



Metal Hydride Gas Cylinder Leakcheck July 2022

In the US the DOT regulations 49CFR§ 173.24 General requirements for packagings, state that compressed gas cylinder cannot be shipped if it is leaking

(b) Each package used for the shipment of hazardous materials under this subchapter shall be designed, constructed, maintained, filled, its contents so limited, and closed, so that under conditions normally incident to transportation -

(1) Except as otherwise provided in this subchapter, there will be no identifiable (without the use of instruments) release of hazardous materials to the environment;

To comply with this regulation, the most common leak test method used by compressed gas companies is a soap solution which can be sensitive to 10^{-5} cc/sec leak. Note that sensitivity is lower for water soluble gases.



Fig. 1: 3.2×10^{-5} cc/sec (after 5+ minutes)

Other methods include hydrochloric acid vapors that are sprayed at an ammonia cylinder valve or ammonia vapors at a hydrogen chloride cylinder valve. In both cases dense white ammonium chloride fumes would be created if there is a leak. For phosgene, DOT (173.192 Packaging for certain toxic gases in Hazard Zone A, (C)(3)) requires the cylinder to be immersed in a heated water bath and observed for bubble formation over a period of 30 minutes.

The Electronic Specialty Gas (ESG) industry is concerned with leaks from the metal hydride gases such as diborane that are highly toxic and/or pyrophoric. These gases have been involved in numerous and significant incidents caused by leakage during transit. Many have TLV's that



are much less than 1 ppm. Detection of leaks at these levels requires the use of chemical specific electronic devices.

The Electronic Specialty Gas (ESG) industry does not have a standard procedure to leak test cylinders after they are filled. NFPA 318 “Standard for the Protection of Semiconductor Fabrication Facilities”, 2022 edition 7.1.2 requires a leak test of a cylinder before it is offloaded from the transport vehicle at the user site. There is no requirement on how this is to be done.

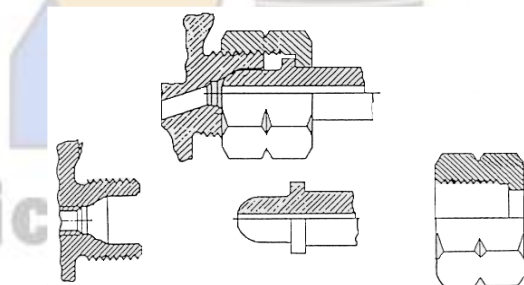
Gas Leakage

All mechanical fittings such as the tapered thread of a cylinder valve inserted into the cylinder will leak at a certain rate. In many cases these are too small to easily measure.

Gas leakage is commonly measured at cc/sec which is expressed as a power of ten

- 0.1 cc/sec is 1×10^{-1}
- 0.01 cc/sec is 1×10^{-2}
- 0.00003 cc/sec is 3×10^{-3}

Metal connections that are repeatedly used such as the standard CGA 350 connection used for Germane or Silane is not capable of routinely providing such a high leak integrity. This bullet connection relies on a nut mechanically compressing a metal nipple into the valve outlet connection. The gas seal is formed by deformation of the nipple and/or outlet connection. The surfaces over time will become scratched and may not be capable of providing a high leak integrity connection. Stainless steel surfaces are more prone to this as they will work harden each time it is deformed, making it more difficult to seal. Leak rates for the connection after repeated use is typically 10^{-5} cc/sec.



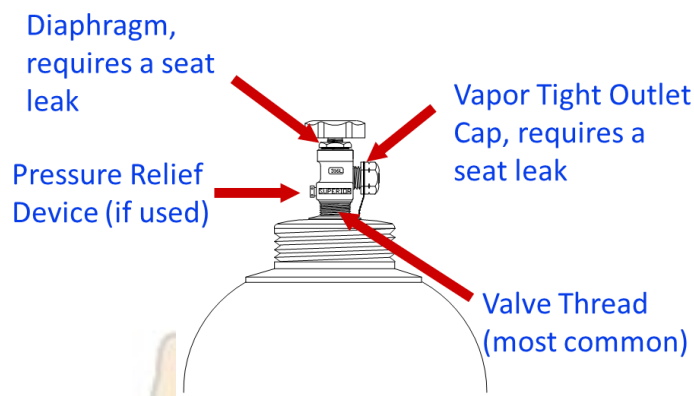
CGA 350 Outlet Connection, Bullet

High integrity mechanical systems which have polished face seal metal flanges and replaceable metal gaskets (VCR and DISS) have reduced these leak rates to 10^{-9} to 10^{-11} cc/sec (0.029 to 0.00029 cc's of gas per year).

1×10^{-10} cc/sec leakrate of a metal hydride gas is non detectable (<5 ppb) with MDA Paper tape systems that are sampling the air at a precise flow rate.

Cylinder leakcheck

It is difficult to properly leak check a cylinder using an electronic leak detector as there are numerous leak points on a cylinder valve. For maximum sensitivity the gas probe must be positioned and held over the leak point for >10 secs. This is difficult to do around the 2 most likely leak points, cylinder valve threads and the valve outlet.



Cylinder leak Points

To assist in this effort, many companies will use a plastic bag to envelop the entire valve to accumulate any leakage over a period of time. This will not only capture the leakage from any point but will also increase the sensitivity.



Bagging Cylinder Valves for Leak testing

To protect the valve from contamination, many gas suppliers will bag the valve. This will accumulate any leakage during transit.



Cylinder Valve Bagged and Wire Shut

Some leaks will be so small that there will be no visual indication. The silane leak below had no visible indication, white SiO_2 solids or smoke. It was detected during an incoming leak test at 6.7 ppm. To confirm this soap solution was applied to the valve threads. This accumulated the leak into a bubble that burst periodically causing a finger of a flame



Soap Solution Gathered The Leak Into bubble that Popped when the Bubble burst

Valve Crossport Leaks

If a cylinder valve is not closed tight enough, gas can leak across the soft valve seat. During the 1970's a number of incidents occurred during transit when the cylinder valve loosened. Silane (Union Carbide) explosion of railcar, Asia Freighter Arsine acute exposure of 10 crewmen (Air Products). Testing after these incidents revealed the potential for cylinder valves to vibrate open during certain handling conditions. The gas industry implemented a best practice of wiring the cylinder valve handwheel shut to prevent this from happening. DOT also mandated the use of a vaportight outlet cap for pyrophoric and toxic gases to act as a secondary seal.

Gases such as

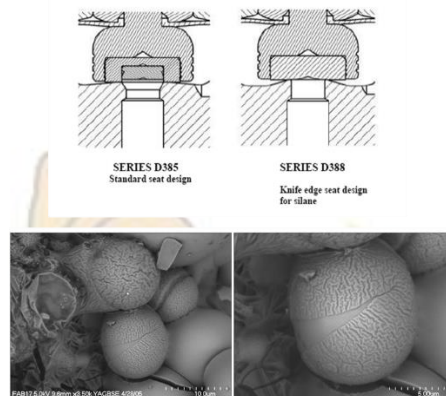
Diborane

Disilane

Silane

Trimethylboron

React with moisture or oxygen to form solid byproducts which can be trapped under valve seats or sealing surfaces causing small leaks across the seat.



Solids Embedded In Soft valve Seat

A silane cylinder valve seat with 1×10^{-6} cc/sec seat leakage will pressurize the vaportight outlet cap to 110 psig in 3 months. When the vapor tight cap is loosened this can “pop”



Silane “Popper”

In the worst case, explosions with an overpressure of 128 db have been measured at a distance of 30’ outdoors. In the past this was a common event, now with better valve design and system purging the probability is low. More sensitive leak testing of the valve outlet further reduces



the probability. Needless to say that when this now happens, a user will initiate an Emergency Response and expect the gas supplier to deal with the cylinder as an ER.

For the highly toxic gases, the users will typically use a gas leak detector to sample the vapor tight outlet cap as it is loosened in the gas cabinet. Any detection will trigger a Emergency Response.

Cylinder Valve Thread Leaker

The most likely leak is from the cylinder valve threads. These are. If the threads of the valve and the cylinder are not perfectly matched, a delayed leaker can occur because the cylinder pressure “cold” flows the PTFE tape or paste which are used to lubricated the NGT are tapered threads during valving. These can occur up to a month after valving. In 1991 a valve and cylinder thread mismatched caused leakage with Arsine cylinders and a recall of hundreds of cylinders worldwide. Some customers required an ER team with an ERCV to pickup the cylinder, these areas were evacuated and shutdown during this time.

Solkatronic Leak Check Cap

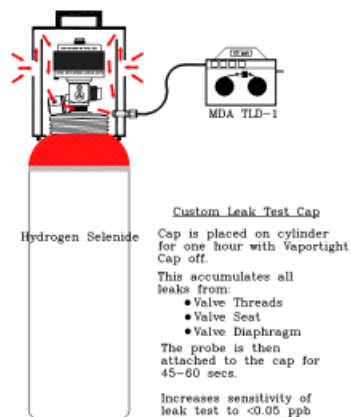
In early 1990's an Arsine cylinder from Solkatronic Morrisville, PA was shipped to a customer in St. Paul, MN. Since it was a small cylinder (2 liter) it was packaged in a cardboard box. As part of their receiving procedure the customer poked a hole in the box and sampled the internal volume using a metal hydride leak detector. There was a positive response of >100 ppb. An immediate evacuation of the R&D facility of >1,000 people occurred. Fire and Police Depts were dispatched to secure the site.

A ER team was dispatched from Solkatronic with ER Equipment. They confirmed the detection but when they removed the cylinder they could not detect a leak using the most sensitive leak detector available (5 ppb). It was not until a plastic bag was placed over the valve for a period of time that a detection occurred.

After this incident, I designed a metal leak check cap that could be easily placed onto a cylinder. I required that it be used to leak test any metal hydride gas shipment. This was placed on the cylinder with the vaportight cap removed for one hour. The air was then sampled. Any detection was cause for rejection. The Arsine cylinder from the incident had a detection of 50 ppb after 30 minutes. It was retained for over 10 years for use as a “calibrated” leaking cylinder and was used to periodically test the method.

Metal Hydride Gas Leak Check Cap

- Accumulates any leak for 60 minutes which will increase the sensitivity of the leak test from ppb to ppt
- Will detect a leak from any potential leak point
 - Valve Threads
 - Outlet Cap/Valve Seat
 - Valve Diaphragm



Jan 2015

Gas Detection

All Solkatronic and distributor locations worldwide had 20-30 of these caps for routine leaktesting of Metal Hydride gas cylinders. These were easy to use and very sensitive to leaks. (ppt)

An ISO container with a group of Arsine cylinders from Solkatronic arrived in at the distributor in Taiwan in 2000. During their incoming leak testing no leakage was found yet a few cylinder valves and collars were coated with a black deposit (elemental Arsenic). Leakage of a small amount of AsH_3 reacted with the moisture in the air decomposing it into elemental arsenic.

The leak check cap was used and after an hour a concentration of 50+ ppb was detected for the cylinders. This triggered an ER which required a US based team to fly to Taiwan and empty the cylinders.



Leak of Arsine over a 3 month period decomposing to Black Arsenic

These types of leaks are minute and do not present a potential exposure and safety problem however many users are very conservative, any detection will trigger an immediate ER. Many users have a protocol to seal the cylinder cap vent hole when the cylinder is received. After some period of time they sample the cylinder cap.

Sometimes despite all of the testing the cylinder can leak. The following 20% AsH₃/H₂ mixture valve had a double failure. It leaked across the valve seat and the vaportight cap into the plastic bag. Reaction with the moisture and air formed the yellow solids.



Leak Through Valve Seat and Outlet Cap, 20% AsH₃/H₂ Mixture

Gas Supplier Metal Hydride Gas Leaktest Method

The current leak test method at another gas supplier is to place a plastic bag over the cylinder valve with the vaportight outlet cap removed. A piece of MDA Hydride tape is placed inside the bag. It is not known how sensitive this method is. It is not as sensitive as the Solkatronic Leak



Check cap nor as precise. While leaks have been found using this method, additional information is not available to evaluate the effectiveness.

Customers receiving metal hydride gases have an expectation that there will be no leakage under any condition. Their SOP's require them to leakcheck prior to offloading from a truck using the most sensitive leak test method available. Some of their methods will be similar to the bagging that is currently done at many gas suppliers.

A handwritten signature in black ink that reads "Eugene Ngai".

Eugene Ngai

