REPORT:

A3.1.2: Review of valves currently used on cylinders for hydrogen sampling

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Summary

This report was written as part of activity 3.1.2 from the EMPIR Metrology for Hydrogen Vehicles 2 (MetroHyVe2) project. The three-year European project commenced on 1st August 2020 and focused on providing solutions to four measurement challenges faced by the hydrogen industry (flow metering, quality assurance, quality control, sampling and fuel cell stack testing). For more details about this project please visit website address.

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Contents

1. Introduction

The quality of the hydrogen fuel from hydrogen refuelling stations (HRSs) can be monitored using two sampling techniques. These are by online sampling (or continuous monitoring) and offline (or spot) sampling [1][2]. Continuous monitoring does not use sampling vessels and will not be discussed in this report.

Offline sampling at an HRS is when a sample of the hydrogen fuel is taken from the HRS and stored in a sampling vessel before being sent to an analytical laboratory for analysis. The sampling vessel is generally a metal cylinder fitted with a valve to allow the hydrogen to be collected and stored for transport. Shipment of an offline sample to an analytical laboratory allows more in-depth analysis of the hydrogen fuel. Analytical laboratories can use the more sensitive equipment. However, the sample vessel and the sampling procedure may have an impact on the sample composition [3]. This could be caused by loss of analyte to the internal surfaces of the cylinder and the valve. Additionally, the connection from the cylinder to the analytical instrument may have effects on the analytical results due to dead volume in between the sample cylinder connection and the analytical instrument.

The purpose of this report is to provide an overview of the cylinder valve used on sampling cylinder. This report will provide an overview of the various type of valves, the valves currently used for hydrogen sampling and what passivation treatments are available. If known the dead volume of the valves will also be given.

2. Definition of a valve

Gas cylinders themselves are open ended vessels. In order to allow the gas within the cylinder to be sealed inside the cylinder, a valve must be fitted to the opening of the cylinder. Most gas cylinders have a single opening, normally at the top of the cylinder but some have more than one (e.g. at either end of the cylinder). The valve of a gas cylinder allows the cylinder to be opened and closed to either release or contain the gas within the cylinder or to allow it to be filled with gas.

Depending on the type of valve used the function can either be fully open/fully closed or the valve may be possible to open gradually to allow some control of the gas flow in or out of the cylinder.

2.1 Valve terms

Below are descriptions of specific valve terms that are used in this report for clarity.

Stem/spindle: The stem of a valve generally refers to the part of the cylinder valve that allows motion or force to be transferred from either the handle of the valve or another moving part (such as a spring) of the valve. Stems generally allow external control of the valve.

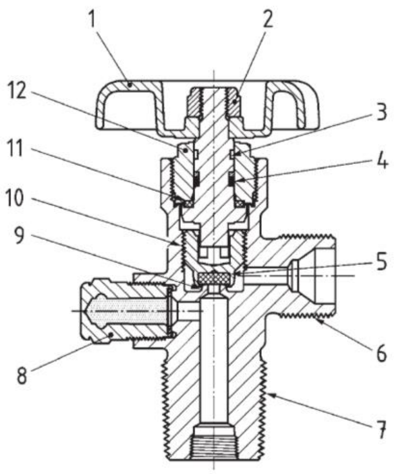
Seat: This is the term used to describe the part of the valve that contacts the moving parts of the valve to provide the seal. The seat is a stationary part of the valve.

3. General valve types

Several types of valve are available and can be fitted to cylinders. This section provides a brief explanation of some of the more common types of valves available for use.

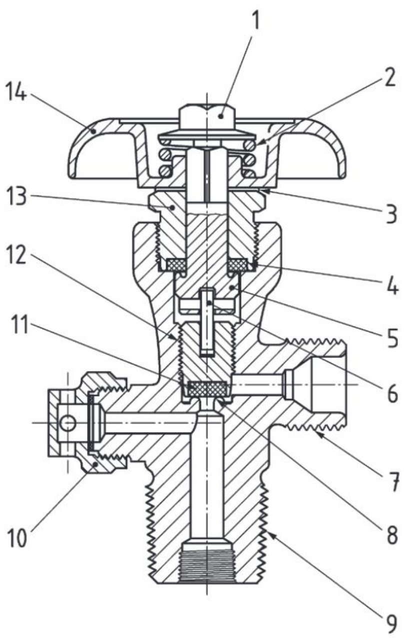
3.1 O-ring valve and pressure seal valves

O-ring valves and pressure seal valves have similar principles, an upper and lower stem are used to seal the valve. An o-ring valve uses an o-ring as the point of seal on the upper stem in the valve where a pressure seal valve uses a washer. Lubricated threads can be used in this type of valve. As the o-ring and washer are often non-metallic seal points they cannot be passivated. The presence of lubricated threads in the wetted surface (where the gas can pass) in both of these types of valves could also raise concerns about possible contamination of very pure gases being used with these valves [4].



1 Handwheel
2 Handwheel retaining nut/stem nut
3 Upper spindle/upper stem
4 O-ring
5 Seat insert
6 Valve outlet connection
7 Valve inlet connection
8 Pressure relief device
9 Body seat
10 Lower spindle/lower plug
11 Washer
12 Gland nut/bonnet

Figure 1: Diagram of an O-ring seal type valve (non-metallic sea handwheel operated) [5]



1 Handwheel retaining nut/stem nut
2 Pressure seal loading spring
3 Washer
4 Packings
5 Upper spindle stem
6 Tang
7 Valve outlet connection
8 Body seat
9 Valve inlet connection
10 Pressure relief device
11 Seat insert
12 Lower spindle/lower plug
13 Gland nut/bonnet
14 Handwheel

Figure 2: Diagram of a pressure seal valve (non-metallic seal handwheel operated) [5]

3.2 Packed seal valve

A packed seal valve uses an upper and lower stem combined with packing (such as Teflon) to create a gas seal. Unlike pressure seal and o-ring valves a lubricant is not used in the area of wetted surface, but the packing material is non-metallic and so is unlikely to be able to be passivated. It is also noted that that packed seal valves have a large number of dead volume in the valve where particles or other contaminates may adhere to [4].

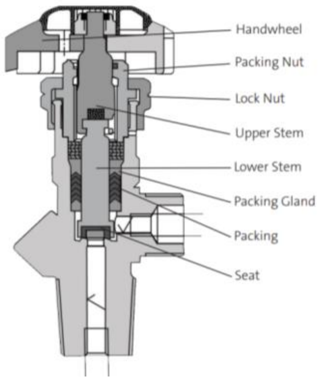


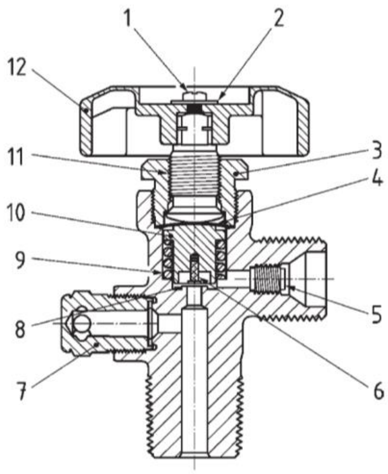
Figure 3: Diagram of a packed seal type valve [4]

3.3 Reverse seated valves

A reverse seated valve is a valve in which the stem moves in a direction that is considered 'out' of the valve to close it. 'Normal seated' valves have the stem moving in a direction that is considered 'into' the valve to close it.

3.4 Diaphragm valve

A diaphragm valve is a valve which contains a diaphragm which closes on a seat (also called a 'weir' or 'saddle'). The diaphragm within the valve is flexible and the valve is generally opened and closed with use of a stem connected to a handwheel on the valve. The term 'membrane valve' can also be used to refer to this type of valve. The diaphragm used for the seal can be metallic or non-metallic depending on the valve. Where the diaphragm is metallic it is still a moving part which can cause difficulties in ensuring passivation treatment remains on the diaphragm. The movement in this part could cause the treatment to be lost. Some passivation treatment involves heating processes that may cause changes in the properties of the metal. If the overall impact of the passivation treatment is not fully studied, it may have impact on the pressure rating and safety of the valve or cause concerns over the seal effectiveness.
Tied-diaphragm valves are a type of diaphragm valve in which the diaphragm is mechanically connected to the upper stem in the valve which removes the need for a spring.



1 Handwheel retaining screw
2 Washer
3 Gland nut/bonnet
4 Diaphragms
5 Flow restrictor (when specified)
6 Seat insert
7 Pressure relief device
8 Body seat
9 Seat opening spring
10 lower spindle/lower plug
11 upper spindle/upper stem
12 Handwheel

Figure 4: Diaphragm of a gland seal valve (non-metallic seal, handwheel operated) [5]

3.5 Needle valves

Needle valves are a type of valve that uses a tapered ‘needle’ resting in a valve seat to control the flow into and out of the cylinder by restricting the opening in the valve. The needle is raised and lowered using the valve handle to open the flow path of the gas to the desired amount and is often directly attached or part of the valve stem. Needle valves allow a much more fine control of outlet flow of the gas from the cylinder.

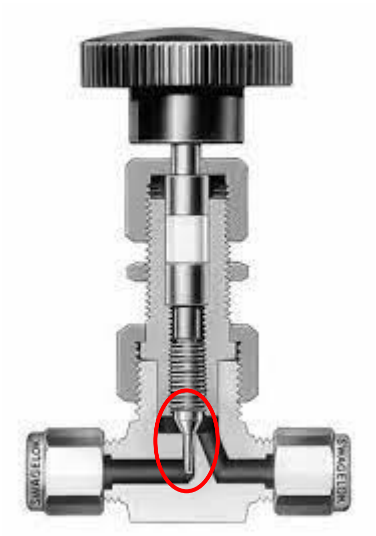


Figure 5: Diagram of a Swagelok 31 series needle valve [6] the ‘needle’ is circled for clarity

3.6 Ball valves

Ball valves are valves in which a central ball with an opening inside it can be turned to an ON or OFF position to either allow or cut off flow (i.e. 2-way ball valve) or to allow flow to one or more openings (e.g. 3-way ball valve).

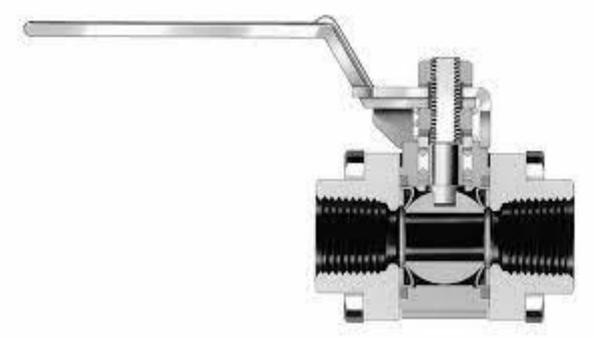


Figure 6: Diagram of a Swagelok 60 series 2-way ball valve [7]

3.7 Twin outlet valves

Twin outlet valves are valves that have two outlets as opposed to one. This allows the cylinder to be open to more than one system at any one time from the same valve. Often the two outlets of twin outlet valves are labelled ‘gas/vapour’ and ‘liquid’ as they are commonly used with liquified gases. They are often also fitted with ‘dip-tubes’.

A dip tube is an extension to the valve that extends into the cylinder body. For example, the tube can be used to extend the valve to access the bottom of a cylinder rather than the top. A dip tube fitting is more commonly found on the ‘liquid’ side of a twin outlet valve (to allow access to the liquid phase at the bottom of a cylinder of liquified gas) but can also be fitted to single outlet cylinders in some cases if desired. Dip tubes are commonly metallic so could potentially be passivated depending on the passivation required and the material they are made from.

4. Standards for valves for use with hydrogen sampling

4.1 Hydrogen sampling standards

Valve requirements that have been noted in hydrogen sampling guide documents are listed below.

4.1.1 ISO 19880-1 Annex K

This standard states in section K3.2 that brass valves should be avoided in the sample collection system [8] and recommends the use of stainless steel [8]. It also notes in section K4.2 that a typical cylinder valve connection that is used in sampling is a DIN 477 No. 1 valve when the Linde Qualitizer sampling system is used [8]. Valves to be used with the Linde Qualitizer sampling system require a DIN 477 No. 1 outlet to be available on the type of valve chosen.

The compatibility of the pressure rating of the valve with the pressure reduction of the sampling system is also highlighted [8]. The pressure rating of the valve needs to be checked with the manufacturer to ensure it is suitable for the sampling system and sample collection pressure.

4.1.2. ISO 21087

In section 8.2 of this standard it is noted that vessels with passivated internal surfaces are strongly recommended [9]. Possible passivation of valves should, therefore, be investigated as the internal surfaces of the valves can be considered as part of the internal surfaces of the sample vessel as a whole. Therefore the passivation of the valves may be critical for reactive species at low amount fraction.

4.1.3 ASTM D7606-11

Section 6.8 of this standard states that the valves in use with the sample cylinder for this procedure are internally coated with silicon [10]. It also states that inlet and outlet valves of the cylinder have 'quick connect' connections fitted [10]. This means the valves for use with this type of sampling need to have a suitable outlet connection that can be fitted with the required 'quick-connect' connections.

4.2 General valve standards

ISO 10297 [5] lists the safety tests required for valves and ISO 1114-1 [11] lists compatibility tables for cylinder valve materials for use with different compounds. The materials listed as suitable for valves for use with hydrogen can be found below in Table 1.

Table 1: Materials listed in ISO 11114-1 [11] that are suitable for use in cylinder valves for use with hydrogen

Material	Notes
Brass and other copper alloys used for the manufacture of cylinder valves (B)	Brass is only acceptable as a valve body but not as a general valve component material.
Carbon steels used for the manufacture of cylinder valve bodies (CS)	For gas mixtures containing gases causing embrittlement the risk of hydrogen embrittlement only occurs if the partial pressure of the gas is greater than 5 MPa (50 bar) and the stress level of the cylinder material is high enough.
Austenitic type stainless steels used for manufacture of seamless and welded cylinders and some valve bodies and valve components (SS)	Stainless steel may be used for valve diaphragms and springs when there is operating experience that shows the design is suitable and safe. Alternatively, use is also authorized if failure of the stainless-steel springs or stainless steel diaphragms does not result in an unsafe condition. Some stainless-steel alloys are sensitive to hydrogen embrittlement. For gas mixtures containing gases causing embrittlement the risk of hydrogen embrittlement only occurs if the partial pressure of the gas is greater than 5 MPa (50 bar) and the stress level of the cylinder material is high enough. 316 type stainless steels recommended
Aluminium alloys specified in ISO 7866 when used for the manufacture of seamless cylinders; for aluminium valve bodies, alloys not specified in ISO 7866 may also be used (AA)	Risk of embrittlement due to the presence of mercury from certain production processes has to be considered, especially with aluminium alloys.

Hydrogen embrittlement seems to be the main concern with regards to the materials to be used for hydrogen sampling valves. Moreover most hydrogen sampling involves taking sample at pressure above 5 MPa. It is recommended to check with the manufacturer if valves are suitable for use with hydrogen.

5 Valves currently in use for hydrogen sampling

Following a review of the current practices worldwide, the following valves have been highlighted as currently in use for hydrogen sampling.

Table 2 below lists valves that are currently known to have been used/ are currently in use with hydrogen sampling. Passivation treatments, manufacturers and internal dead volumes are listed where known.

Valve name/ reference	Valve manufacturer	Valve type	Valve passivation available	Internal dead volume	Sample cylinder size (Manufacturer)	Outlet type
D304	Rotarex	Diaphragm type valve	Dursan, SilcoNert, Silcolloy	Estimate of dead volume known by the manufacturer	10 L (Luxfer)	Single outlet, Din 477 No.1 connection available
D349	Rotarex	Diaphragm type valve	Dursan, SilcoNert, Silcolloy	Estimate of dead volume known by the manufacturer	10 L (Luxfer)	Twin outlet, Din 477 No.1 connection available
-	Swagelok	Needle valve	Sulfinert (Resteck)	Unknown	1 L (Swagelok)	Single outlet and inlet
NDSS-NS4-8PETGCV	Fitok	Needle valve	Passivation considered secondary to Lubricant sealant type by users -Krytox sealant used	Unknown	2.25 L and 10L	Singe outlet and inlet. NPT connection
Inlet: SS-16DKM4-F4-1 Outlet: SS-14DKS4	Swagelok	Needle valve	SilcoNert (Silcotek) Silonite (Entech)	Unknown	1 – 3.78 L (Luxfer – 316 ss or Swagelok 304L-HDF4-1000)	Single outlet and inlet. Inlet: NPT fittings Outlet: Swagelok fittings
314 series	Alta Robbins	Needle valve	SilcoNert, Dursan, Silcolloy, SilcoKlean, SilcoGuard, Dursox (Restek for all)	Unknown	1 – 3.78 L (Swagelok)	Single outlet and inlet, NPT
DSP21	Neriki	Diaphragm type valve	Wetted surface is machined only, EP grade stainless steel	2.5 cc	47L (Benkan Kikoh)	Singlet outlet

6. Summary and recommendations

The feedback shows main valve types used are diaphragm and needle valves. Needle valves are used more commonly on cylinders of smaller volumes (e.g. 1L vessels) and diaphragm valves seem to be more common on cylinders of larger volumes (10L and the 47L vessels). It also seems that most valves are already able to be passivated and quite a few have multiple passivation treatments available. It seems, however, that knowledge of the dead volume within the valves is less widely known.

Since most valves can be passivated already it should be possible to test if passivated valves have a significant effect on sampling by testing sampling vessels with and without treated valves.

This report highlights few challenges around gas cylinder valves:

- Lack of information on dead volume: it may be important to determine or estimate the dead volume from each cylinder valve. Once the dead volume in the valve is known, it will allow studies to determine if it has an impact on the actual gas composition and stability. It will be interesting to determine if the valve with larger internal dead volume suffers a greater loss of contaminant. A better knowledge of valve dead volume will allow a comparison between valve suppliers.
- Lack of study on valve passivation: it seems that valve manufacturers are able to treat the valves. When contacted about different passivation treatments the manufacturers can recommend treatments based on which contaminants are being looked for/expected to be present but there is a lack of studies comparing treated/passivated valves against nontreated/passivated valves.
- Comparison of valve type as two different valves are in use in hydrogen area (needle and diaphragm). It would be interesting for the industry to have a better understanding on the potential influence of the valve.

These studies would help to understand if the actual cylinder surface or the valve surface has the largest influence on the gas composition and stability. There is an important research activity on the cylinder surface passivation or treatment, however, it seems that the valves have not been studied extensively.

Moreover, it would be interesting to look into new evolution of new types of valve or alternative systems to deliver gas, for example gas cylinders with inbuilt regulators. The cylinder with inbuilt regulators may be an alternative to valves as most users will attach the cylinder valve to a regulator. This new system may be interesting to study in similar exercise in the perspective of understanding how the inbuilt regulator system may influence the gas composition and stability. An inbuilt regulator has other components that would be in contact with the gas in the cylinders. It shows advantages in terms of safety and ease of use but requires investigation to ensure the gas composition and stability is maintained.

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