Mercury Vapor Analyzers: Finding the Right Fit for Your Needs

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The toxic effects of mercury vapor on human health have been well documented throughout the years, and the Environmental Protection Agency (EPA) regulates and sets strict limits on the amount of mercury vapor which can be present in air: 1µg/m³ for residential properties, and 25µg/m³ for industrial properties. To ensure compliance with these regulations, industrial hygienists, clean-up crews and government agencies must rely on portable instrumentation to measure mercury vapor levels on site. There are many different technologies which can be used to detect mercury, and some may be more appropriate in certain environments than others. This paper will explain differences between gold film sensors, atomic absorption spectroscopy and atomic fluorescence spectroscopy, focusing on how these technologies work, what interferences they have and how sensitive they are to low levels of mercury vapor.

Gold Film Sensor Technology

How it works

Gold Film Sensors were the first reliable forms of mercury detectors due to gold’s affinity for elemental mercury. Arizona Instrument (AZI) took advantage of this affinity and coupled it with gold’s inherent electrical conductivity to create the Jerome 431 & J405 mercury vapor analyzers. If a mercury rich air sample is swept over a thin gold film, the mercury will deposit on the gold and change the electrical resistance of the foil. This change in resistance is directly proportional to the mass of mercury vapor taken from a known volume of air, which can be calculated in mg/m³. If the gold becomes saturated over time, the instrument offers a ‘regeneration’ feature that bakes the foil at an elevated temperature where the mercury deposits are vaporized and collected in the scrubber. The schematic below demonstrates how this works.

![Schematic](image)

Interferences

The ‘green’ box above represents the Acid Gas Filter, an activated carbon filter designed to remove hydrogen sulfide gas. Hydrogen sulfide (and mercaptans) along with ammonia and chlorine gas will react with the gold film and produce a false positive. However, along with the internal gas filter, several other external filters can be purchased from AZI to remove ammonia and chlorine gas if it ever poses a major interference without reducing the mercury concentration in your sample.

Jerome® J431 Gold Film Mercury Vapor Analyzer

Sensitivity

Arizona Instrument has been manufacturing its patented Gold Film Sensor mercury vapor analyzers for over 30 years, during which time the technology has proven to be effective for diverse applications.
and detection limits. The Jerome® J405 has many updates from the older 431 model, but both are useful for different detection limits. The J431 has a detection range from $3\mu g/m^3$ to $999\mu g/m^3$ with a resolution of $1\mu g/m^3$. This detection limit falls just short of the EPA residential specification but is well below the industrial specification of $25\mu g/m^3$. This instrument is better suited for industries concerned with exposing their employees and surrounding residents to harmful mercury vapor.

**Jerome® J405 Gold Film Mercury Vapor Analyzer**

The Jerome® J405 is our latest gold film analyzer, equipped with an on-board data logging (20,000 data point storage) system and an optional USB data communication port. The J405 has a detection range from $0.5\mu g/m^3$ to $999\mu g/m^3$ with a resolution of $0.01\mu g/m^3$. This newest model of gold film MVA allows you to adhere to both industrial and commercial mercury regulations because it can read below $1\mu g/m^3$. Both units offer continuous modes for surveying potential hot spots in the field, and are robust enough to withstand daily use in challenging environments.

**Environments of Likely Interferences**

Gold film interferences include hydrogen sulfide, ammonia and chlorine, however internal and external filters are available to remove these chemicals from interfering with your analysis. One potential environment where gold film would not be ideal is an environment rich in both ammonia and chlorine. Since only one external filter can be used during analysis it would be difficult to measure mercury without a getting a signal from either the ammonia or chlorine. Another potential environment not suitable for gold film would be an environment completely void of oxygen. The gold film sensor requires the presence of some oxygen to be effective. Since most industrial hygienists are measuring in environments where personnel could be exposed, it is unlikely that any environment would void of oxygen.

**Atomic Absorption Spectroscopy**

**How it works**

Cold Vapor Atomic Absorption Spectroscopy (CVAAS) is another method used for mercury detection. In mercury CVAAS, a light source of known wavelength and intensity (~$254nm$, middle ultraviolet spectrum) is radiated through a sample of air where the light eventually encounters a detector. If mercury is present, electrons from within the mercury atoms will absorb some of this energy from the light source. The difference between the initial energy of the light source and the energy measured by the detector gives you an indirect measurement of how many mercury atoms were present. The schematic below demonstrates the path of the radiated light. Several mirrors and photo multiplier tubes (PMTs) are used to amplify the signal difference.

**Indirect method relies on how much energy was absorbed**

**Interferences**

Unfortunately, atomic mercury in CVAAS is not the only chemical species to absorb this wavelength. Many other substances can also absorb this
wavelength and produce false positive readings. The chart below lists a handful of some of the known interferences for CVAAS. It is important to note that 'hydrocarbons' is a very broad description of many different forms of organic compounds.

<table>
<thead>
<tr>
<th>CVAAS Interferences</th>
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<tbody>
<tr>
<td>Inorganic</td>
<td>Organic</td>
</tr>
<tr>
<td>Chloride/chlorine</td>
<td>Dust</td>
</tr>
<tr>
<td>Sulfides</td>
<td>Smoke</td>
</tr>
<tr>
<td>Copper</td>
<td>Hydrocarbons *</td>
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<tr>
<td>Tellurium</td>
<td>Some Organic Solvents</td>
</tr>
<tr>
<td>Hydrocarbons *</td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>Acyclic Hydrocarbons</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>Polycyclic Aromatics</td>
</tr>
<tr>
<td>Toluene</td>
<td>Petroleum Hydrocarbons</td>
</tr>
<tr>
<td>Xylene</td>
<td></td>
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</tbody>
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Along with these interferences, the reflective mirrors could also become dislodged, soiled by material condensation (including humidity) or degraded by surface corrosion.

**Sensitivity**

Because atomic absorption spectroscopy measures on the atomic level, the sensitivity range is lower. Portable mercury CVAAS analyzers such as the Nippon® EMP-2 and the Lumex® 915 M claim to offer a low-end sensitivity of 0.1µg/m³ and 0.002µg/m³ (respectively), both of which fall below the EPA regulations for residential specifications. However, with positive interferences being such a problem for CVAAS it is more than likely the instruments will be analyzing chemical species other than the intended mercury vapor (especially at that low level). If the readings are taking place in a clean and dry environment, more merit could be given to the results. However, most environments where mercury vapor analysis is required (laboratories, landfills, industrial chemical facilities) are rarely void of the interferences listed. Moreover, the delicate placement of the internal mirror system may not be robust enough to be brought into hazmat situation.

**Environments of Likely Interferences**

When using atomic absorption spectroscopy to detect low levels of mercury contamination, it is imperative that your instrument is detecting a true signal and not just 'noise' from other chemical species. An example of a common low-level mercury analysis application is the process of decommissioning laboratories and hospitals. These old buildings have been usually been abandoned for many months or years and have collected a fair amount of dust and construction debris. Before demolition can begin, the entire square footage of the building must be below a certain limit of mercury vapor. It is difficult to confidently measure low-end mercury vapor over dust and smoke if the environment you are sampling from is substantially contaminated with these particulates in the air.

Mercury analysis in the petroleum processing industry is also quite common. Industrial hygienists must monitor the naturally occurring mercury levels emanating from crude oils wells and processing plants. Common interferences with low-level mercury analysis using atomic absorption in this industry are petroleum hydrocarbons. Crude oil aromatic hydrocarbon vapors along with the toluene/xylene co-solvents used in processing are major sources of interferences for atomic absorption spectroscopy. Many double bonds and resonance electron structures within these hydrocarbons absorb ultraviolet light and would be read as a mercury vapor. Because of these interferences, atomic absorption spectroscopy is not a suitable fit for mercury vapor analysis in this industry.

**Atomic Fluorescence Spectroscopy**

**How it works**

Atomic fluorescence and absorption are two terms that are related but have two different meanings. Cold Vapor Atomic Fluorescence Spectroscopy (CVAFS) is an improvement upon the traditional CVAAS. When a mercury atom absorbs the energy
from the UV wavelength, an electron transitions from a stable ground state to an unstable ‘excited’ state. This excitation event describes the atomic absorption as discussed in the previous section. However, when the energy source is removed the excited electron returns to its ground state. In doing so, a photon of light is emitted during the loss of potential energy. This fluorescence of light is often unique for various chemical species. Mercury in particular absorbs light at 254nm and fluoresces light at the same wavelength. Because the light absorbed and emitted are at the same wavelength, this form of fluorescence is referred to as resonance fluorescence. Other chemicals such as chlorides, sulfides and hydrocarbons absorb light at 254nm but either do not fluoresce or fluoresce at a different wavelength.

Arizona Instrument took advantage of the unique resonance fluorescence of mercury to detect ultra-low concentrations of mercury vapor while minimizing the interferences involved with atomic absorption alone. The Jerome® J505 Atomic Fluorescence Spectroscopy Mercury Vapor Analyzer is the first hand-held instrument of its kind. Although other chemical species may still absorb the energy from the light source, the J505 only detects the specific wavelength that is fluoresced radially from an air sample. The amount absorbed is inconsequential because the mercury concentration is revealed by the amount of light fluoresced at a 90° degree angle. This technology is a more direct method of analysis since the instrument is quantifying individual photons of excited mercury atoms in a sample. The diagram below outlines how this done without having to amplify the signal through a series of mirrors.

Direct method relies on how much energy was fluoresced

Interferences

Because the J505 only measures radial resonance fluorescence of 254nm, only a chemical species that is excited at 254nm and then fluoresces at 254nm will be measured. This stringent criteria eliminates nearly all sources of interferences ensuring you get accurate and repeatable results in the field. The only positive interference ever to be reported is a high concentration of acetone vapor. Fortunately, most areas of potential mercury contamination are void of such levels of acetone vapor.

Sensitivity

The J505 has a detection range from 0.05µg/m³ to 500µg with a resolution of 0.01µg/m³, which is well below the EPA, OSHA, and NIOSH standards for ultra-low mercury vapor specifications. Moreover, the J505 does not share any common interferences with traditional CVAAS technologies. The J505 is a robust analytical tool that can be used in a variety of fields. There are no amplifying mirrors like the CVAAS units and unlike the gold film sensor instruments, no regeneration is ever required. The instrument stores
up to 10,000 tests on its internal memory board, which can easily be downloaded from a USB port. Like the J405, one time or continuous sampling can be performed on the instrument to aid in searches for hot spots of contamination.

**Environments of Likely Interferences**

Atomic fluorescence spectroscopy selects for a very narrow criteria of chemical species that can absorb and fluoresce at the 254nm wavelength. Industries which use large quantities of acetone as a solvent could potentially present environments in which the J505 might have difficulty exclusively detecting mercury vapor. Such environments could potentially be encountered in certain types of chemical processing plants or paints and coatings settings.

**Conclusion**

Arizona Instrument takes pride in the instruments we manufacture and wants to educate our current and future customers on what form of analysis might be appropriate for their needs. In this paper we covered three very different technologies of mercury vapor analysis. Gold film is a proven, reliable form of low and high-end mercury detection with few interferences (hydrogen sulfide, chlorine, and ammonia). However, each of these interferences can be filtered away without changing the accuracy of your results. The indirect detection of atomic absorption spectroscopy was shown to be useful at ultra-low levels of mercury analysis, but with many different types of interferences that cannot be filtered. This form of analysis raises the question: if there are so many potential interferences, how can you sure your signal is really mercury? The solution to this problem was designing an instrument with very strict parameters for mercury analysis. Utilizing the unique resonance fluorescence of mercury, the Jerome® J505 is able to directly measure mercury atoms during their excitation phase. Not one method is perfect, but an understanding of how the available technologies behave differently in your unique application setting will be a key factor in making the decision that is right for you.
Appendix: Mercury Vapor and Human Health

Elemental mercury (Hg) is the only metal on the periodic table that remains in its liquid phase under standard temperature and pressure (STP); giving it the appropriate nickname of ‘quicksilver’. Many of us may envision this form of mercury as this shiny silver puddle evading capture, but mercury can be found in many other forms in our everyday lives. Fluorescent lighting, antique switches, dental fillings and thermometers are just a handful of items that contain the toxic metal, not to mention its many uses in industrial processing (chlorine, cement, and gold purification). Most of these items are sufficient at sequestering or minimizing the exposure of the dangerous metal, but accidents can and do happen. Thermometers break, old bulbs and switches are crushed in landfills, and industrial mercury incidences can occur. So why is it so bad for us to be exposed to this metal?

Elemental mercury has an unusually high vapor pressure for a metal (0.0018 mm Hg) at room temperature which corresponds to approximately 2.4 part per million. Studies have shown that skin contact and ingestion are dangerous methods of exposure, but inhalation of mercury vapor is perhaps the most lethal form of absorption. Symptoms of mercury exposure include seizures, dementia, and in some cases even death. Because of these risks, several guidelines and regulations have been developed to limit the amount of mercury people can be exposed to along with special methods for cleaning up mercury if an accident should occur. Currently, the time weighted average limit for mercury varies depending on regulating agency. For OSHA, the limit is 0.1mg/m³; NIOSH sets the limit at 0.05mg/m³; while ATSDR sets its limit at 0.001mg/m³. Because these agencies all differ in application and exposure limit, the environmental protection agency (EPA) has a standard minimum limit of mercury exposure to 1µg/m³ for residential and 25µg/m³ for industrial properties.