

Mercury Vapour Analysers: Finding the Right Fit for Your Needs

The toxic effects of mercury vapour on human health have been well documented throughout the years.



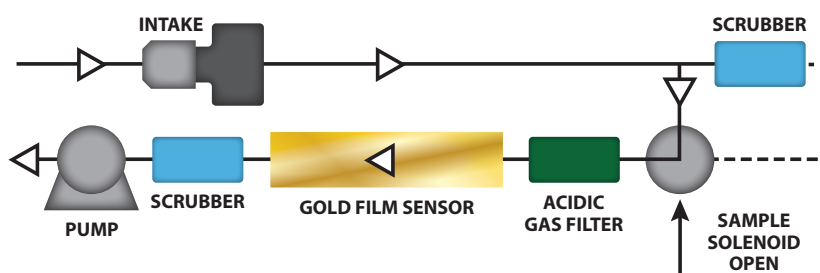
Agencies such as the Environmental Protection Agency (EPA) regulate and set strict limits on the amount of mercury vapour which can be present in air: $1\mu\text{g}/\text{m}^3$ for residential properties and $25\mu\text{g}/\text{m}^3$ for industrial properties. To ensure compliance with these regulations, industrial hygienists, clean-up crews and government agencies rely on portable instrumentation to measure mercury vapour 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 three different methods of mercury detection: gold film sensors, atomic absorption spectroscopy and atomic fluorescence spectroscopy. Gold film sensors were the first truly reliable instruments for lo and high-end

mercury detection with few interferences that can be filtered, while atomic absorption spectroscopy is useful for low level mercury analysis but has many different types of interferences that cannot be filtered. Atomic fluorescence spectroscopy, the most common method used in benchtop mercury analysis, is by far the most reliable with its strict parameters for mercury analysis. By focusing on how these different technologies work, what interferences they have and how sensitive they are, you will gain insight into which method of mercury detection would be most suitable for your unique application. Gold Film Sensor Technology.

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. Coupling this affinity with gold's inherent electrical conductivity, Arizona Instrument created the Jerome 431 & J405 mercury vapour analysers. When a mercury rich air sample passes over a thin gold film, the mercury deposits on the gold and changes the electrical resistance of the foil. This change in resistance is directly proportional to the mass of mercury vapour taken from a known volume of air, which can be calculated in mg/m^3 . If the gold becomes saturated over time, the instrument offers a regeneration feature that bakes the foil at an elevated temperature at which the mercury deposits are vaporized and collected in the scrubber. The schematic below demonstrates how this works.



Registered Address

ABLE Instruments & Controls Ltd
Cutbush Park, Danehill, Lower Earley,
Reading, Berkshire, RG6 4UT. UK.

Reading

Tel: +44 (0)118 9311188 | Email: info@able.co.uk

Aberdeen

Tel: +44 (0)1224 725999 | Email: ab@able.co.uk

Web

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The green box above represents the Acid Gas Filter, an activated carbon filter designed to remove hydrogen sulfide gas. Hydrogen sulfide, mercaptans and 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 that have the ability to remove ammonia and chlorine gas without reducing the mercury concentration in your sample.

Jerome® 431 Gold Film Mercury Vapour Analyser

Arizona Instrument LLC has been manufacturing its patented Gold Film Sensor mercury vapour analysers 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 431 has a detection range from $3\mu\text{g}/\text{m}^3$ to $999\mu\text{g}/\text{m}^3$ with a resolution of $1\mu\text{g}/\text{m}^3$. Although this detection limit falls just short of the EPA residential specification, it is well below the industrial specification of $25\mu\text{g}/\text{m}^3$. This instrument is well suited for industries concerned with exposing their employees and surrounding residents to harmful mercury vapour.

Jerome® 431 Gold Film Mercury Vapour Analyser

Jerome® J405 Gold Film Mercury Vapour Analyser

The Jerome® J405 is the latest gold film analyser from Arizona Instrument. It is equipped with an on-board data logging system that can store up to 20,000 data points and has an optional USB data communication port.

The J405 has a detection range from $0.5\mu\text{g}/\text{m}^3$ to $999\mu\text{g}/\text{m}^3$ with a resolution of $0.01\mu\text{g}/\text{m}^3$. Because it can read below $1\mu\text{g}/\text{m}^3$, the J405 allows you to adhere to both industrial and commercial mercury regulations. Both the 431 and J405 offer continuous modes for surveying potential hot spots in the field and are robust enough to withstand daily use in challenging environments.



Jerome® J405 Gold Film Mercury Vapour Analyser

Environments of Likely Interferences

Gold film interferences include hydrogen sulfide, ammonia and chlorine. However, both internal and external filters are available to prevent these chemicals from interfering with your analysis. One potential environment in which 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 in this environment without getting a signal from either the chemical that is not being filtered out. Another potential environment that may not be suitable for gold film sensing technology is one that is completely void of oxygen. Gold film sensors require the presence of some amount of oxygen to be effective. Since most industrial hygienists are measuring in environments where personnel could be exposed, it is unlikely that any environment being tested would be completely void of oxygen.

Atomic Absorption Spectroscopy: How it works

Cold Vapour Atomic Absorption Spectroscopy (CVAAS) is another method used for mercury detection. In mercury CVAAS, a light source of known wavelength and intensity ($\sim 254\text{nm}$, 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 initially present. The schematic below

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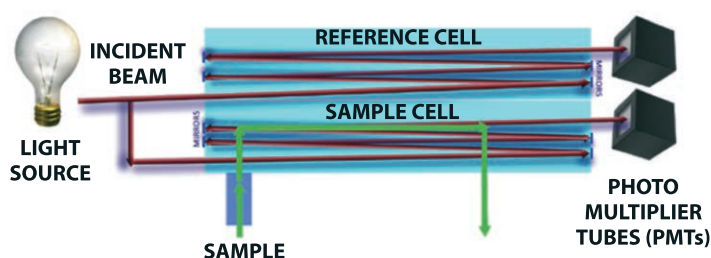
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demonstrates the path of the radiated light. Several mirrors and photo multiplier tubes (PMTs) are used to amplify the signal difference.



Indirect method relies on how much energy has 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 the known interferences for cold vapour atomic absorption spectroscopy. It is important to note that, in this case, 'hydrocarbons' is a very broad description of many different forms of organic compounds that can cause interferences.

CVAAS Interferences	
Inorganic	Organic
Chloride / Chlorine	Dust
Sulphides	Smoke
Copper	Hydrocarbons*
Tellurium	Some Organic Solvents
Hydrocarbons*	
Benzene	Acyclic Hydrocarbons
Ethylbenzene	Polycyclic Aromatics
Toluene	Petroleum Hydrocarbons
Xylene	

Along with these interferences, it is also possible for the reflective mirrors to 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 analysers 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 that the instruments will be analyzing chemical species other than the intended mercury vapour, especially at that low level. If the readings take place in a clean and dry environment, more merit can be given to the results. However, most environments that require mercury vapour analysis – 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 used in a 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. When old buildings are abandoned for an extended period of time, they tend to collect 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 vapour. It is difficult to confidently measure low-end mercury vapour over dust and smoke if the environment in which you are sampling is substantially contaminated with these particulates.

Mercury analysis in the petroleum processing industry is also quite common. Industrial hygienists must monitor the naturally occurring mercury levels emanating from crude oil wells and processing plants. Common interferences with low-level mercury analysis using CVAAS 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

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resonance electron structures within these hydrocarbons absorb ultraviolet light and would be measured as a mercury vapour. Because of these interferences, atomic absorption spectroscopy is not a suitable fit for mercury vapour analysis in this industry.

Atomic Fluorescence Spectroscopy: How it works

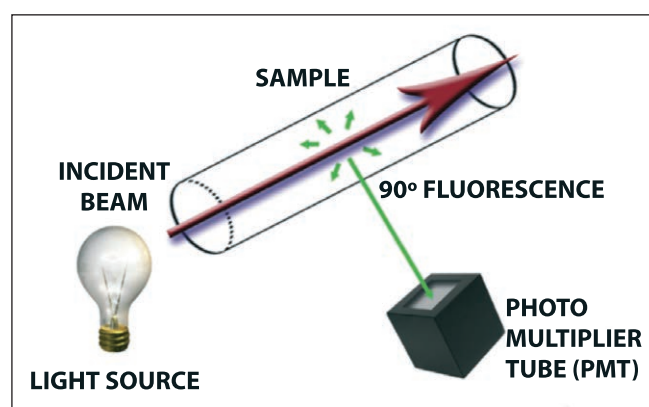
Although atomic fluorescence and atomic absorption are related, they really have two very different meanings. Cold Vapour Atomic Fluorescence Spectroscopy (CVAFS) is an improvement upon the traditional CVAAS. When a mercury atom absorbs the energy from the UV wavelength, an electron transitions from a stable ground state to an unstable 'excited' state. This excitation event describes 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.

Jerome® J505 Atomic Fluorescence Spectroscopy Mercury Vapour Analyser

The Jerome® J505 Atomic Fluorescence Spectroscopy Mercury Vapour Analyser is the first hand-held instrument of its kind. Utilizing the unique resonance fluorescence of mercury, Arizona Instrument designed an instrument that can detect ultra-low concentrations of mercury vapour while minimizing the interferences involved with atomic absorption alone.

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 is done without having to amplify the signal through a series of mirrors.



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 vapour. Fortunately, most areas of potential mercury contamination are void of such levels of acetone vapour.

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 vapour 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 such as in CVAAS units and,



**Jerome® J505
Atomic Fluorescence
Spectroscopy Mercury
Vapour Analyser**

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Cutbush Park, Danehill, Lower Earley,
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Reading

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Aberdeen

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unlike 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 and the 431, the instrument can perform one time or continuous sampling to aid in searching 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 in which large quantities of acetone are used as a solvent could potentially present environments in which the J505 might have difficulty exclusively detecting mercury vapour. 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 used to perform mercury vapour 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 be 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 Vapour 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 vapour pressure for a metal (0.0018 mm Hg) at room temperature which corresponds to approximately 2.4 parts per million (ppm). Studies have shown that skin contact and ingestion are dangerous methods of exposure, but inhalation of mercury vapour is perhaps the most lethal. 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.

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