10	9
Genesis 2	70	83	105	76	83	15	18

* All data in $\mu\text{g}/\text{m}^3$ Hg unless noted

Table 4 – Experiments to Determine Sensitivity to “Potentially Interfering” Organic Substances

Hg Conc	Temp	Benzene	AZ 431-X(a)	Genesis(b)	Nippon(a)	AZ 471(b)	Tracker(b)	Genesis(b)
$\mu\text{g}/\text{m}^3$	$^{\circ}\text{C}$	ppm						
5	25	0.1	0.006	0.0	0.004	3.9	5.5	3.8
5	25	50	0.007	0.0	0.004	4.0	8.4	11.0
250	25	0.1	0.205	171.6	0.219	107.0	227.3	201.4
250	25	50	0.215	160.6	0.224	109.0	226.8	211.5

Hg Conc	Temp	Toluene	AZ 431-X(a)	Genesis(b)	Nippon(a)	AZ 471(b)	Tracker(b)	Genesis(b)
$\mu\text{g}/\text{m}^3$	$^{\circ}\text{C}$	ppm						
5	25	2	0.006	0.0	0.009	9.5	7.2	3.6
5	25	400	0.009	89.7	0.078	64.5	60.4	88.3
250	25	2	0.209	174.5	0.220	103.3	226.3	182.0
250	25	400	0.199	233.1	0.268	155.3	276.3	244.1

Hg Conc	Temp	Naphtha	AZ 431-X(a)	Genesis(b)	Nippon(a)	AZ 471(b)	Tracker(b)	Genesis(b)
$\mu\text{g}/\text{m}^3$	$^{\circ}\text{C}$	ppm						
5	25	30	0.005	0.0	0.006	4.1	6.0	5.1
5	25	500	0.044	0.0	0.008	13.1	9.8	13.2
250	25	30	0.211	204.6	0.242	103.1	233.1	183.7
250	25	500	0.221	195.1	0.249	110.1	270.5	178.1

(a) Read-Out in mg/m^3 (b) Read-out in $\mu\text{g}/\text{m}^3$

Table 5 – Primary effects for organic interferents

Instrument	Primary variable effects					
	Benzene test		Toluene test		Naphtha test	
	Hg*	Benzene	Hg*	Toluene	Hg*	Naphtha
AZ 431-X	203	6	196	-4	192	25
Genesis 1	166	-5	159	74	200	-5
Nippon EMP-1A	218	2	201	58	238	4
AZ 471	104	1	92	54	98	8
Tracker	220	1	218	52	244	21
Genesis 2	199	9	167	73	172	1

* $\mu\text{g}/\text{m}^3$

Table 6 – Experiments to Determine Sensitivity to “Potentially Interfering” Inorganic Substances

Hg Conc	RH	NH ₃	AZ 431-X (a)	Genesis (b)	Nippon (a)	AZ 471 (b)	Tracker (b)	Genesis (b)
$\mu\text{g}/\text{m}^3$	%	ppm						
5	10	0.5	0.021	4.1	0.006	4.5	4.6	2.1
5	90	35	0.021	4.1	0.006	4.5	4.6	1.5
250	10	35	0.193	165.3	0.233	77.9	234.0	145.1
Hg Conc	RH	SO ₂	AZ 431-X (a)	Genesis (b)	Nippon (a)	AZ 471 (b)	Tracker (b)	Genesis (b)
$\mu\text{g}/\text{m}^3$	%	ppm						
5	10	0.2	0.006	0.0	0.004	3.7	4.6	1.9
5	90	5	0.006	0.0	0.006	4.4	5.0	4.0
250	90	0.2	0.206	179.2	0.229	77.9	244.0	186.6
250	10	5	0.185	166.7	0.211	76.0	243.0	196.0
Hg Conc	RH	NO ₂	AZ 431-X (a)	Genesis (b)	Nippon (a)	AZ 471 (b)	Tracker (b)	Genesis (b)
$\mu\text{g}/\text{m}^3$	%	ppm						
5	10	0.3	0.018	0.0	0.005	4.0	4.5	2.5
5	90	5	0.167	0.0	0.005	3.8	4.4	2.5
250	90	0.3	0.165	170.3	0.214	77.4	230.8	178.9
250	10	5	0.202	176.8	0.221	78.2	222.6	182.5
Hg Conc	RH	H ₂ S	AZ 431-X (a)	Genesis (b)	Nippon (a)	AZ 471 (b)	Tracker (b)	Genesis (b)
$\mu\text{g}/\text{m}^3$	%	ppm						
5	10	0.1	0.276	0.0	0.004	3.3	4.8	5.0
5	90	15	8.8.8	0.0	0.005	3.6	4.7	4.1
250	90	0.1	0.000	190.2	0.227	82.7	231.5	187.6
250	10	15	0.106	160.7	0.232	82.3	240.2	179.6

(a) Read-Out in mg/m^3 (b) Read-out in $\mu\text{g}/\text{m}^3$ **Table 7 – Primary effects for inorganic interferents**

Instrument	Primary variable effects					
	SO ₂ test		NO ₂ test		H ₂ S test	
	Hg*	SO ₂	Hg*	NO ₂	Hg	H ₂ S
AZ 431-X	190	-10	91	93	-89	-81
Genesis 1	173	-6	174	-3	175	15
Nippon EMP-1A	215	-8	212	4	225	3
AZ 471	73	-1	74	1	81	1
Tracker	239	0	222	-4	231	4
Genesis 2	188	6	178	-2	179	-5

All data in $\mu\text{g}/\text{m}^3$ Hg

Table 8 – Effect of Extended Lengths of Sampling Tubing

<i>Conditions of Test</i>	Mercury introduced to Instrument at	Hg Conc'n ($\mu\text{g}/\text{m}^3$)	Length of Tubing Added	Volume of Tubing		
		13	None	Zero		
Results of Test						
Rdg after...	AZ 431-X (a)	Genesis (b)	Nippon (a)	AZ 471 (b)	Tracker (b)	Genesis (b)
0.5 min	0.013	0.0	0.013	10.3	10.2	0.0
1 min	0.015	0.0	0.013	10.4	11.3	8.8
2 min	0.016	0.0	0.013	10.5	11.6	11.2
5 min	0.012	0.0	0.013	10.5	11.7	11.8
10 min	0.011	0.0	0.013	10.3	11.8	11.6
Sample Rate	0.9 L/min	0.2 L/min	0.8 L/min	2.0 L/min	1.15 L/min	0.2 L/min

<i>Conditions of Test</i>	Mercury introduced to Instrument at	Hg Conc'n ($\mu\text{g}/\text{m}^3$)	Length of Tubing Added	Volume of Tubing		
		13	5.0 M	8 cm ³		
Results of Test						
Rdg after...	AZ 431-X (a)	Genesis (b)	Nippon (a)	AZ 471 (b)	Tracker (b)	Genesis (b)
0.5 min	0.012	0.0	0.013	1.1	10.2	0.0
1 min	0.011	0.0	0.013	1.9	10.8	8.5
2 min	0.015	0.0	0.013	2.2	11.8	10.8
5 min	0.014	0.0	0.013	2.5	12.0	11.8
10 min	0.011	0.0	0.013	2.8	12.1	11.8
Sample Rate	0.9 L/min	0.2 L/min	0.8 L/min	0.2 L/min	1.15 L/min	0.2 L/min

<i>Conditions of Test</i>	Mercury introduced to Instrument at	Hg Conc'n ($\mu\text{g}/\text{m}^3$)	Length of Tubing Added	Volume of Tubing		
		13	10.0 M	16 cm ³		
Results of Test						
Rdg after...	AZ 431-X (a)	Genesis (b)	Nippon (a)	AZ 471 (b)	Tracker (b)	Genesis (b)
0.5 min	0.008	0.0	0.012	--	10.6	0.0
1 min	0.012	0.0	0.013	--	11.8	10.2
2 min	0.014	0.0	0.013	--	12.2	11.1
5 min	0.017	0.0	0.013	--	12.3	11.3
10 min	0.012	0.0	0.013	--	12.4	11.5
Sample Rate	0.9 L/min	0.2 L/min	0.7 L/min	0 L/min	1.15 L/min	0.2 L/min

(a) Read-Out in mg/m^3 (b) Read-out in $\mu\text{g}/\text{m}^3$

Table 9 – Experiments to Determine Rate of Recovery of Monitors after High Mercury Concentrations

Conditions of Test	After presenting $600 \mu\text{g}/\text{m}^3$ of mercury vapor to each monitor for 10 minutes, clean air was presented and instrument response recorded as a function of time.					
	Results of Test					
Rdg after ...	AZ 431-X (a)	Genesis (b)	Nippon (a)	AZ 471 (b)	Tracker (b)	Genesis (b)
	0.535	682.9	0.528	187	547.7	552.5
0.5 min	0.000	248.4	0.000	3.7	30.1	235.6
1 min	0.001	36.3	0.001	1.5	17.1	40.4
2 min	0.000	6.3	0.000	1.0	12.0	4.6
5 min	0.000	0.0	0.000	0.5	6.6	0.0
10 min	0.001	0.0	0.000	0.0	4.1	0.0

(a) Read-Out in mg/m^3 (b) Read-out in $\mu\text{g}/\text{m}^3$

Table 10 – Comparison of Monitor Specifics

	AZ 431-X	Genesis	Nippon	AZ 471	Tracker
Height (in)	4	6	8	8	6
Width (in)	6	7	4.5	6	10
Length (in)	13	10	10	19	17
Footprint (in^2)	78	70	45	114	170
Weight (lb)	6.9	9.2	7.3	15.0	14.0

	AZ 431-X	Genesis	Nippon	AZ 471	Tracker
Method	Gold Film Sorption	UV Absorbance	UV Absorbance	UV Absorbance	UV Absorbance
Lowest Reading	$0.001 \text{ mg}/\text{m}^3$	$0.1 \mu\text{g}/\text{m}^3$	$0.001 \text{ mg}/\text{m}^3$	$0.001 \mu\text{g}/\text{m}^3$	$0.1 \mu\text{g}/\text{m}^3$
Sample Rate	0.92 L/min	0.21 L/min	0.67 L/min	2.00 L/min	1.15 L/min
Warm-Up Time	1 min	20 min	20 min	20 min	3 min
Battery	internal	external slide-in	internal	internal	internal
Claimed Battery Life	6 hr	5-6 hr	8.5 hr	3 hr	6 hr
Recharge Time	14 hr	3 hr	3 hr	3 hr	10 hr
Run on AC	yes	no	no	yes	yes

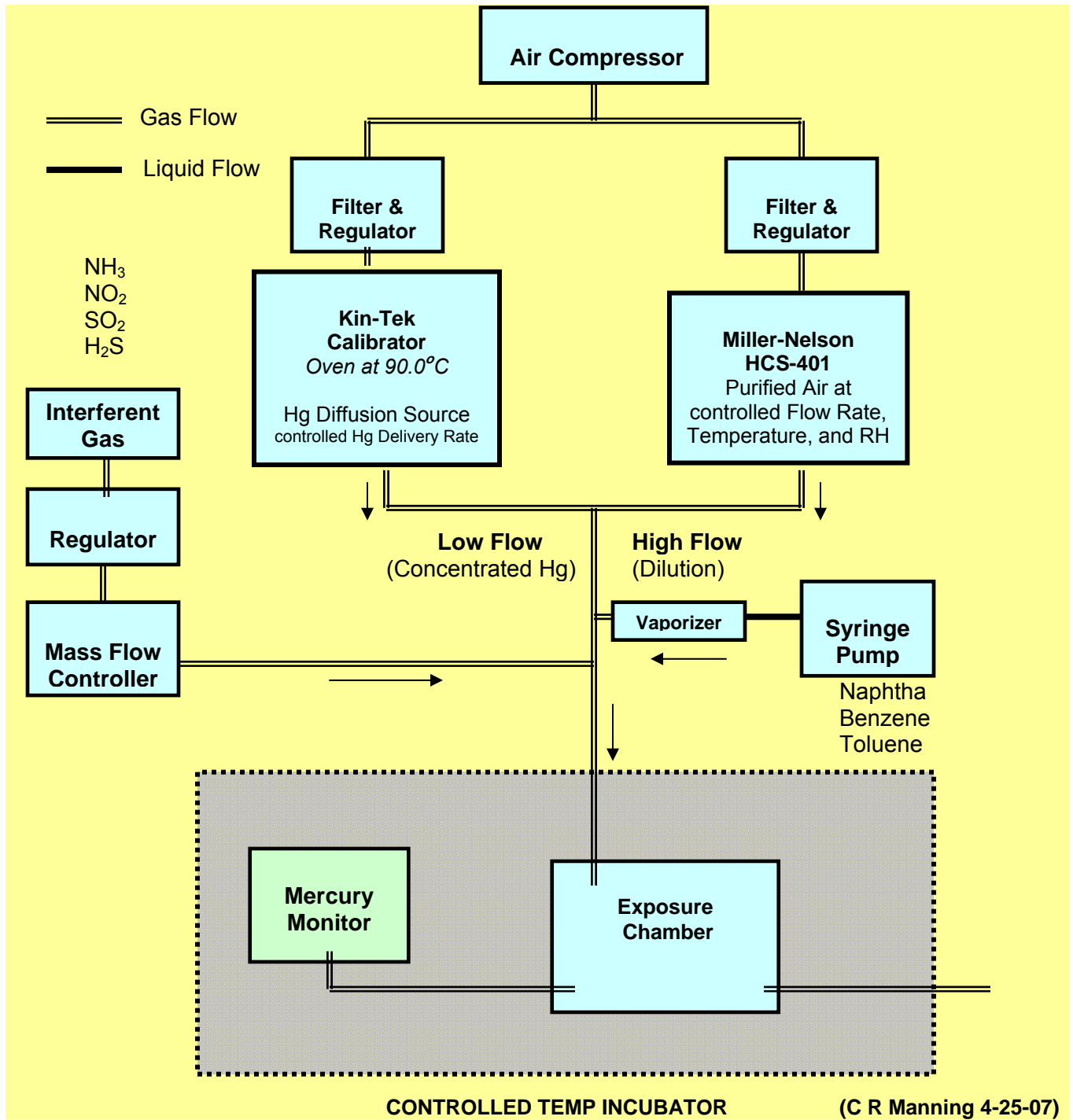


Figure 1 – Schematic of the test chamber set up

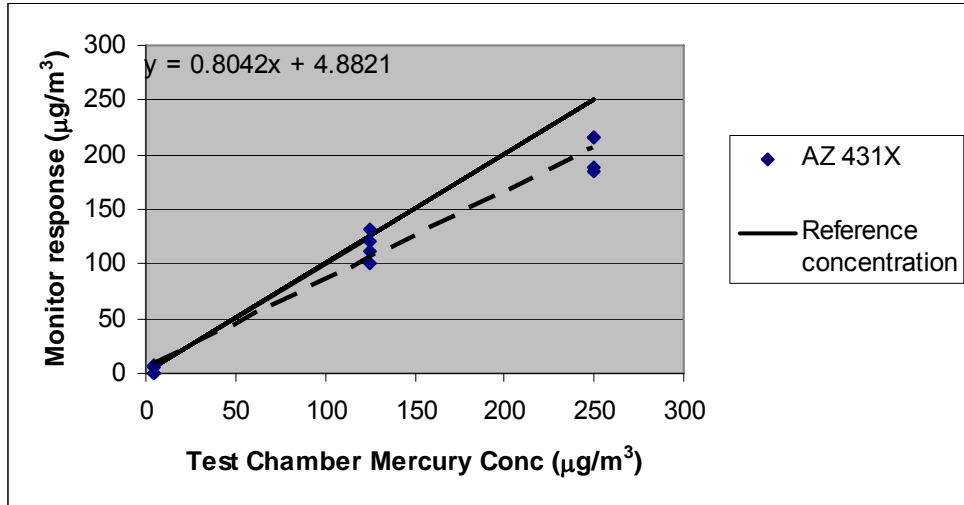


Figure 2 – AZ 431-X response curve

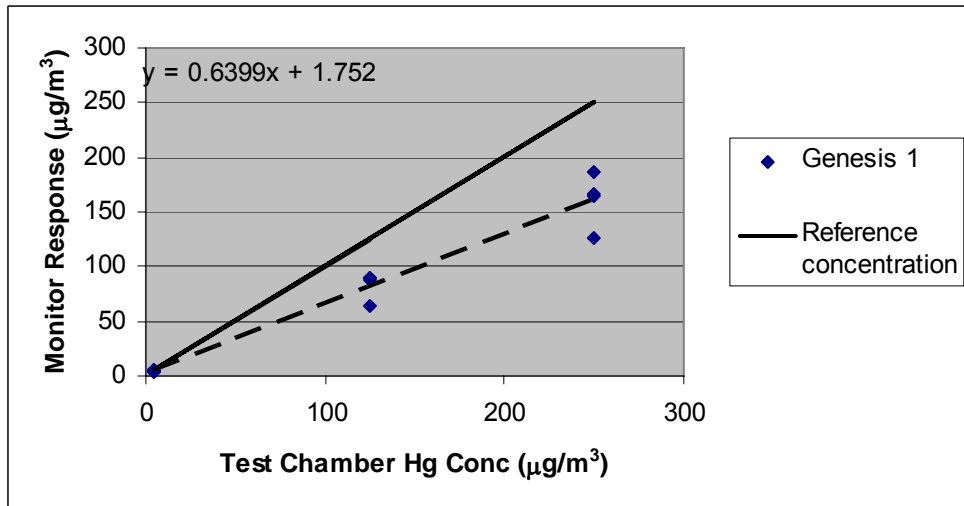


Figure 3 – Genesis 1 response curve

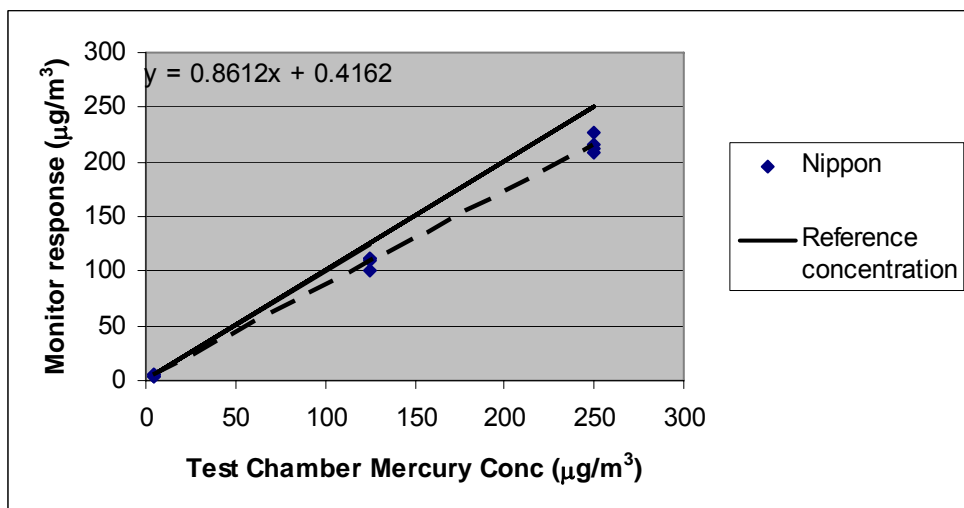


Figure 4 – Nippon response curve

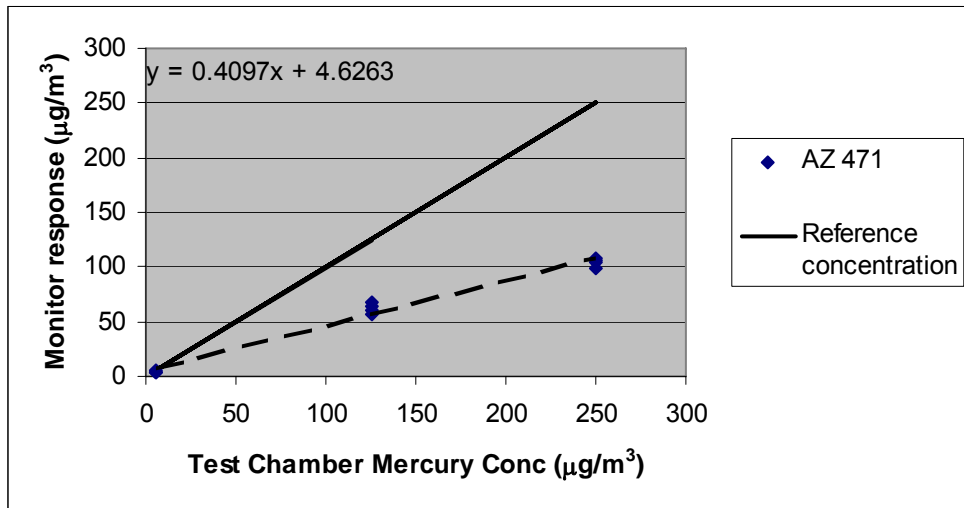


Figure 5 – AZ 471 response curve

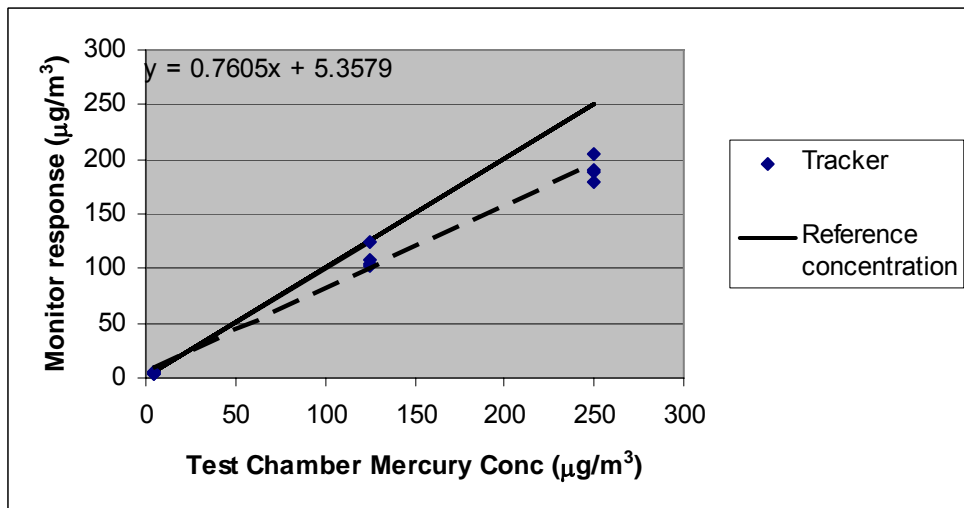


Figure 6 – Tracker 3000 response curve

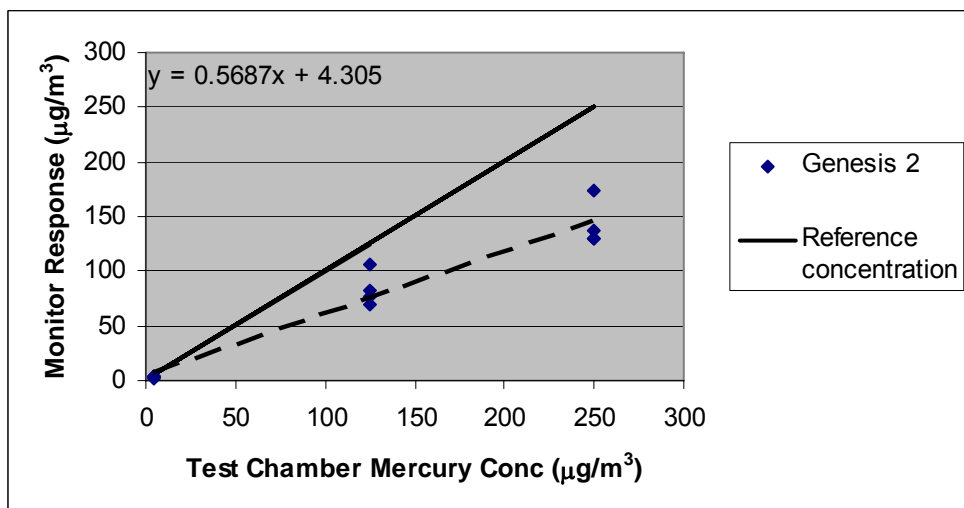


Figure 7 – Genesis 2 response curve

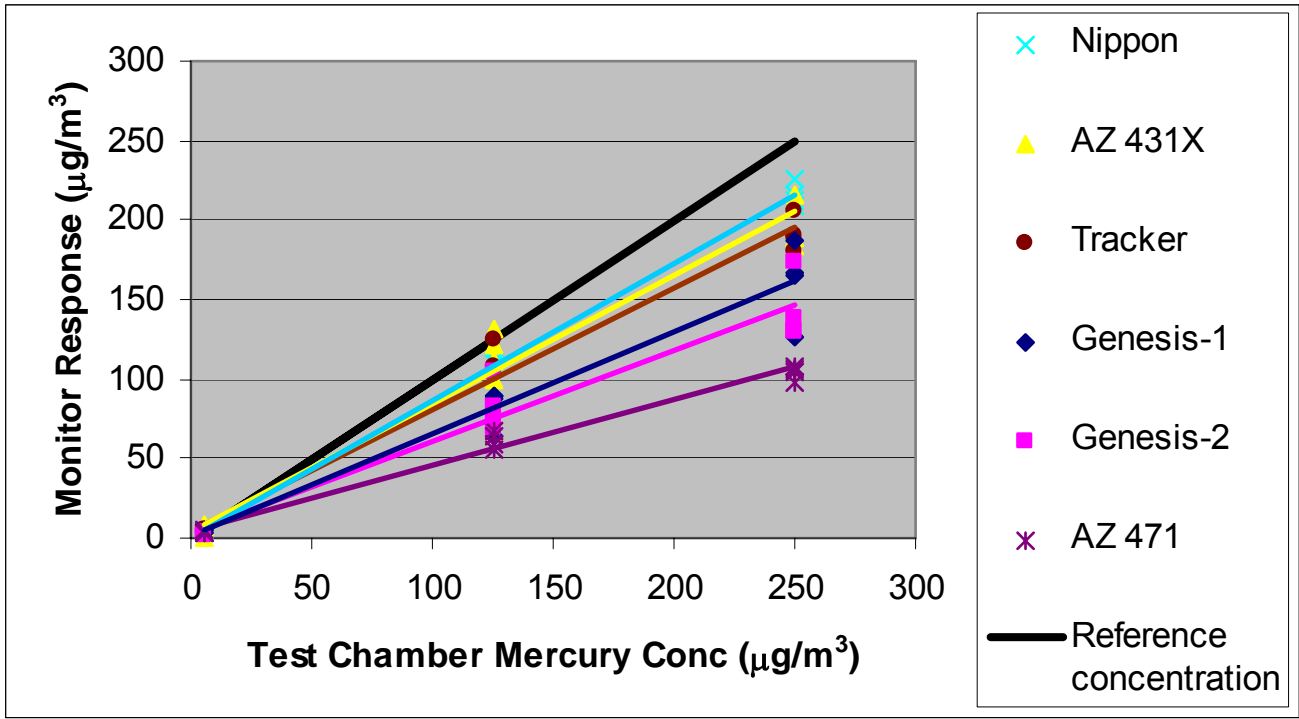


Figure 8 – Response curves for all monitors