



Net zero: Hydrogen monitoring review

Chief Scientist's Group report

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Dr Robert Bradburne Chief Scientist

Contents

Executive summary	6
Introduction	9
Hydrogen landscape	9
Objectives of this work	10
Scope	10
Rationale	11
Chapter 1: Emission scenarios	12
The hydrogen value chain	12
Hydrogen production	14
Hydrogen transport and storage	17
End-uses for hydrogen	20
Summary	21
Chapter 2: Data reporting requirements	29
Defining the data requirements for regulatory compliance	30
Chapter 3: Monitoring of hydrogen	34
The constituents of a method	34
Commercially available instruments	35
Emerging systems	49
Future method development	51
Case study for monitoring hydrogen emissions	56
Case study 1: Monitoring of hydrogen in a production facility	56
Case study 2: Hydrogen monitoring in a Green production facility	61
Conclusions	62
References	64
List of abbreviations	70

ossary72

Executive summary

Low carbon hydrogen has clear climate benefits compared to conventional fossil fuels, and is envisaged to play a crucial role in achieving net zero. It can be adopted as an alternative energy conveyor through which alternative and green energy sources can be widely used, both at industrial and domestic levels. Hydrogen leakage remains a challenge, as it can act as an indirect greenhouse gas by prolonging the lifetime of methane in the atmosphere. This has the potential to offset some of the climate benefits of a hydrogen economy if not mitigated. Therefore, mitigating hydrogen emissions is important.

Mitigation of climate risk is not the only driver for monitoring hydrogen emissions. Hydrogen gas has a wide range of flammable concentrations in air and may ignite more easily than natural gas. In addition, some metals and alloys can become brittle when exposed to hydrogen gas, particularly in high pressure environments. This further increases the risk of significant leaks occurring. There is an additional economic purpose for minimising hydrogen leaks as it is a valuable commodity.

Understanding potential hydrogen leakage scenarios and emission sources is currently based on predictions and expectations of how a hydrogen economy may function in the future, combined with current understanding of how leakage scenarios and emission sources arise in the contemporary natural gas economy – the closest comparator. Measuring hydrogen emissions using validated methods is important to provide data that can be trusted.

Examples of emission sources include direct sources such as the venting and purging of hydrogen, and fugitive sources (unintentional leakage), particularly if hydrogen is incorporated into the contemporary infrastructure currently in use for natural gas.

There are three overall purposes for monitoring hydrogen:

- To identify, locate and repair leaks, thus improving safety, minimising the loss of a valuable commodity, and reducing the impact on the climate.
- To provide evidence data for regulatory compliance.
- To carry out exploratory monitoring to provide emissions scenario data based on actual measurements rather than predictions, help define reporting requirements that better reflect the different emission scenarios, and an opportunity to develop and test monitoring methods in realistic conditions.

Currently there are no established methods for monitoring hydrogen emissions to atmosphere, however, there are instruments available on the market that measure hydrogen concentration. Such instruments form only one part of a method. In addition, there needs to be a sampling strategy (which describes how the measurement data are collected, assimilated and reported), a means for converting concentration to emission rate, an agreed and established protocol and quality system and way to validate method performance. Measurements and reporting of data will need to cover a wide spatial range (components to site level) and temporal range (snapshot in time to continuous monitoring). Reconciliation of data across a wide range of spatial and temporal scales can be challenging, for example assimilating many measurements into a site total where some areas could be missed due to physical inaccessibility.

The National Physical Laboratory (NPL) has recently tested a number of hydrogen measurement instruments to provide preliminary assessment of their performance as leak detection and measurement systems as part of a Knowledge Assets Grant Fund (KAGF) funded project that was undertaken by NPL. The scope was to undertake preliminary tests across a range of instruments that exploit different technologies to understand their basic performance and limitations.

Their performance characteristics and design point to which emission scenarios they could monitor and data reporting requirements they could fulfil. For example, two of the instruments' may be better suited to detection and localisation of leaks depending on the concentration range. Some of the instruments are able (according to the manufacturer) to measure both at high concentrations up to pure hydrogen and in no oxygen environments. At face value these could be suited to the monitoring of vents for example. However, further testing is needed to understand instruments' performance against these concentration ranges and within the conditions expected for a particular scenario. The instrument design, for example portability and ability to operate in a hazardous area, may require further development.

The instruments tested (apart from one desktop instrument) were designed as hand portable instruments. Such instruments could be developed into a method similar in principle to Leak Detection and Repair (LDAR). Such a method would aim to take a number of snapshot measurements at component level and then combine these into a site total emission estimate for a period of time (month, quarter or year). Methods for monitoring methane, for example, use existing correlation curves to determine emissions rate, but no such data exists for hydrogen. An alternative is to develop an existing high flow method for methane (such as the Bacharach Hi Flow® sampler) into a hydrogen method.

An alternative (and complementary) approach is to develop methods that can measure and report over larger scales, such as those that are based on current optical open-path techniques used to measure methane. Direct optical absorption in the infrared wavelength region is widely used as the basis for a range of techniques for measuring methane, but due to the limited absorption of hydrogen in the infrared, such techniques are not available for monitoring hydrogen. Alternatively, a technique based on Raman scattering could offer potential, but it is at a low technology readiness level and therefore not ready for use. Another approach could be based on distributed point sensors which consists of an instrument connected to a distributed network of sampling tubes spread across a site.

For the monitoring of direct emissions (for example: vents and stacks) the existing monitoring structure using Continuous Emission Monitoring Systems (CEMS), based on a number of standards such as EN 14181 (European Standard, 2015) and EN 15267 (European Standard, 2023) could be extended to include hydrogen. This would require emission limit values and performance requirements for the hydrogen CEMS to be

defined. It would be necessary to develop a reference method which would be used during the CEMS certification field trials and for calibration of CEMS under EN 14181 (European Standard, 2015). There are few instruments that are currently available to continuously monitor hydrogen in stacks.

Much work is required to develop hydrogen monitoring methods, however, many of the techniques, processes and knowledge gained from other gases such as methane can be applied. The next step is to understand the performance and validate methods within a field environment against a controlled release for both fugitive emissions (leaks) and directed emissions (stack). These methods should cover the temporal and spatial scales needed to monitor hydrogen for example, using LDAR to monitor individual components and techniques to monitor vents to distributed sampling techniques to cover whole sites. The next step would be to carry out exploratory monitoring at selected sites. Such work may inform the development of environmental assessments and the Low Carbon Hydrogen Standard.

Introduction

Hydrogen landscape

Hydrogen is widely accepted to form part of a pathway to achieving Net Zero carbon emissions through its use as an alternative energy conveyor through which alternative and green energy sources can be widely used, both at industrial and domestic levels (House of Commons Science and Technology Committee, 2022; HM Government, 2021). Uses for hydrogen include a source of fuel for turbines, process industry, transport and potentially for residential and commercial heating. However, atmospheric hydrogen still has some short-term climatic impact, largely as a consequence of its reaction with the hydroxyl radical (OH), the main source of atmospheric methane removal (Warwick et al., 2022). Increases in atmospheric hydrogen would therefore lead to reductions in global OH concentrations, indirectly extending the lifetime of methane in the atmosphere and prolonging its greenhouse effect. Therefore, understanding the potential emission sources and emission scenarios for hydrogen is important. As hydrogen emissions have been identified as having potential to cause harm due to the indirect global warming potential of the hydrogen molecule, environmental regulators, such as the Environment Agency (EA), may require operators of regulated sites to identify and quantify these emissions.

There are established practices to estimate emissions calculated from measurable activity data from methane and non-methane Volatile Organic Compound (VOC) emission sources. The reporting of methane emissions has historically relied on the use of generalised emission factors. Emission factors are used to estimate emissions arising from a given industry or process by relating emissions with measurable operational activity data (Innocenti et al., 2023). The Intergovernmental Panel on Climate Change (IPCC) defines three tiers of emission factor (representing activities at different spatial scales) for national greenhouse gas inventory reporting: from generalised emission factors to site-specific emission factors at a process scale (IPCC, 2006). Typically, general emission factors at either a global or national scale have been used to report emissions. However, a lack of comprehensive measurement data and incomplete monitoring means that emission factors can vary widely leading to large discrepancies in national inventories (Gao et al., 2022). This has led to a clear need to measure methane emissions for reporting emissions. Measuring hydrogen emissions is important too, more so since there is less evidence data as hydrogen production, storage, transport, and use is an emerging industry and no validated monitoring methods exist.

Mitigation of climate risk is not the only driver for monitoring hydrogen emissions. There are reasonable concerns regarding the safe use of hydrogen gas. Hydrogen gas is flammable over a wide range of concentrations in air and may ignite more easily than natural gas. In addition, some metals and alloys can become brittle when exposed to hydrogen gas (Li et al., 2022), particularly when exposed to high-pressure gaseous hydrogen environments. This further increases the risk of significant leaks occurring. Adequate leak detection is therefore of key importance for health and safety. There is also an economic purpose for avoiding hydrogen leaks. Leaks lead to the irretrievable loss of

hydrogen gas as a commodity; gas that could otherwise be used for multiple purposes and from which economic and environmental benefits could be derived.

Objectives of this work

- To understand where hydrogen leakage could be expected at different areas of the value chain, during the production, storage, transport, and use of (combustion of) hydrogen. This work is presented in Chapter 2.
- To identify the drivers for hydrogen monitoring and then anticipate the associated data reporting quality objectives. This work is presented in Chapter 3.
- To identify the required specifications for hydrogen monitoring methods and associated measurement instruments. This work is presented in Chapter 3.
- To identify commercially available hydrogen monitoring techniques and emerging systems and to summarise testing that NPL has conducted on some commercially available instruments under a Government Office for Technology Transfer programme. This work is presented in Chapter 3.
- To identify the technological and methodological gaps between what is available on the market and needed to fulfil the reporting requirements. This work is presented in Chapter 3.
- To provide a hypothetical case study to help bring all the different factors discussed (such as methods, emission scenarios and data reporting quality objectives) and demonstrate how material in this report could be applied.

Scope

The low carbon hydrogen economy is at a nascent stage of development, with limited numbers of operational projects in the UK. Understanding potential hydrogen leakage scenarios and emission sources must therefore be based on predictions and expectations of how such an economy may function in the future, combined with our current understanding of how leakage scenarios and emission sources arise in the contemporary natural gas economy – the closest comparator.

Currently there are no established methods for monitoring hydrogen emissions to atmosphere, however, there are instruments available on the market that measure hydrogen concentration. Such instruments form only one part of a method. In addition there needs to be a means for converting concentration to emission rate, an agreed and established protocol for operating these instruments and a way of validating their performance. This report, based on current information, takes a speculative view on how methods could be developed and a view on emerging technologies.

The work in this report therefore reflects the experience and expertise built over many decades for monitoring and reporting methane emissions and applies that knowledge in the context of future possible hydrogen gas economies.

Rationale

There are many differing requirements for reporting methane emissions globally, as well as a diverse range of emission source sectors, emission source types, and methods for measuring emissions. It is envisaged the same could apply to hydrogen. There is no common basis for describing these factors and confusion concerning language, definitions and terminology is commonplace. This leads to overall reduced compliance and inhibits the development of standardised practices which adhere to the core metrological principles of data quality, accuracy, and integrity.

There are spatial scales which will be referred to throughout this report:

- Component: defined as an entity that forms part of a process or system; on an approximate spatial scale of centimetres to metres (for example, a flange that joins two pipes).
- Functional element: defined as a spatially separate entity that performs a specific purpose; on an approximate spatial scale of metres to hundreds-of-metres (for example, a process tank, boiler unit, or storage unit).
- Site: defined as a spatially separate premises that performs an activity consisting of several functions or consists of one (or more) functional elements; on an approximate spatial scale of hundreds-of-metres to a kilometre (for example: a hydrogen production plant).

There are a wide range of commercially available instruments that can measure the concentration of hydrogen; however, these instruments would need to be integrated into a system (i.e., a method) than can measure emissions rate. A method should also include factors such as a clear definition of its scope, a quality process and characterisation of its performance to ensure that the data produced can be trusted to make informed decisions from it.

The instruments exploit different techniques for measuring concentration including catalytic combustion, thermal conductivity, and mass spectroscopy. These techniques have their strengths and weaknesses in terms of their different performance characteristics, therefore particular instruments will be better suited to fulfil different roles such as detection and localisation or quantification, for example.

Chapter 1: Emission scenarios

This section contains a literature review of hydrogen emission scenarios. The review primarily considers information from Frazer-Nash (2022) on hydrogen emissions from a UK-based hydrogen economy. Additional context and updated information are taken from wider literature and may not be UK specific.

There is the potential for hydrogen emissions to occur wherever gaseous or liquid hydrogen is being handled, and hence emissions can come at any point along the hydrogen value chain. The following studies have attempted to identify components within the value chain which have the potential for emissions and assess whether emissions are the direct result of a deliberate or expected process, or whether they result from unintentional or fugitive leaks (Colella et al., 2005; van Ruijven et al., 2011; Petitpas, 2018; Cooper et al., 2022; Fan et al., 2022; Frazer-Nash, 2022; Esquivel-Elizondo et al., 2023). Of these studies, some examined specific types of emission sources for example, Petitpas (2018) looked at emissions from boil-off from liquid hydrogen, whilst others collated information across the entire value chain in a particular context, for example Frazer-Nash (2022) used a UK context. However, it remains difficult to predict and anticipate the amount of hydrogen that may be emitted from many sources due to a current lack of empirical and contextual evidence regarding actual emissions.

Emissions can be broadly classified as direct emissions (which are the direct result of an intentional process or activity), or fugitive emissions (which are the result of unintentional leakage).

The hydrogen value chain

Currently assessments of emission scenarios are based on predictions for long-term growth of the hydrogen economy, coupled with modelling and emission estimates based on contemporary understanding of emissions within the natural gas value chain. However, it should be noted that, whilst much more is known about emissions from the natural gas chain, there are still many uncertainties and unknowns, as well as a high degree of variability in emissions across different regulatory regimes, operators, and distributors.

Cooper et al. (2022) provided some of the first estimates of the potential emission profile across the hydrogen value chain. Several supply chains, based on pilot projects and trials, were evaluated, and disaggregated to identify likely high-emission activities. Hydrogen emissions were estimated for three distinct supply chains:

- 1. Blue hydrogen (in which hydrogen is produced using energy from fossil fuels).
- 2. Green hydrogen (in which hydrogen is produced using energy from renewable sources).
- 3. Biomass (in which hydrogen is produced using biomass-derived methane)

Other elements within the value chain (such as storage, transport, shipping, transmission) were also considered but were broadly similar across different supply chains. Hydrogen

emissions were estimated using a method analogous to that used to estimate methane emissions for national emissions inventory reporting (IPCC, 2006).

The Frazer-Nash (2022) report used the UK National Gas Grid's "Future Energy Scenario: System Transformation predictions" (National Grid, 2021) to anticipate the infrastructure required for large-scale hydrogen usage by 2050. Frazer-Nash (2022) separated the value chain into three distinct components: 1) hydrogen production, 2) hydrogen transport and storage, and 3) hydrogen end-use. Within this, they allowed for the full repurposing of the UK's National Transmission System, which is currently used for transporting natural gas, for 100% hydrogen. Hydrogen emissions were estimated using current natural gas emission estimates from analogous processes and infrastructure (estimates which themselves are highly uncertain).

Esquivel-Elizondo et al (2023) presented a recent synthesis and review of other emission estimates for the possible hydrogen value chain, including the Frazer-Nash (2022) report and results in Cooper et al. (2022). Three other studies were included in the synthesis: Van Ruijven et al. (2011), a report for the European Commission, Arrigoni and Diaz (2022), and a report for the Columbia Centre on Global Energy Policy, Fan et al. (2022). For their synthesis, Esquivel-Elizondo et al (2023) separated the hydrogen value chain into five distinguishable elements: 1) hydrogen production, 2) hydrogen conversion (compression or liquefaction), 3) hydrogen transport, 4) hydrogen storage, and 5) hydrogen end-use. Regasification is not mentioned by Esquivel-Elizondo et al. (2023) despite the potential for hydrogen emissions during this process.

The following subsections describe hydrogen emissions within the different areas of the supply chain: production (including preparation for onward supply), transport, storage and end-use.

The project steering group set up between NPL and the Environment Agency identified the following scenarios as of particular interest:

- The production of hydrogen.
- The end-use of hydrogen (e.g., combustion).
- Pipelines if located on a site (or installation).

Other areas that could be considered:

- Storage and transport: Above ground storage, pigging on pipelines (these have potential emissions but may not be regulated in some cases, for example, depending on the final emission point from the pipeline system.
- End-use: pipelines going to a boiler, emissions from burners, hydrogen slip from combustion processes, gas turbines and other direct uses in industrial processes or furnaces.

Hydrogen production

There are four main sources for hydrogen production: natural gas, oil, coal, and the electrolysis of water. Of these, production from natural gas is the most common globally, whilst electrolysis accounts for relatively low amounts of hydrogen production.

- Natural gas (which is mostly methane) is reacted with high-pressure steam in the presence of a catalyst to produce hydrogen. Carbon monoxide and carbon dioxide are by-products. This process is often referred to as steam methane reforming.
- A synthesis gas (like natural gas) can be produced from other fossil fuels (oil and coal), as well as biomass, using a process called gasification. This produces a mixture of hydrogen and carbon monoxide.
- Water can be split into hydrogen and oxygen. This can be achieved through electrolysis or via several methods under active development: thermochemical (high temperature chemical reaction), photobiological (microbial consumption of water), or photoelectrochemical (sunlight-driven semiconductors) splitting. Currently, two types of electrolysis technologies are commercially available (alkaline and proton exchange membrane), but others exist and operate at different temperatures, pressures, and efficiencies.

The hydrogen source, or the energy source used to split water, influences the description of the type of hydrogen produced. Types of hydrogen include:

- Grey: hydrogen produced from fossil fuels where emissions are released to atmosphere.
- Blue: hydrogen produced from fossil fuels where emissions are captured through gas reforming.
- Green: hydrogen produced from renewable energy sources, for example, splitting of water powered by electrolysis from wind or solar, or hydrogen produced from landfill gas. 'Green' is sometimes referred to for electrolysis where the electricity supply may come from the mixed source grid.
- Pink: hydrogen produced via splitting of water powered by nuclear energy.

In addition, there is biomass (see Cooper et al., 2022), which is included in the Green hydrogen, and White hydrogen formed by natural processes inside the Earth's crust.

Frazer-Nash (2022) analysed two types of hydrogen production: electrolytic production (non-specific energy source) and Blue hydrogen production. Esquivel-Elizondo et al. (2023) only distinguished between Blue and Green hydrogen, with the rest of the supply chain examined as part of later components in the value chain. Cooper et al. (2022) looked at multiple different production scenarios for hydrogen. Production routes were analysed in conjunction with a specific supply chain, including:

- Hydrogen produced from biomass and used locally in the US (with pipeline transmission or storage needed).
- Blue hydrogen produced from coal in Australia and exported as a liquid to Japan.
- Blue hydrogen produced from natural gas in Qatar and exported as a liquid to Japan.

- Green hydrogen produced using offshore wind in the North Sea (Dutch) and used locally.
- Green hydrogen produced using onshore wind in Australia and exported as a liquid to Japan.
- Green hydrogen produced using solar energy in Saudi Arabia and exported as a liquid to Japan.
- Green hydrogen produced using solar energy in Saudi Arabia and exported as ammonia (through the Haber-Bosch process) to Japan.

As discussed above, emission sources can be broadly classified as direct (emissions are the direct result of an intentional process or activity) or fugitive (emissions are the result of unintentional leakage). It should be clear to an operator whether an emission was direct or fugitive.

Direct sources of emission during production identified in the literature include:

- Venting of hydrogen during start-up of and shutdown of equipment. This is done to prevent the formation of explosive air mixtures (>4% hydrogen in air) and may involve addition of nitrogen gas (to dilute the hydrogen). Frazer-Nash (2022) estimated emissions to be between 0.05%-0.6% of total hydrogen produced.
- Operational purging (or bleeding) processes for maintenance purposes, during fault conditions, or during processing to remove impurities. This is relevant for electrolytic, or steam methane reforming processes so could be a significant continuous source if there is no combustion plant or catalytic recombination to convert the hydrogen back to water. To meet hydrogen fuel standards, moisture and oxygen must be removed from the produced hydrogen gas. The hydrogen recovery rate when using pressure swing adsorption for purification is approximately 90%, meaning 10% of the produced hydrogen may be released. This is an active area of research and improvements to the capture rate are expected to be made. Frazer-Nash (2022) estimated emissions to be 0%-10% of total hydrogen produced.
- Venting of residual hydrogen in by-products (carbon dioxide for steam methane reforming, or oxygen for electrolysis). This is relevant for electrolytic hydrogen and would be a continuous emission. A small fraction (~0.03%) of produced hydrogen could be released with any carbon dioxide. When using CCS, this hydrogen would be sequestered along with the captured carbon dioxide. Crossover of hydrogen gas into the oxygen gas stream (through a membrane or separator) is unavoidable during electrolysis. Frazer-Nash (2022) estimated emissions to be 0.05%-0.15% of total hydrogen produced.

Indirect, or fugitive, sources of emission during production identified in the literature include:

• Leakage of hydrogen from equipment (for example, casing). This is foreseen to be a relatively minor contributor. Permeation rates through different materials are known to vary significantly and hydrogen embrittlement can compromise structural integrity over time.

- Leakage of hydrogen from pipework.
- Any unintentional leakage of hydrogen during processing.

Fugitive emissions are predicted to be lower than direct emissions assuming that the infrastructure is purpose built for hydrogen. However, there is limited evidence at this stage of the development of the industry to support the validity of this assumption, therefore there may be a need to carry out exploratory monitoring to validate these assumptions. It is also possible that repurposed infrastructure could be used, which could increase leakage. H2 is a smaller molecule than other gases so could be more vulnerable to leak in infrastructure not specifically built for hydrogen.

Some technologies or activities may be used to reduce the amount of hydrogen released to the atmosphere (mainly in the case of direct emissions). The viability, and the extent of adoption of these technologies, is generally unknown:

- Flaring of hydrogen. Flaring of hydrogen is preferred over direct venting, as flaring converts hydrogen into water vapour. A very small amount of unburnt hydrogen may remain (depending on the flaring efficiency), but this is predicted to be negligible due to the high flammability of hydrogen. It may not be feasible for smaller facilities to conduct flaring due to additional safety concerns. It is likely that intentional venting of hydrogen will occur at least at start up and shutdown of processes. There will be a cost benefit versus environmental damage versus availability of suitable flare equipment which will determine whether flaring of venting occurs, more likely at smaller sites.
- Oxidation of hydrogen using a catalyst. Any purged or vented hydrogen could be theoretically passed over a catalyst in the presence of oxygen to re-form water.

Frazer-Nash (2022) concluded that a central scenario involving scaled-up hydrogen production would likely result in 0%-0.5% emissions of the total hydrogen produced. Cooper et al. (2022) estimated a high degree of variability in hydrogen emissions across different supply chains, with a lower estimate of 1.5% loss for biomass-derived hydrogen in the US, and higher estimates of 5% losses for Green hydrogen produced in various locations.

Hydrogen preparation for onward supply

Conversion of gaseous hydrogen into other forms or into other substances may be done to facilitate transportation or storage. Hydrogen gas may be compressed, converted into liquid hydrogen (using liquefaction), or converted into ammonia (via the Haber-Bosch process). Equally, converted hydrogen may be regasified prior to end-use. Conversion of hydrogen is not directly assessed in the Frazer-Nash report, whilst Cooper et al. (2022) assessed conversion as part of several distinct supply chain examples.

Direct sources of emission during conversion identified in the literature include:

• Venting and purging of equipment.

Indirect, or fugitive, sources of emission during conversion identified in the literature include:

• Leakage through pipework and equipment and compressor seals.

Cooper et al. (2022) estimated high hydrogen emissions from liquefaction (0.33% across four supply chain examples) and no emissions from the Haber-Bosch process (one supply chain example). Regasification was estimated to result in much lower emissions of approximately 0.002%.

'Blue' and 'green' hydrogen production routes were identified as being of particular interest by the project steering group. Figure 1 illustrates the emission scenarios for the production sector. Green colour type shows emissions specific to 'green' hydrogen, blue colour type specific to blue hydrogen and black colour type common to both.

Figure 1: Green and Blue production emission scenarios.



Hydrogen transport and storage

Transport

Hydrogen can be transported through various means:

• Pipelines: this can be as part of a national transmission network, or a local distribution network. These pipeline networks are distinct, with different gas pressures, pipeline section lengths, pipeline materials, and associated infrastructure (for example, compressor stations). These factors likely affect the potential range in

possible emissions (as is known for emissions of natural gas from pipelines). For their scenario, Frazer-Nash (2022) assumed that the existing UK National Transmission System for natural gas would be directly converted to transport 100% hydrogen.

- Road network: hydrogen can be transported over road either as a gas (in a tube trailer) or as a liquid (in a truck). Esquivel-Elizondo et al. (2023) assessed these separately, whilst Frazer-Nash (2022) analysed the two together.
- Shipping: hydrogen-transporting ships often use the hydrogen boil-off as a fuel. This could equally be considered an end-use for the hydrogen.

Direct sources of emission during conversion identified in the literature include:

- Venting or purging (potentially using nitrogen gas) of pipelines for maintenance or other operations and may involve the addition of nitrogen in the purge gas.
- Venting or purging of associated equipment for maintenance (for example, compressors).
- Vented boil-off of gaseous hydrogen from liquid hydrogen. The amount of boil-off depends on the size and type of storage being transported; Frazer-Nash (2022) estimated the boil-off rate to be 0.1%-5% per day, with typical values around 1%. Hydrogen boil-off may be captured and transported elsewhere (Cooper et al., 2022).

Indirect, or fugitive, sources of emission during conversion identified in the literature include:

Leakage through pipework and equipment. Estimates of methane leakage from the UK National Grid are uncertain and range from 3.4 kilotonnes (kt)/year (European Union Greenhouse Gas Inventory, 2020) to 220 kt/year (DNV GL, 2021). Anecdotally, estimated leakage of methane from the National Transmission System is likely to be around 15 kt/year (Frazer-Nash, 2022). Frazer-Nash (2022) estimated leakage from compressors to be 4.5 kt (CH₄)/year and leakage from the gas distribution network to be approximately 0.5% of transported hydrogen.

Converting current estimates for natural gas leakage into estimates of potential hydrogen leakage is not trivial. The leakage rate depends on the established flow regime (turbulent or laminar) which will differ for different gases and for different pipeline pressure scenarios as well as the pipeline material. Frazer-Nash (2022) estimated that total pipeline leakage would be 3-7 kt/year for hydrogen, equivalent to 0.02%-0.04% of total hydrogen throughput. Any estimate for hydrogen leakage based on natural gas leakage estimates will be dependent on the leakage rates through materials and standards employed for rejoins and welded pipes.

Another likely source of emissions is during the "pigging" process, where a device is propelled due to the flow of product down a pipeline, for operations such as inspection or maintenance.

Hydrogen storage

Hydrogen may be stored as a gas or a liquid, above or below ground. For below ground storage, different storage options may be available, including the storage of hydrogen in salt caverns. During storage, direct emissions can occur through venting and purging (often with nitrogen gas) of storage equipment (such as for shutdown during maintenance or for emergencies). Emission of some vented hydrogen may be mitigated using gas flares.

Direct sources of emission during storage identified in the literature include:

• Venting and purging from equipment (during shutdown, maintenance, emergencies etc.). Venting from a typical surface plant servicing 15-20 below-ground storage facilities was estimated to be around 25 tonnes/year, equivalent to roughly 0.04% of stored hydrogen (Frazer-Nash, 2022).

Indirect, or fugitive, sources of emission during storage identified in the literature include:

- Natural leakage from salt caverns due to the permeability of the substrate. This was
 predicted to be negligible by Frazer-Nash (2022). Leakage due to the permeability
 of the substrate and gas migration pathways through the subsurface and emissions
 through ground water are not fully understood (Zhu et al., 2023). Salt caverns have
 been used for several decades for hydrogen storage, although only six salt caverns
 have been created for hydrogen storage, most in the USA (Moss Bluff, Clemens
 Dome, Spindletop) and one in the UK (Teesside). However, these may need to be
 assessed to check that they are fit for purpose for storing hydrogen if they were
 originally developed for another purpose, for example natural gas storage.
- Leakage from pipelines and equipment. Leakage from high-pressure storage was estimated to be 0.12%-0.24% per day (Frazer-Nash, 2022).

Cooper et al. (2022) estimated total losses across both storage and transmission to be 1.22%-2.42% depending on the supply chain.

Figure 2 illustrates the emission scenarios for the storage, transport and conversion sector.

Figure 2: Emission scenarios for the storage, transport and conversion sector.



End-uses for hydrogen

Frazer-Nash (2022) identified multiple end-uses for hydrogen, including: hydrogen-vehicle refuelling stations, hydrogen fuel cells; hydrogen use in an internal combustion engine; residential and commercial use of hydrogen in boilers, hobs, and ovens; use as a fuel in gas turbines; use in process industry (steel, glass, chemical production). Of these, very little information was found to be available regarding the potential use of hydrogen in the process industry. Hydrogen fuel cells are like hydrogen electrolysers but operate in reverse; the fuel cells *produce* water and electricity and *consume* hydrogen and oxygen.

Direct sources of emission during use identified in the literature include:

- Venting or purging during normal operation (start-up, shutdown), maintenance, or for emergencies.
- Venting of residual hydrogen in oxygen gas stream (hydrogen fuel cells). Frazer-Nash (2022) estimated this at 0.15% of hydrogen used but acknowledged that most hydrogen would be consumed by the process.
- Unburned hydrogen in combustion processes (internal combustion, gas turbines, heating). This may also be referred to as engine slip. Frazer-Nash (2022) assumed this to be negligible, but Cooper et al. (2022) reported loss rates of up to 12% (average of 0.5%) with the highest losses occurring at low engine loads.

Indirect, or fugitive, sources of emission during use identified in the literature include:

- Leakage from pipework and equipment (for example, casing).
- Leakage from high-pressure storage tanks.
- Leakage during compression processes (often via permeation through seals). This has been estimated at 0.05%-0.25% (Frazer-Nash, 2022).

Figure 3 illustrates the emission scenarios for the end-use sector.

Figure 3: Emission scenarios for end use: residential and commercial heating, gas turbines, process industry, refuelling stations, fuel cells and the internal combustion engines



Summary

To summarise the emission scenarios have been grouped as follows:

- Direct emissions from venting or purging that could contain high concentrations of gas or pure gas.
- Emissions from flares or exhausts and hydrogen slip from combustion processes.
- General fugitive emissions from components (such as seals, pipe joins) and functional elements such as storage containers, process units, compressors etc.
- Fugitive emissions from repurposed infrastructure or infrastructure containing blended gases. There is a lot of uncertainty regarding such emissions and scenarios where other gases are being processed such as methane which could be a source of interference. It is important to understand the emission properties where there are likely to be blends of hydrogen and natural gases, and the appropriate methods to monitor these emissions.

Scenario	Туре	Leakage path	Estimated emissions	Fugitive / Direct	Notes / mitigation
Production Electrolytic (Green)	Electrolytic (Green)	Venting at start- up and shutdown.	0.05% - 0.60% of H ₂ produced.	Direct	Technology to recombine with O ₂ to produce water –
		Venting due to H ₂ cross-over through membrane and into vented O ₂ .	0.05% - 0.15% of H ₂ produced.	Direct	considered on a large scale. Physical access
		Operational purging during purification.	Up to 10% of H ₂ produced.	Direct	requirements to vents – to be considered.
	Leakage through casing.	Predicted to be negligible.	Fugitive	BS ISO 22734 (International Standard, n.d) for testing leakage.	
					Fugitive leaking mitigated through use of welded joints.
Blue	Leakage from pipework and equipment.	Predicted to be negligible.	Fugitive	Fugitive leaking mitigated through use of welded joints.	
		Operational and maintenance procedures including purging during purification.	Up to 10% of H₂ produced.	Direct	Direct emissions could be flared.
		Venting at start- up and shutdown.	Unknown	Direct	
		Processing, including gas stream analysis.	Predicted to be negligible.	Direct + fugitive	

Scenario	Туре	Leakage path	Estimated emissions	Fugitive / Direct	Notes / mitigation
		Post-processing for carbon capture of CO ₂ (some residual H ₂ in stored CO ₂).	Up to 10% of H ₂ produced.	Fugitive	
		Waste H₂ flared.	Predicted to be negligible.	Direct	Flaring is expected to be efficient due to H ₂ flammability range and flame speed.
Transport and storage	Underground gas storage	Natural leakage due to permeability of substrate.	0.04% of stored H ₂ per day. Depends on frequency	Fugitive	
		Leakage associated with processing on the surface (including venting and purging).	on maintenance, emergencies etc.	Direct + fugitive	
	Above-ground gas storage	Leakage from compressed gas storage.	0.12% - 0.24% of stored H ₂ per day. Depends on storage pressure, storage material etc.	Fugitive	
	National transmission grid	Leakage (repurposed natural gas grid) from pipes, valves, traps, assets etc.	0.02% - 0.04% of transported H ₂ . Highly uncertain leakage from current natural	Fugitive	

Scenario	Туре	Leakage path	Estimated emissions	Fugitive / Direct	Notes / mitigation
		Compressor leakage from seals, planned process venting, start-up purging.	gas grid; conversion factor (to H ₂) uncertain too. Assumptions regarding flow regime and leakage paths. 0.1% - 0.23% of transported H ₂ . Lots of uncertainty I. and	Direct + fugitive	
		Other emissions including venting of pipelines for maintenance.		Direct	
	Distribution network	Leakage (repurposed natural gas grid) similar to national transmission grid.		Fugitive	
		Leakage during completion of mains replacement programme.	assumptions (pipeline pressure etc.).	Direct + fugitive	Temporary for duration of programme.
	Road trailering (gas or liquid)	Leakage from compressed gas storage.	0.12% - 0.24% of transported H ₂ . May be more significant.	Fugitive	
		Boil-off from liquid hydrogen (vented).	0.1% - 5% of transported H ₂ . Depends on size and type of storage.	Direct	Technologies (reliquification and recompression) could be used to reduce emissions for larger applications.
End-uses	Residential and	Vented unburnt H2 from boilers	0.13%.	Direct	

Scenario	Туре	Leakage path	Estimated emissions	Fugitive / Direct	Notes / mitigation
commercial heating	commercial heating	during start-up and shutdown.			
		Leakage from pipework.	Very uncertain. Depends on age of pipework. Estimated 0.33%.	Fugitive	
		Leakage during installation and maintenance.	Unknown	Direct + fugitive	
	Leakage from casing.	Predicted to be negligible.	Fugitive		
Gas turbines	Venting during start-up and shutdown.	Predicted to be negligible due to small volumes of inlet pipes.	Direct	More likely to run continuously so this could be minimal.	
		Leakage from exhaust whilst idle (initial part-load after start-up).	5% - 10% during first 5 minutes of operation when combustion efficiency is lower.	Fugitive	
	Process industry	Unburnt gas exiting furnaces.	Up to 0.5% but limited		
		Leakage and exhaust loss from blast furnaces.	mornation.		

Scenario	Туре	Leakage path	Estimated emissions	Fugitive / Direct	Notes / mitigation
F		Other processes – limited information.			
	Refuelling stations	Compressed gas leakage.	Relatively low. 0.12% - 0.24% of stored H ₂ per day.	Fugitive	
		Purging during normal operation and emergency venting.	Unknown	Direct	
		Leakage during compression processes.	0.05% - 0.25%.	Fugitive	
Fuel cells	Fuel cells	Leakage through casing and pipework.	Predicted to be negligible.	Fugitive	BS ISO 22734 (International Standard, n.d) for testing leakage. Fugitive leaking mitigated through use of welded joints.
		Leakage from compressed gas storage.	0.12% - 0.24% of stored H ₂ per day.	Fugitive	
		Venting during start-up and shutdown.	0.04% - 0.07%.	Direct	
		H ₂ crossover causing contamination of vented O ₂ .	Up to 0.15%.		

Scenario	Туре	Leakage path	Estimated emissions	Fugitive / Direct	Notes / mitigation
		Purging or bleeding during operation.	0.8% - 2.0% during operation.	Direct	Catalytic converter could be fitted to burn H ₂ before emission.
	Internal combustion engines	Unburnt fuel.	Predicted to be negligible.	Fugitive	Unlikely to need a catalytic converter as concentration of H ₂ too low.
		Leakage from compressed gas storage.	0.12% - 0.24% of stored H ₂ per day.	Fugitive	

Table 1: Summary of emission sources identified in the Frazer-Nash (2022) report, their leakage pathways, and their estimated emission ranges.

Figure 4 illustrates a summary of the potential emission sources and scenarios present in a future hydrogen value chain. The information in this figure is adapted from Esquivel-Elizondo et al. (2023) but with additional context from Frazer-Nash (2022) and Cooper et al. (2022).

Figure 4: Schematic of hydrogen emission scenarios associated with elements along the hydrogen value chain. Adapted from Esquivel-Elizondo et al. (2023).



It should be noted that most mentioned emissions estimates are highly uncertain now, due largely to the lack of empirical emission rate measurements for hydrogen for many of these processes. Furthermore, estimates may be based on conversion of current estimates for natural gas emissions, which themselves may be highly uncertain due to the inherent difficulty in measuring them.

Chapter 2: Data reporting requirements

It is important to distinguish between the two types of data requirements:

- The data monitoring requirements (*what* data need to be reported) and frequency of monitoring, for example: for a report containing evidence of compliance that is submitted to a regulator or data to inform a repair process.
- The measurement requirements (*how* the data are to be acquired), for example: sampling strategy, resolution etc.

This section focusses on the former, whereas the latter should be detailed in the definition of the monitoring method, described in the next section. The method should also describe how the measurements are assimilated into a report which could involve data reconciliation across different temporal and spatial scales, the next section discusses this further.

To define the data reporting requirements, it is necessary to identify the drivers of the monitoring to be undertaken. To monitor hydrogen emissions to the atmosphere the anticipated drivers are:

- Regulation: To provide evidence data for regulatory compliance.
- Process improvement: To provide data to manage hydrogen leaks and repairs (i.e., to minimise impact to the environment, minimise loss of a valuable product and improve safety).
- Research: To undertake exploratory monitoring to provide data based on actual measurements rather than predictions, to obtain more accurate emission scenarios. Examples of emissions source properties to measure are the range of emission rates (and instrument sensitivities required) and the temporal (continuous or non-continuous) characteristics of the sources whether continuous monitoring is required, plume size etc. Such monitoring is also an opportunity to develop and test monitoring methods in realistic conditions.

It may be useful to define the stakeholders involved in the monitoring as that could influence the type and complexity of data required. Additionally, it could be helpful to identify the industry and position in the supply chain which may identify specific requirements for the data to be reported.

The project steering group agreed that safety was not in scope for this project. However, safety devices which are currently in operation that could also be used to collect emissions data should be identified and considered if appropriate. Also, any monitoring methods employed should not compromise safety.

The data requirements for leak detection and repair would require a monitoring method that can identify, potentially quantify, and locate fugitive emissions (for example, leaks) at component scale, for example a "handheld sniffer", such that a process can be put in

place to repair the leak. It is recognised that if a leak detection and repair scheme were to be implemented then data from that may be used to contribute to reported emissions.

Reported emissions for compliance would need to include monitoring of direct emissions, assimilation of data from a few measurements taken from the various components and functional elements on site, taking care that individual sources are not duplicated in the report, for example the measurement from one functional element may include downwind emissions from another. Interfering sources need to be considered to ensure that appropriate instruments are chosen that minimise any cross interference from gas species such as methane and water vapour.

Assimilating data obtained at component scale (for example, a valve) into a site total should be verified using a method that monitors at functional element or site scale to ensure that the results agree within defined uncertainties. Definitions of component, functional element and site scale are given in the glossary.

A snapshot measurement (before and, if necessary, after a repair) may be sufficient to manage individual leaks. For evidence data for regulatory compliance, such snapshots of data would need to be a representative sample of the site conditions and continuous monitoring may be preferred.

Defining the data requirements for regulatory compliance

It is envisaged that quantification of hydrogen emissions will need to be reported to the relevant regulatory authority (i.e., the Environment Agency) by site operators. The nature of this reporting will depend on the value chain type and whether the hydrogen project is covered under The Environmental Permitting (England and Wales) Regulations 2016. The data quality metrics (for example uncertainty, emission rate, spatial scale, frequency etc.) of the reported hydrogen emissions need to be defined. This report explains how those metrics could be defined.

The UK Low Carbon Hydrogen Standard, (Department for Energy Security and Net Zero, 2023) provides useful information to form a basis for defining the data reporting requirements during hydrogen production. This standard is not a regulatory requirement or under the Environment Agency's remit. The standard has been published by the Department of Energy Security and Net Zero (DESNZ) and is regularly updated to incorporate the latest advancements and understanding in technology. Complying to the LCHS is a requirement for all hydrogen projects receiving DESNZ funding, however it is voluntary for projects not supported by DESNZ.

The standard sets out the method for calculating emissions associated with hydrogen production, guidance for reducing emissions and the requirements producers are expected to meet to prove that hydrogen production is compliant with the low carbon hydrogen standard. Currently, producers must meet a hydrogen emission intensity of 20 gCO_{2e}/MJ_{Lower Heating Value} (or approximately 2 g Hydrogen per MJ; Warwick et al., 2022).

This value includes emissions associated with the supply of material and energy, waste, and non-CO₂ fugitive emissions. Producers are expected to minimise and report on fugitive hydrogen emissions through a Fugitive Hydrogen Emissions Risk Reduction Plan and Annual Report. It is recommended that hydrogen emissions are reported monthly (with annual third-party verification) to check whether sites are compliant with the Standard. Producers should report actual data based on the performance and emissions measured or calculated through the production of hydrogen. In some cases, projected or default data may be accepted.

Fugitive emissions are likely to be reported as total annual releases from a whole site including any releases from planned or unplanned events. Monitoring and reporting frequencies will be determined during the environmental permitting process informed by existing best available techniques. Leak detection and repair (LDAR) plans and results of surveys would need to be reported for a new site, initially on a more frequent basis and then extended if the data indicates this would be appropriate. This data may be used to inform total annual releases. There are currently no standards for the monitoring of fugitive hydrogen emissions.

For direct releases (via process vents, sampling points, hydrogen slip from combustion) the measurement of flowrate, either via monitoring or calculation, plus concentration monitoring in the vent stack to MCERTS (Environment Agency's Monitoring Certification Scheme) standards should be considered. Depending on the size of emission, this would be periodic (likely monthly/quarterly) or (less likely) continuous monitoring. The generic standard used for CEMS certification and testing could be extended to include hydrogen. However, it is still necessary to develop a reference method which would be used during the CEMS certification field trials and for calibration of CEMS.

To obtain MCERTS certification for analysers or accreditation for methods for monitoring hydrogen a periodic monitoring method would need to be developed, possibly via a fast-track British Standards Institution (BSI) standard. The time frame would be approximately 2 years. Alternatively, a generic MCERTS framework for certifying analysers could be applied. However, this may need to be supplemented with performance requirements applicable to hydrogen monitoring.

Table 2 shows indicative data reporting requirements for compliance to regulatory authority. This table illustrates example data that would be reported by the site operator to a regulatory authority, for emissions of a complete site. It is assumed that such a report would include the total emissions for a site, the type of site (for example electrolysis production), the types of functional elements and components on site and their emissions and locations.

Table 2: Indicative data reporting requirements for compliance to a regulatoryauthority.

Properties	Categories / Values
Temporal granularity	Monthly or quarterly with annual 3 rd party verification.
	Assume indefinitely.
Spatial granularity	An emission rate for identified components and functional elements that have been assimilated into a site total.
Species selectivity	Ability to distinguish hydrogen from other potential sources of interference such as water vapour and other combustible gases (for example methane).
Target uncertainty	Ultimately a cost versus performance judgement. Assumption: Target uncertainty <30% of the mean of a defined set of measurements. Below the lower quantification limit the target uncertainty would be fixed at 30% of this quantification limit. Based on methane emissions monitoring for onshore oil and gas (see Environment Agency, 2021).
Class and type	Quantification of emission rate
Range of emission rates	Not yet defined. To be determined as the minimum level of sensitivity that would be needed for a method to be useful.

Properties	Categories / Values
Output type	List of sites, functional elements and components surveyed and their emission rates and locations.
Specifics	To cover Fugitive and Direct releases and unplanned and planned events.
Costs	The costs associated with equipment and method implementation.
Practical use	Portability (walk over survey). All weather operation, no restrictions on time or day or year. Ability to operate in explosive atmospheres.

Chapter 3: Monitoring of hydrogen

When monitoring hydrogen, the concentration of hydrogen gas in the atmosphere is one factor to be measured (although it should be noted that this concentration can vary drastically in time and space surrounding the emission point). Whilst measuring the concentration can help to detect the presence of a leak (via enhancements in concentration above the local background), to quantify the amount of hydrogen over a specified time (emission rate), a measure of flow rate needs to be combined with the concentration. This flow rate could be measured directly (for example: flow through a vent) or can be estimated indirectly via a model that has been derived for example from wind measurements, or from a mass balance approach (see Environment Agency, 2022) where the emissions are calculated from the mass of flow into the site (or functional element).

The spatial granular scale defines how data are measured or reported. For example, component-scale is a measurement or report for each component within a site such as a flange or join in a pipe. Site scale is a single measurement or report that covers the entire site; the report could conceivably (depending on whether there are suitable technologies in the future) be obtained from a single measurement, but in practice a more likely scenario is to assimilate data from several measurements at component or functional element level. This will involve monitoring a potentially large number of functional elements and/or components on site, then assimilating the data into a site mass emission rate total. However, there are several factors to consider about calculating a site total (and annualising the data). This includes contribution from irregular or discontinuous events that are not typically representative of the site, difficult to reach or hazardous areas that could be missed, or areas that are not being monitored due to them being out of scope or not appropriate for the method deployed. In addition, interfering hydrogen emission sources and the background hydrogen concentration needs to be considered. Therefore, reconciliation of datasets to ensure consistency of data measured and reported across different temporal and spatial scales can be challenging.

Continuous monitoring may need to be used to increase the probability of capturing emissions from less frequent events (such as maintenance). However, monitoring continuously may be cost prohibitive and therefore snapshot methods may be preferred with targeted monitoring of important activities.

The constituents of a method

This sub-section describes what a method should consist of. A monitoring method that reports hydrogen emissions rate must consist of the following:

• A measurement instrument or complementary set of instruments that measure concentration. An instrument will have its own properties, for example resolution, range, sensitivity etc.

 A sampling strategy, describing how the measurement data are collected and represented, as well as the platform used to collect the data. The term *strategy* is used as this encompasses many aspects of how the method is implemented for example: choice of platform(s), how data is assimilated, specific acquisition procedures. Whereas a sampling procedure would be a defined set of specific instructions for a human activity or software code, for example ensuring that (given a sampling time) the whole leaked gas is sampled.

There are two types of sampling strategy: point sensor and remote sensor which is an inherent property the instrument. Point sensors (for example a "sniffer" type instrument) need to be located within the area being monitored, which may not be feasible in difficult to reach or hazardous areas. The sampling strategy would define the platform (or vehicle) for monitoring, for example whether the instrument is portable and therefore monitors components or functional elements in turn or whether it consists of several distributed fixed sensors that monitor continuously. For remote sensing of methane and non-methane VOCs, optical instruments are used, for example a beam of light traverses the area of interest. There are no such commercially available remote sensing techniques for hydrogen monitoring, however a technique based on Raman scattering may offer a solution. Further details are described below in the section "Emerging systems".

• Emissions rate quantification. This describes how the concentration measurements are converted into an emission rate.

A method should define the measurement requirements (i.e., *how* the measurements are to be acquired and reported):

- A clear definition of the physical magnitude to be measured: direct measurements, or estimations (for example based on models).
- The spatial granularity at which to measure and report data: i.e., component, functional element, or site.
- Measurement period: should it monitor continuously, periodically (with gaps), or will a single snapshot provide representative data?
- A determination of the measurement uncertainty.
- Species covered.
- Detection limit and minimum quantifiable emissions rate.

Commercially available instruments

There are a wide range of commercially available instruments that can measure concentration of hydrogen. As previously mentioned, to provide a measure of emissions rate these instruments would need to be integrated into a system that can also measure flow rate and combine this with the concentration measurements, however there are no such systems that are commercially available.

The instruments tested exploit different techniques for measuring concentration including catalytic combustion, thermal conductivity, and mass spectroscopy. These techniques have their strengths and weaknesses in terms of selectivity (ability to distinguish hydrogen from other gases), sensitivity, linearity and range of concentration that can be measured; therefore, particular instruments will be better suited to fulfil different roles such as detection and localisation or quantification. Optical absorption is a widely used technique for measuring methane, but such techniques would not provide sufficient absorption for hydrogen.

All the commercially available instruments (apart from ultrasonic cameras) would need to be located within the area to be measured, meaning that their scope could be limited to areas that can be physically accessed.

The next subsection describes work carried out by NPL to test instruments that exploit different technologies (for example mass spectrometry) and to understand their basic performance and limitations. The testing was undertaken as part of a KAGF funded project that was undertaken by NPL; no testing was carried out under the Hydrogen monitoring project commissioned by the EA. Due to limited project costs under the programme proposed, future testing is then described. There are commercially available instruments that were not tested under this programme. These instruments were not tested either because they were not available for testing at the time or used a technology that has already been included within the scope of testing.

Instrument testing

NPL is currently developing its hydrogen test facilities, monitoring capabilities, and transferring expertise from other areas (for example methane) under the KAGF funded project undertaken by NPL. Part of this project has involved testing seven hydrogen measurement instruments that cover a wide range of technologies within the laboratory and field, to provide preliminary assessment of their performance as leak detection and measurement systems. A shortlist of eight commercially available instruments that could detect hydrogen was drawn up. Each instrument has been designed for a specific purpose, meaning that they differ in their working ranges for measuring gas concentrations, possible cross interferences (including atmospheric humidity), selectivity, etc. They also have different advantages and limitations, for example: portability, if they have an ATmospheres EXplosibles (ATEX) certification, and whether their output suffers from drift. These differences are intrinsically related to the physicochemical nature and mechanisms of the sensor used inside each instrument.

The rationale behind the selection of the detectors was to use an instrument (and so a sensor) of each kind, to test them and thus obtain performance data of their use for the proposal of detection and monitoring methods for hydrogen and H₂-enriched natural gas fugitive leaks. It is worth noting that no existing report on performance assessment of these kind of instruments in the presence of blended gases (as $H_2 + CH_4$) has been found so far.
One of the 8 instruments (i.e. a Sensit HXG-3/3P, semiconductor sensor) was not available for the laboratory testing at the time the tests were undertaken, and for that reason it was the only instrument on the shortlist not tested. All instruments tested were commercially available at the time of testing. Further information is given below (next sub section) on other commercially available instruments that were not tested by NPL. Table 3 compares performance metrics of the instruments that were tested under the KAGF funded project that was undertaken by NPL.

- Riken Keiki: GP 1000, (Riken Keiki Co Ltd, n.d.(a)) Technology: Catalytic combustion. The GP 1000 is a portable, handheld gas detector which uses catalytic combustion to detect the presence of combustible gases (such as methane, hydrocarbons, hydrogen etc.).
- Riken Keiki: GX Force, (Riken Keiki Co Ltd, n.d.(b)) Technology: Catalytic combustion. The GX Force is another handheld device for the detection of combustible gases.
- Riken Keiki: NP 1000, (Riken Keiki Co Ltd, n.d.(c)) Technology: Thermal conductivity. The NP 1000 is a portable, handheld gas detector which uses thermal conductivity to detect the presence of combustible gases (such as methane, hydrocarbons, hydrogen etc.). Thermal conductivity devices (TCDs) detect a change in the thermal conductivity of a gas relative to a reference gas.
- Inficon: Extrima and Sentrac Strix, (Inficon, n.d(a/b)) Technology: Palladium alloy Field Effect Transistor (FET) sensor. The Extrima and Sentrac Strix instruments use field-effect transistor-type (FET) gas sensor to detect hydrogen. FET-type sensors can be directly integrated within certain electronic circuits which are designed to control changes in signal and calibrate changes in environmental conditions during sensing, Hong et al. (2021). FET-type sensors can also be extremely small and produced very cheaply. The Sentrac Strix is designed as a leak detector by using a specific hydrogen gas mixture (5% hydrogen, 95% nitrogen) as a tracer gas.
- Inficon: XL 3000 (Inficon, n.d.(c)) Technology: Mass spectroscopy. The Inficon XL 3000 is a mass spectrometer. Mass spectrometry is an analytical technique for measuring the mass-to-charge ratio of ions. Mass spectrometers are therefore able to distinguish between chemicals which have different molecular masses.
- Teledyne: GS 700, Teledyne (n.d.)

Technology: Catalytic bead sensor and thermal conductivity (for hydrogen) and IR (for methane).

The Teledyne GS 700 uses both a catalytic bead sensor and a thermal conductivity sensor for detecting hydrogen. Catalytic bead sensors work in very similar ways to catalytic combustion devices.

 Table 3: KAGF funded project undertaken by NPL - Instrument comparison.

Instrument	GP 1000	GX- Force	NP 1000 H2	Extrim a	Sentrac Strix	GS 7 (IR sense	00 , or)	XL 3000
Selectivity	×	×	×	✓	✓	~	×	✓
Cross interference to methane Reading at 25,000 ppm exposure	P Designed for methane, natural gas and other flammable gases. These gases will interfere with hydrogen measurements.		3 ppm					
Sampling pump?	~	✓	~	×	×	~		~
Maximum concentrati on - claimed by the manufactur er. (ppm)	50,000	50,000	1,000,00 0	500	1,000,000 S		Not pecified	
Can operate in low O ₂ concentrati on	×	×	~	~	~	V	×	~
H₂ Linearity 4,000 to 40,000 ppm	~	*	~	Linear p Non- (parabo p	5 to 100 pm -linear blic) >100 pm	~		Linear > 5 ppm

Instrument	GP 1000	GX- Force	NP 1000 H2	Extrim a	Sentrac Strix	GS 700 (IR, sensor)	XL 3000
Sensitivity	Lower	Lower	Lower	Higher		Lower	Higher
H₂ + CH₄ Linearity 4,000 to 40,000 ppm	~	~	No linear response		~	Not tested	

The instruments tested were all non-optical. Optical instruments that could be used to monitor hydrogen are up to Technical Readiness Level (TRL) 4, UK Research and Innovation. (n.d.). Currently there are no commercially available systems.

The performance metrics tested were:

• Selectivity.

Selectivity is defined as the ability of an instrument to measure the gas species of interest without being affected by other (interfering) gas species and water vapour. Selectivity is a function of the instrument sensor's technology. For example, Palladium-Alloys are sensitive to changes in hydrogen concentration, but much less so for methane and are chosen for their simplicity and efficient sensing properties (Koo et al., 2020), whereas metal oxide semiconductor sensors are not able to differentiate between hydrogen and methane and many other gases (Korotcenkov et al., 2009).

From the emissions scenarios investigated the most likely interfering gas species could be the presence of combustible gases (other than hydrogen) such as methane, where methane and hydrogen have been blended, water vapour for measurements made in the atmosphere, or pollutants such as ammonia or sulphuric acid that are likely to impact most sensors. Therefore, it is important that the performance of candidate instruments is assessed against the range of gases that could be present at sites across the value chain. The scope of these tests limited testing to cross sensitivity to methane and limited tests against water vapour. Due to the scope of this testing, *selectivity* in Table 3 is the ability of the instrument to distinguish between hydrogen and methane. However, the results can be extrapolated to natural gas.

The GP 1000, GX Force and NP 1000 by virtue of their technology are not able to distinguish between methane and hydrogen.

The Sentrac and Extrima instruments have a Palladium-Alloy sensor, these types of sensors are chosen for their selectivity to hydrogen (Koo et al., 2020) and therefore should be much less sensitive to methane than hydrogen. At 25,000 ppm exposure to methane these instruments reported 0.5 ppm hydrogen due to cross sensitivity.

The GS 700 has two sensors: an optical infrared sensor that is selective to methane and a catalytic bead and thermal conductivity sensor intended for hydrogen. The inclusion of an infrared sensor therefore helps the instrument distinguish between these two species.

The XL 3000 is not designed to measure methane, however at 25,000 ppm exposure to methane the instrument reported 3 ppm hydrogen, due to the CH₄ partial decomposition at the ionisation source surface.

Four of the seven tested instruments have the ability to discriminate between methane and hydrogen. Further testing would need to be undertaken against water vapour for all applications where measurements are undertaken within the atmosphere or vented or purged emissions that could contain water vapour. In any case, care must be taken to avoid exposure to atmospheres or flue gases with compounds potentially harmful for specific sensors. For instance, exposure to ammonia or sulphuric acid could compromise and damage catalytic, semiconductor or Pd-alloy surfaces.

Further testing would be required to investigate whether a similar proportion of cross sensitivity extends across the concentration range of the instrument. This is an important consideration if these instruments were to be used where methane could be an interfering source.

- Incorporation of a sampling pump. Five of the instruments tested have sampled pumps where the atmosphere being sampled is drawn through a probe (and tube) and then across a sensor, whereas the other instruments use sensors that are passive. Instruments with sampled pumps are preferred, since assuming the probe tip is pointing towards the leak source then the sampled atmosphere (combination of leaked gas and air) will likely contain more leaked gas and less air than a volume sampled by a passive sensor.
- Maximum concentration declared by the manufacturer.

Maximum concentration declared by the manufacturer and the ability of the instrument to measure in oxygen depleted atmospheres which could be important for vented or purged emissions, or in case of unacceptable large leaks.

The tests conducted were limited to below the lower explosive limit for methane and hydrogen for safety reasons. Table 4 shows the maximum concentrations declared by the manufacturer. The NP 1000, Sentrac and GS 700 (according to the manufacturer) measure up to 1,000,000 ppm. These instruments are potential candidates for monitoring emissions that have high concentrations or up to pure hydrogen, for example vented or purged emissions. However, further tests will be required to confirm this declaration by the manufacturer and determine their performance at higher concentrations, for example linearity.

Another consideration is the instrument's ability to measure in the absence of Oxygen. Catalytic conversion requires Oxygen to function, therefore the ability to function in Oxygen-depleted atmospheres excludes the GP 1000, GX Force and GS 700 instruments. The other instruments (according to the manufacturers) can measure in Oxygen-depleted atmospheres, but this needs to be verified.

For three of the instruments the manufacturers claim that the instrument can measure up to pure hydrogen. Although this will require further testing to validate and determine performance (for example, linearity and measurement stability) at these concentrations.

• Linearity to different concentrations of hydrogen.

Linearity may influence the uncertainty of the method and range of concentrations that are quantifiable.

These tests were performed 3 times between 4,000 to 40,000 ppm. The results of these tests should not be extrapolated beyond these limits as further testing would need to be performed.

From the tests conducted all the instruments are capable of measuring within these ranges. According to the manufacturer's datasheet the instruments may be capable of measuring at lower concentrations.

The Extrima and Sentrac instruments indicated a non-linear response to hydrogen within this range, meaning that obtaining accurate quantification from these sensors could be a challenge at these concentration levels. However, at lower concentrations of hydrogen (5 to 100 ppm), these instruments had a linear response. These instruments may be better suited to detecting and locating leaks without any quantification.

All the instruments demonstrated linearity within this range apart from two instruments which instead demonstrated linearity within the range from 5 to 100 ppm. These instruments may be better suited to detection and localising rather

than quantification since a non-linear response could make quantification a challenge.

• Sensitivity - declared by the manufacturer.

The detection limit of the instrument is the minimum concentration that can be measured in direct contact with the sensor.

The limit of detection has not yet been fully assessed for these instruments. For the purposes of comparison in Table 3 a qualitative label has been given: "Higher" sensitivity or "Lower" sensitivity:

- "Higher": From a limited set of tests, it has been found that the Infricon Extrima, Sentrac and XL 3000 could have limits of detection down to approximately 1 ppm level. However, conditions in the field (for example humidity) can have a significant effect on the values reported at these concentration levels. For example, for Sentrac and the XL 3000 the effect of humidity on the measurement became dominant below 5 ppm hydrogen concentration.
- "Lower": means that these instruments can only measure down to approximately 10,000 ppm (1 % v/v). However linearity testing indicated that this range could actually be lower down to 4,000 ppm (depending on how the manufacture undertook their tests).

Four instruments have sensitivities down to approximately ppm level, the others have sensitivities down to approx. 1% v/v (10,000 ppm), although linearity testing indicated that this range could extend down to 4,000 ppm.

• Linearity to a blend of hydrogen and methane at different concentrations.

These tests were conducted to between 5,000 to 50,000 pm methane and 4,000 to 40,000 ppm hydrogen. The Inficon Extrima and Sentrac and XL 3000 are not designed to measure methane and were therefore not tested. The NP 1000 was not tested as it is not selective between methane and hydrogen. All other instruments indicate a linear response within these ranges. Linearity to blended mixtures will be important for quantifying blended gases.

Table 4 provides examples of relevant specifications provided by the manufacturers for the instruments tested under the KAGF funded project undertaken by NPL. The physical properties shown (for example weight and size) show the instruments' suitability to being used as a handheld portable instrument. The Technology Readiness Level (TRL) of each instrument may depend on the intended application. In terms of the quantification of hydrogen concentration or determination of emissions further technology validation is required in the laboratory and field. Therefore, according to UK Research and Innovation. (n.d.), these instruments are at least TRL 4 (i.e., technology basic validation in a

laboratory). The instruments not tested would require laboratory testing, therefore still at TRL 3.

Table 4: KAGF funded project undertaken by NPL - Example manufacturersspecifications of the Extrima, Sentrac, GS 700 and XL 3000 instruments.

Instrument	GP 1000	GX- Force	NP 1000 H2	Extrim a	Sentrac Strix	GS (II sen	700 R, sor)	XL 3000
Species the instrument is designed to measure	H₂ (other gas options available)		H2	H2	CH₄	H2	H2	
Response time (seconds)	3 to 15	< 10	30	NA	30	2s meto tub useo to met	per er of ing d (up 30 ers)	1
Handheld and battery operated	~			✓			Desktop	
Weight (kg)	0.3		4.5	4	1.3		38	
IP rating	IP67			IP 67	NA	IP	55	None
Explosion proof (for example ATEX)	Yes			Yes	No	Y	es	No
Price per unit	NA	NA	NA	NA	£13,000	£3,	500	£24,000

NA - information not available

The performance data provided by the manufacturer can differ from the performance data obtained in the laboratory or in the field. For example, the sensitivity levels quoted by the manufacturers typically do not consider the effect of varying levels of humidity on measurements at low concentration of hydrogen; it can therefore be difficult to make judgements based on datasheets alone.

Performance metrics not tested.

There are several parameters generally measured for these kinds of instruments:

- The response time is a parameter usually provided by the manufacturer (as shown in Table 4). The response time, known as "t90", is the time to reach 90% of the steady state reading after exposed to a constant gas concentration. Therefore, it can be reasonably estimated only when the instrument is fed by a homogeneous gas with constant concentration. However, the variability of the gas concentration in the neighbourhood of any leak source in actual field conditions does not allow it to reach any steady state measurement, and the usual response time (several seconds) is generally good enough to report the maximum value during monitoring. BS EN 15446 (European Committee for Standardization, 2018) indicates leaving the instrument probe inlet at this maximum reading location for approximately twice the instrument's response time. In all the tests performed, NPL used more than 1 minute to ensure that enough time elapsed to obtain a valid reading. The response time will determine the minimum temporal granularity that could be measured.
- Limit of Detection (LOD): This is a quantity strongly dependent on the experimental conditions in which the assessment is performed. The tests conducted have shown that LOD of the most sensitive sensors (Mass Spectrometer and Pd-alloy), are affected by environmental humidity, presence of other gases and possibly temperature. An accurate LOD can be determined under controlled laboratory conditions, but this LOD is not applicable to the typical outdoor conditions found in industrial environments. An estimate LOD will need to be obtained for field conditions during future tests.
- Short- and long-term drift tests: Drift tests are required to determine how the reported concentration changes when the instrument's sensor is exposed to a known and fixed level of concentration. Short term tests are typically in the order of a few minutes and long term over a day. Such tests will inform how the instrument will be used, for example calibration or corrections that may be required.

<u>Summary</u>

These preliminary tests undertaken for the KAGF funded project undertaken by NPL indicate:

- Instruments that can discriminate between methane and hydrogen will be an important performance factor where there are blended gases or where methane could be an interfering gas from a neighbouring process.
- Some instrument technologies (for example thermal conductivity and mass spectrometers) have the potential to measure (quantify) concentrations of hydrogen higher than 40,000 ppm even in the absence of oxygen, while catalyticbased instruments will require oxygen. However, any attempt to assess the performance of these types of instruments when exposed to higher concentrations of hydrogen must be experimentally tested, and the linearities and repeatability

must be quantified. To do that further work is required to develop the needed infrastructure and address the corresponding health & safety issues, as well as the relevant risk assessments. It will be important to define and test the intended concentration range of instruments and their intended use, for example whether measuring hydrogen or blends of gases.

- Some of the instruments might be better suited to leak detection and identifying the location of a leak rather than quantification.
- Most of the instruments are portable and battery operated (designed for "walk over" monitoring) whereas the mass spectrometer would be more suited to a fixed installation or potentially inside a mobile platform.

These tests alone do not provide sufficient information to recommend any instrument or determine whether they can fulfil the monitoring requirements since there are factors (listed above) to consider as well as the instrument's performance. These instruments only provide concentration measurements, therefore there needs to be an emissions rate quantification element, for example to combine measured flow rate with the concentration measurements. There also needs to be a sampling strategy, for example: to determine how the measurements from each component or functional element are combined to produce a site total.

Further testing is required to determine response time, limit of detection, linearity in the whole range of interest and drift within a field test setting. For any proposed method, the assessment of the mentioned performance parameters must be undertaken to both direct measurements (concentrations, volumes, sampling times or sampling rates) and indirect measurements (emission rates or leak rates).

Proposed future testing

All these instruments are meant to detect the presence of the target gas above a threshold limit and sometimes below a certain maximum concentration, both limits are imposed by the intrinsic nature of each sensor and by the quality of the electronic signal processing.

In most cases the instruments can be used to measure the target gas concentrations in a specific range, and their readings are stable when exposed to a homogeneous gas with a constant composition. To measure concentrations each detector must be previously calibrated, and it is advised to perform the calibration before the use (typically on a daily basis).

Cross interferences are expected to mask or distort the readings causing failure to measure the actual concentrations. This happens to all the non-selective detectors, and it can also happen to some of the selective ones to some extent.

These instruments are not devised to measure leak rates, although most can be used to quantify leaks if an appropriate sampling method is used. The Bacharach Hi Flow ® (Connolly et al., 2019) and the "bagging" methods are examples of sampling methods for leak rate measurements for methane. They would need to be validated for hydrogen and

H₂-enriched natural gas because the leak rate measurement relies on the sampling strategy, not only on the operational features of the instruments.

NPL, through several ongoing projects, is planning to test and validate the Hi Flow® method for H_2 and H_2 +CH₄ blends (mimicking H_2 -enriched natural gas) for the quantification of leak rates. Ranges and features of the leaks to be assessed are still under definition due to technicalities and health & safety issues. It is anticipated the testing will be performed with 2 or 3 different commercial instruments.

Commercially available instruments not tested

A literature search identified additional instruments capable of measuring hydrogen (as well as those tested above), such as:

• Tiger Optics Halo Hydrogen instrument (Process Insights, n.d.)

This instrument measures hydrogen concentration by combining oxygen and the sampled hydrogen over a catalyst to produce water. The resultant water vapour is then measured using a laser-based Cavity Ring Down Spectrometer. This is a desk-based instrument. It was considered for incorporation into NPL's Hydrogen Fugitive Emissions Detection System (FEDS), National Physical Laboratory (n.d.); however, it is designed for dry gas (i.e., low / no water vapour concentration), not ambient gas. NPL therefore concluded that it would require a significant amount of additional engineering.

• Ultrasonic cameras.

An ultrasound imaging camera that has been designed to locate gas leaks from several meters away, it has proven its capacity for hydrogen detection. An example would be a remote sensing technique, manufactured by Distran (n.d.), which could provide a solution to monitoring difficult to reach areas.

- Semiconductors (Metal Oxide Semiconductors). The Sensit Instrument was not available on time for the NPL laboratory test. The results for Hydrogen are expected to be similar to those of the Pd-alloy sensors. These kinds of sensors are likely to be affected by natural gas and methane cross interference.
- OFCEAS. Optical feedback cavity enhanced absorption spectroscopy for hydrogen requires large scale instrumentation, is suited for continuous monitoring, but not suitable as a portable device.

Other instruments that are available but will require further investigation

- Pfeiffer, ASM340. Mass spectrometer.
- Horiba HyEVO. Mass spectrometer.
- Asea Brown Boveri (ABB) EL3060 continuous gas analyser and ABB advance Optima A0200 which are modular systems that can exploit the benefits of different technologies and detect a wide range of gases, such as optical techniques for monitoring flammable gases, oxygen, and a thermal conductivity sensor for hydrogen.
- Gas chromatographs such as the Ametek TA5000 and Peak Laboratories Performer 1 which are more likely suited for laboratory analysis of sampled gas rather than field work.

Technologies discounted for monitoring hydrogen

- Thermoelectric (catalyst). Only unsupported devices were found, no recent versions of the use of this technology were found.
- Laser Spectroscopy and standard Infrared. Hydrogen does not respond to standard laser absorption while portable Raman spectrometers for hydrogen are not available.
- Optical sensors. Sensitive to cross interference from flammable gases and even affected by ambient light and to temperature changes, so unsuitable for in field monitoring.

In addition to the technologies already mentioned, there are several other kinds of hydrogen sensors, such as the Sound-resonance hydrogen sensor (Dong et al., 2003), Surface Acoustic Wave and the Microresonance-Based Sensors (Soundarrajan and Schweighardt, 2009). However, these technological approaches are not discussed because (as far as we know) there are no available commercial detectors based on these technologies.

Several examples can be found in the literature of efforts to develop mechanical sensors (Hübert et al., 2011), such as the Micro-Electro-Mechanical Systems (MEMS) using microcantilevers for hydrogen detection at sub ppm concentrations in laboratory-controlled conditions (Gurusamy et al., 2019). Recently, Nevada Nano has offered a detector for multiple gases (including hydrogen and methane) based on MEMS (more detail below). The manufacturer claims that this sensor should be able to detect LEL% for multiple gases and locate fugitive emissions within a mix of hydrogen and methane (Energy Networks Association, n.d.). Furthermore, they comment that the sensor will be able to quantify fugitive emissions, but no sampling method is mentioned besides the detection and the concentration measurement capabilities.

Finally, it is foreseen that some of these technologies will have intrinsic limitations (interferences, mechanical stability, linear response, etc.) to deployment as portable detectors to detect and measure gas concentrations, being restricted to laboratories or for fixed industrial uses, unless heavy digital corrections and compensations (data analysis) could be developed.

Emerging systems

Table 5 below lists emerging technologies that are not currently commercially available.

Name	Notes
Aerodyne Hydrogen	The same concept as the Tiger Optics Halo (mentioned in the previous section) but incorporating a novel sampling scheme to remove ambient water vapour that could exceed the hydrogen derived water and affect the measurement (Hydrogen Insight, 2023). UKRI TRL3 (basic validation in a laboratory environment required for emissions monitoring)
Raman scattering	 Hydrogen detection by Raman scattering is an optical technique where the scattered light from a laser is shifted in frequency due to an inelastic scattering process and has the potential to be used in a remote detection technique. There are a number of organisations that are developing such systems. They are all at early stages of laboratory testing and NPL are currently reviewing these developments. For example, the Fraunhofer Centre for Applied Photonics have recently reported a proof-of-concept system which can detect 0.1 % (v/v) hydrogen at ranges greater than 30 m (Fraunhofer Centre for Applied Photonics, n.d.). Further work would be required to assess how this technique could be deployed in a hydrogen energy economy and in an industrial environment. Conceivable future use: Laser-based remote sensing, potential eye safety issues for field deployment. UKRI TRL3 (basic validation in a laboratory environment required for emissions monitoring)
Hi Flow® sampler	Based on a Bacharach Hi Flow® sampler (Connolly et al., 2019) for quantifying natural gas. Leaking components are loosely enclosed using a dedicated adaptor and measured flow of ambient air is drawn past the leaking component into the sampler. The resulting concentration is then measured by an instrument. Using the measured concentration and flow rate, a mass emission can then be calculated. NPL are in the process of developing a hydrogen version of the Hi Flow® sampler to provide a novel capability to detect and quantify

Table 5: Example emerging instruments or technologies

Name	Notes
	hydrogen leaks. UKRI TRL3 (basic validation in a laboratory environment required for emissions monitoring)
Hydrogen FEDS	A Fugitive Emission Detection System (FEDS), National Physical Laboratory (n.d.) for methane has been deployed in field environments and is therefore at UKRI TRL 7. A number of sampling inlets are distributed around the target site and connected to a central instrument via tubes. The instrument measures concentration which is then combined with wind flow to obtain mass emissions using reverse dispersion modelling. The system provides near-continuous monitoring over a site (limited by the placement of tubing). NPL are investigating whether low-cost sensors can be used to complement the FEDS to minimise any temporal and spatial data gaps and hence provide continuous coverage and enhanced spatial coverage of a site. NPL are in the early stages of developing a hydrogen version of the FEDS as part of the development of a continuous monitoring capability for hydrogen emissions under the KAGF funded project undertaken by NPL. UKRI TRL4 (basic validation in a laboratory environment required for hydrogen emissions monitoring)
Nano's MPS multi-gas sensor	Nevada Nano Multiple complementary chemical sensors on a single Si chip. Called Molecular Property Spectrometer (MPS [™]). This is an example of a Micro Electro Mechanical System (MEMS), made by an array of micro-cantilevers. The manufacturer claims that this gas sensor measures a variety of properties of sampled vapours, liquids, and particles, then a custom software identifies the types of molecules present in an unknown sample.

There is much current research into the use of Unmanned Aerial Vehicles (UAVs), or colloquially drones, for concentration mapping and leak detection from natural gas pipelines (Shaw et al., 2021). Detecting (and potentially quantifying) leaks from the extensive natural gas network (many thousands of kilometres) likely requires a mobile method capable of rapid sampling near to the surface. Drones may find utility here. However, whilst commercial drones have rapidly improved in capability over the past decade, miniaturisation of hydrogen measurement instruments has not. Consequently, combining high performance hydrogen measurements with drones is not yet a possibility. Furthermore, accurately measuring emissions of methane using drones is still an active area of research, and standardisation of procedures has yet to take place.

Future method development

This subsection provides a review of the potential development of hydrogen monitoring methods.

Hydrogen monitoring temporal and spatial coverage

Figure 5 illustrates the different temporal and spatial measurement scales involved in covering a site. The y-axis represents temporal scale from a 'snapshot' measurement to continuous measurement. A snapshot measurement would typically be undertaken by a mobile system or walk over survey taking a measurement of each component in turn, whereas continuous measurements would typically be undertaken by an instrument at a fixed location such as a Continuous Emissions Measurement System (CEMS). Periodic could mean regular snapshots or a near continuous measurement but with gaps in coverage. The x-axis represents spatial scale: i.e. component (for example a flange); functional element (for example a storage tank); site and multiple sites clustered together.





Walk over type instruments that are battery operated and handheld portable would cover the lower left box in the figure. Acoustic cameras could also be classed as "walk over" type instruments or be engineered into a mobile platform. They have the benefit of being able to detect and localise leaks that could be difficult to access or hazardous by monitoring from a remote location. The instruments that have been tested are all point source instruments where the instrument (or sampling tube connected to it) must be positioned within the area being monitored. Most (except the Inficon XL 3000) of the instruments that have been tested are handheld and battery operated (refer to Table 4), they have been designed to fulfil the role as a "walkover" type instrument that covers the lower left of the temporal and spatial map in Figure 5. Due to the physical size of the mass spectrometer, it is not practical to fulfil the role of a 'walk over' type instrument, however it could conceivably be installed in a mobile platform (for example a vehicle) and measure snap shots around a site and assimilate that data into reports for functional elements or a complete site. Whether the instruments tested could be deployed at a fixed location and measure continuously depends on the instrument design (for example packaging, how information is communicated) and how the technique is applied (for example calibration, zero offsetting) and the environment and conditions in which it would need to operate.

Continuous Emissions Monitoring Systems (CEMS) can provide a continuous measurement at component scale of a direct source, for example a vent. The temporal and spatial coverage is shown in the top left on Figure 5. For the monitoring of direct emissions (for example: vents and stacks) the existing monitoring structure using Continuous Emission Monitoring Systems (CEMS), based on a number of standards such as EN 14181 (European Standard, 2015) and EN 15267 (European Standard, 2023) could be extended to include hydrogen. This would require emission limit values and performance requirements for the hydrogen CEMS to be defined. It would be necessary to develop a reference method which would be used during the CEMS certification field trials and for calibration of CEMS under EN 14181 (European Standard, 2015). There are few instruments that are currently available to continuously monitor hydrogen in stacks.

Remote sensing methods, for example Solar Occultation Flux (SOF), Flux sense (n.d.) or DIAL (Innocenti et al., 2017) can cover the regions shown in blue in Figure 5, for methane and non-methane VOCs. These methods are operated as mobile platforms that can cover a larger area from a single measurement compared to a point sensing instrument, they can also monitor difficult to reach or hazardous areas. In principle they could be deployed at a fixed location and measure continuously. There are no commercially available instruments that remotely sense hydrogen.

An emerging technology exploits Raman scattering (Fraunhofer Centre for Applied Photonics, n.d.). Hydrogen detection by Raman scattering is an optical technique where the scattered light from a laser is shifted in frequency due to an inelastic scattering process and has the potential to be used in a remote detection technique where the Raman scattered light is detected at range over an open path. Further work would be required to assess how this technique could be deployed in a hydrogen energy economy and in an industrial environment, to assess the required performance and to resolve potential eye safety issues when used as a remote sensing technique. Eye safety issues are an issue since the laser light is transmitted into the atmosphere. Currently, to obtain sufficient sensitivities, laser power levels need above eye safety limits. Figure 5 shows how it could be conceptually deployed across a range of required temporal and spatial coverages. Depending on performance, Raman spectroscopy could conceivably be

deployed to continuously monitor a component, or, depending on the ranges over which the required sensitivity can be achieved, a functional element (as shown at the top left of Figure 5); or on a mobile vehicle to provide snapshot measurements similar to NPL's Differential Absorption Lidar system.

A distributed system consists of an analyser connected to a network of tubes and sampling points that are positioned across a site. The analyser measures concentration from each sampling point in turn, for example if there are 12 sampling points (and connecting tubes) each location could be sampled for 5 minutes every hour and the cycle repeated. In practice there would be limitations as to where the sampling points could be located, hence such a system would in practice be limited in spatial coverage and would only fill the central region of the map in Figure 5. Such as system is a Fugitive Emission Monitoring System (FEDS; National Physical Laboratory, n.d.) that has been used to measure methane and is to be developed for hydrogen. It is envisaged that its temporal and spatial coverage could be enhanced by the deployment of low-cost sensors which are routinely calibrated and corrected against an analyser.

Leak detection and repair (LDAR)

One conceivable approach to hydrogen leak detection and emission estimation could be to develop a LDAR programme for hydrogen based on Method 21 (Environmental Protection Agency, 2017) and/or BS EN 15446 (European Committee for Standardization, 2018). An LDAR programme would aim to take a number of snapshot measurements at component level and then combine these into a site total emission estimate for a period of time (month, quarter or year).

The monitoring of diffuse Volatile Organic Compound (VOC) emissions to air from components within industrial facilities is undertaken through the implementation of LDAR surveys using techniques prescribed by the Best Available Technique Reference (BREF) documents published by the Industrial Emissions Directive (IED; European Commission, 2010). The standard EN15446 describes the method for LDAR. The first step is detection using a handheld analyser to determine gas concentration. Emissions are then estimated either by capturing a sample of the gas for subsequent analysis (bagging) or the use of correlation curves that have been obtained from a large number of previous measurements.

The frequency of surveys will need to be determined, which will be a compromise between increasing the number of surveys that has been found to increase the number of new leaks found (Pratyush, 2020) and reducing the associated costs. The frequency and location of the monitoring will depend on the details of the characteristics of the emissions sources (temporal characteristics, areas that potentially could have higher emissions such as repurposed infrastructure whereas for infrastructure that has been purposely built for hydrogen there should be less need for monitoring).

It is suggested that an emissions source inventory is built to identify the content of such an inventory and its categories. The inventory should include details such as physical size of

the source, whether it is a continuous or non-continuous source, plume characteristics (point or diffuse) and information that describes the local environment (for example topology). The purpose of such an inventory is to start to build a picture of what sources need to be monitored and their characteristics; such information (along with the reporting requirements) would inform the location, detail and frequency of monitoring and the type of technology that would be most suitable. This inventory could be initially populated with information from studies undertaken (for example the Frazer-Nash 2002 report) including a measure of confidence in that data and include site visits to gain an understand of physical attributes such as hazardous or difficult to reach areas. The inventory could flag the need for investigative monitoring to determine the frequency, location and resolution required.

Producing a component inventory and identifying significant sources of emissions could help target surveys more effectively. The cost of an LDAR programme will include equipment purchase or hire, training, implementation of a quality system (for example record keeping) and labour costs (Pembina Institute, 2015).

Each measurement of a component (for example during a portable walkover survey) will be a snapshot measurement, therefore it is important to ensure that the snapshot measurement is representative of the component throughout the reporting period by correlating it with site operational activity data.

The first step could use a handheld hydrogen instrument such as the GS 700 to determine gas concentrations. However, there are no existing correlation curves that could be used to determine hydrogen emission rate and such data would need to be compiled (and validated) if this approach was to be adapted. In the case of hydrogen, it will be necessary to specify, test and validate a sampling method able to capture a representative gas aliquot (a portion of the leaked gas blended with an unknown amount of atmospheric air) whose concentration can be correlated with emission rate.

In the case of local leaks (with a defined source point or small area) another option is to put in place a methodology, comprising both sampling and measurement, which can directly determine the emission rates without the need for the emission factor estimation. This is the case for the Bacharach Hi Flow® sampler method which is currently being tested for hydrogen at NPL in the frame of different initiatives.

The direct use of instruments devised for concentration measurements without the specification and validation of suitable sampling methods is discouraged, since the variability of the reported readings rely on the sampling method and not just on the measurement instrument used.

Work carried out by other organisations.

NPL have found some relevant reports, protocols and projects reports performed by different agencies with regard to Hydrogen monitoring:

• Testing the Performance of Hydrogen Sensors (Marsh & Cleary, n.d.).

- Standard Hydrogen Test Protocols for the NREL Sensor Testing Laboratory. (National Renewable Energy Laboratory, 2011).
- Blending Hydrogen into Natural Gas Pipeline Networks: A Review of Key Issues. (Topolski et al., 2022).
- NREL Hydrogen Sensor Testing Laboratory (Buttner et al., 2022).
- Test Protocol Document, Hydrogen Safety Sensor Testing. Phase I: Non-Flammable Mixtures (Burgess et al., 2008).

These documents correspond to research results of large-scale projects or to literature reviews focused on several aspects related with the new hydrogen industry, however, we haven't found any mention or detail on fugitive leaks of hydrogen or H₂-NG blends and their monitoring methods.

Efforts to understand the basis of the leaks of hydrogen-enriched natural gas leaks have been made in the past (e.g. Jasionowski et al., 1980). Since then, many works covering these issues can be found, but none mention the fugitive leak monitoring methods.

A broad literature can be found in procedures using transient pressure and discharge time transient analysis to detect size and locate leakage in a rigid pipeline of hydrogen and hydrogen–natural gas mixtures (for example Elaoud et al., 2010). However, again, we have not found specific information on monitoring fugitive leaks of hydrogen and methane.

Case study for monitoring hydrogen emissions

Case study 1: Monitoring of hydrogen in a production facility

Overview

Figure 1 (Section: summary of emission leakage scenarios) lists the leakage scenarios in any hydrogen production facility, which are:

- Direct emissions from venting and purging.
- Fugitive emissions.
- Emissions from flaring.
- Fugitive emissions through infrastructure such as pipework.

The most significant sources of emissions (according to Chapter 1) are from direct emissions from venting for electrolysis plant and purging and fugitive emissions from gas reforming plant. Fugitive emissions from pipework and 'hydrogen slip' emissions from flaring are foreseen to be relatively small or negligible (assuming infrastructure is purposebuilt for hydrogen).

This case study focusses on fugitive emissions. The aim is to detect, locate and quantify emissions and this will provide evidence on the hydrogen emissions to verify the predictions drawn so far regarding emissions scenarios. This data would be collected by undertaking exploratory monitoring. The methods suggested could equally be applied to other forms of hydrogen production processes or other areas of the value chain e.g., pipeline systems, depending on the reporting requirements and the specifics (for example ease of access, size etc) of the emissions sources and their environment.

Exploratory monitoring could inform what data requirements are needed for specific purposes.

Rationale

The approach to an exploratory monitoring campaign could be as follows:

- Build an emissions source inventory that details which emissions sources need to be monitored.
- Identify relevant properties that describe these sources to determine which monitoring methods to deploy.
- Identify the methods that should be deployed that can meet the data reporting requirements and are suitable for the emissions sources that need to be investigated.

• Describe how the commercial off the shelf technologies and emerging technologies can meet these needs and summarise what the technological and methodological gaps are.

Build an emissions source inventory.

The inventory could be based on literature surveyed such as Frazer-Nash (2002), site visits, or based on components that are considered the largest contribution to fugitive emissions in the methane and non-methane industry (see Environment Agency, 2021), such as:

- Compressor seals.
- Open-ended lines.
- Pressure release devices.
- Pump seals.
- Valves.

Functional elements could be grouped as:

- Electrolysers.
- Specific vents.
- Compressor.
- Hydrogen treatment area.
- Flare (if applicable).
- Storage tanks.

Identify relevant properties of emission sources.

Identify the properties of each emissions source:

- The location and physical properties of each of these items should be noted which could include access restrictions (for example: whether it's located in a hazardous zone), height and physical size. Include a map of the site.
- The known plume characteristics: the exit velocity, temperature and gas composition, range of emission rates, continuous or non-continuous, type such as diffused, point source (from a vent), and whether it's an elevated source.

Assumptions: It is assumed there are no sources of other combustible gases such as methane.

Identify Methods which could be deployed

For investigative monitoring the site operator could deploy a range of methods to provide coverage of the temporal and spatial scales shown in Figure 5.

Direct measurement of leak sources

A LDAR type survey could be deployed to detect and quantify any leaks at component level, each on a snapshot basis. The inventory and plant operational history and status may provide an indication of how representative such a survey could be. For example, it may be that only a small percentage of components are inaccessible for monitoring, therefore few are missed. Based on the plant status, if a functional element is operating in a continuous (non-varying) state then the method operator could assume that a snapshot measurement would be representative, whereas a snapshot measurement of a flange seal that feeds a non-continuous vent may be not necessarily be representative. Instruments that are commercially available could in principle perform this type of survey, however a means of quantifying emissions rates needs to be established. A potential system is a Bacharach Hi Flow® sampler (Connolly et al., 2019), that currently is in use for methane. Figure 6 shows this type of instrument in operation. Leaking components are loosely enclosed using a dedicated adaptor and a measured flow of ambient air is drawn past the leaking component into an instrument which measures the gas concentration. Using the measured concentration and flow rate, a mass emission can then be calculated. In addition, methodologies to detect leaks and guality hydrogen emissions need to be developed.





Such a system could provide a snapshot measurement for each component, however difficult to access or non-continuous leaks may be missed. In addition, it would be useful to build up a "broader picture – spatially" by having an inventory of emissions from functional elements and site total. Such data could be compared to similar functional elements on different sites to identify any common emission properties and help to validate component measurements that have been assimilated to build a site total.

Remote 'open path' sensing

Potential methods that could help build up a broader picture spatially and provide a means to detect and quantify leaks from difficult to access or hazardous areas (for example flares) is to deploy a remote sensing, open path method. Remote sensing methods (for methane and non-methane VOCs) use optical instruments to measure the concentration across an open path in the atmosphere. Figure 7 illustrates how such a method could be deployed.





In this example a remote sensing, open path instrument is installed on a mobile vehicle, whose position is shown by the rectangle, it moves to location one, two then three, taking measurements at each location. For methane and non-methane VOCs such measurements could be undertaken passively (for example Solar Occultation Flux) where the absorption of light (generated by the sun) at specific wavelengths is measured to determine total concentration along an open path length; or undertaken actively by generating light at a specific wavelength that is absorbed by the gas species of interest along a path. Either the portion of the scattered light is captured by a telescope mounted on the vehicle (for example Differential Absorption Lidar) or some techniques use a detector positioned at the other end of the path or a retroreflector. As discussed, spectroscopic absorption instruments are not suitable for hydrogen, however the principle of using a remote sensing, open path technique along with a suitable instrument (for example Raman) may be an option to explore.

The remote sensing method shown below measures the concentration along a path, which could be total path concentration or range resolved concentration for an instrument that uses a pulsed source (Lidar). This can provide a useful source of information about plume

shapes and sizes. In the example the concentration is measured along Line Of Sight (LOS) 1 (downwind of a flare), LOS 2 (upwind of a flare to measure background), LOS 3 downwind of a process and storage area and LOS 4 downwind of a process area (could be housing electrolysers, treatments area, compressors etc). The concentration measurements could then be combined with wind measurements to obtain emission rates. Therefore, the emissions rate of the storage area would be that obtained from LOS3 minus that obtained from LOS4.

Distributed sampling

The potential methods mentioned acquire a snapshot of concentration (and emissions) in time, therefore, non-continuous emissions may be missed. A potential method that could help build up a broader picture in time and space is to deploy a distributed sampling method as shown in Figure 8. An analyser is connected to a network of distributed sampling points via tubes. The analyser instrument would measure concentration and then combine with wind measurements to obtain emissions rate. Please refer to emerging systems section for more information.





The methods described could be applied across the value chain and are not necessarily limited to the production of hydrogen.

Case study 2: Hydrogen monitoring in a Green hydrogen production facility

Figure 9 shows a block diagram of a green (electrolysis) hydrogen production facility showing the location of direct (vented) emissions, a flare and fugitive emissions from infrastructure components.

The direct emissions could be monitored using Continuous Emissions Monitoring Systems (CEMS), taking into consideration the conditions (for example, range of concentrations and other gases that might be present). The measured concentration would need to be combined with the flow rate to obtain emissions rate. For a green hydrogen facility these types of emissions are likely to be significant.

Fugitive emissions from flares are predicted to be insignificant, a cost versus benefit approach along with exploratory monitoring could be undertaken to determine the monitoring requirements. Flares can be difficult to access and the area surrounding a flare can be hazardous, therefore a 'remote sensing' method might be the best approach, depending on the range and performance of the monitoring system.

The infrastructure components could be monitored using an LDAR type approach, for example using a Bacharach Hi Flow® sampler, however physical accessibility and hazardous zones would need to be considered. Emissions from such components are predicted to be insignificant, so again a cost versus benefit approach along with exploratory monitoring could be undertaken to determine the monitoring requirements.



Figure 9: Green hydrogen production facility

Conclusions

There are currently no standard methods for monitoring hydrogen. There are commercially available instruments that can measure concentration, but these are designed to measure a snapshot in time at component level. These instruments need to be incorporated into methods to be able to measure emission rates. Emerging technologies such as Raman remote sensing, distributed sampling, low-cost sensors and acoustic techniques may be able to provide greater coverage of the spatial (component to site level) and temporal scales (periodic to continuous). Further work is required to establish the required performance of these methods to meet the data reporting requirements and emission scenarios. There are currently few continuous emissions monitoring systems that are commercially available.

Listed below are the suggested areas for future development outlined by this project (in no particular order of importance):

- Development of a method to detect and quantify hydrogen (based on LDAR methodologies) that can provide a snapshot at component level. One possibility is a hydrogen version of the Bacharach Hi Flow® sampler that is used for methane monitoring. This could potentially fulfil the need to manage leaks to improve safety, minimise loss of a valuable product and contribute to the reduction in emissions to atmosphere.
- Development of a standard methodology for monitoring and reporting emissions at a periodic level for a complete site which may involve reconciliation of data at different spatial and temporal scales. This is a current industry development area for whole site methane monitoring and reporting.
- Understand the performance and validate methods within a field environment against a controlled release at a selection of sites. These methods should cover the temporal and spatial scales needed to monitor hydrogen from LDAR, open path to distributed sampling.
- Site specific identification of the most cost-effective monitoring to deploy. This will depend on the specific details of the site. For example, physical characteristics such as elevated sources that could be difficult to physically access; and emissions characteristics, such as point source or diffuse source covering a wide area. A site-specific inventory of potential emissions sources including functional elements and components that are likely to have significant emissions would be needed. This inventory could be used to plan future exploratory monitoring, for example for fugitive emissions, as described in the case study.
- Development of methods that provide continuous coverage such as CEMS and distributed sampling systems (with low-cost sensors) and remote sensing systems such as Raman and acoustic methods.
- NPL are developing a framework for defining and characterising data requirements, emission sources and methods as a standard. This would be initially aimed at methane but could be adapted for hydrogen. It would provide the following benefits:

- A harmonised system for describing and classifying data reporting requirements, emissions sources and monitoring methods. Such a system (with a lexicon) would ensure a more reliable transfer of information and knowledge between stakeholders which would benefit the development of regulations and standardisation of methodologies which are fit for purpose. A harmonised system could also lead to more reliable reconciliation and integration of datasets (for the calculation of useful emissions factors) since stakeholders will have consistent terminology and systems for describing information.
- A means for industrial operators and other stakeholders to select the most costeffective monitoring solutions, or suite of complementary solutions, based on understanding the reporting requirements and source characteristics.
- In future, a database could be developed based on the framework to highlight current standards, emerging techniques, and systems that have evidence of use and validation. Use of such a database could potentially identify gaps in technology, scale, standards, and availability, to ultimately assist in the development and improvement of monitoring methodologies.

Much work is required to develop monitoring methods, however the techniques, processes and knowledge gained from other gases such as methane can be applied.

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List of abbreviations

Abbreviation	Definition
АВВ	Asea Brown Boveri
ΑΤΕΧ	EU safety directives for explosive atmospheres
ВАТ	Best Available Technique
BREF	BAT Reference document
BSI	British Standards Institution
ccs	Carbon Capture and Storage
CEMS	Continuous Emission Monitoring System
CH₄	Methane
CO ₂	Carbon Dioxide
DESNZ	Department of Energy Security and Net Zero
DIAL	Differential Absorption Lidar
EPA	US Environmental Protection Agency
FEDS	NPL's Fugitive Emissions Detection System
FET	Field Effect Transistor
H ₂	Hydrogen
KAGF	Knowledge Assets Grant Fund
kt	Kilo tonnes

Abbreviation	Definition
LDAR	Leak Detection And Repair
LEL	Lower Explosive Limit
LOD	Limit of Detection
LOS	Line Of Sight
MCERTS	Environment Agency's Monitoring Certification Scheme
MEMS	Micro Electro Mechanical System
MJ	Mega Joules
NPL	National Physical Laboratory
он	Hydroxyl radical
ррт	parts per million
SOF	Solar Occultation Flux
TCD	Thermal Conductivity Devices
TRL	Technology Readiness Level
UAV	Unmanned Aerial Vehicle
UK	United Kingdom [of Great Britain and Northern Ireland]
voc	Volatile Organic Compound

Glossary

Term	Definition
Closed path	Closed-path optical spectroscopy is used to measure the concentration of a chemical species within a physical closed system, such as a cell, which contains a sample of the atmosphere.
Component (spatial scale)	An entity that forms part of a process or system; on an approximate spatial scale of centimetres to metres (for example, a flange that joins two pipes).
Continuous emission	An emission that occurs continuously for a period greater than a prescribed threshold. The threshold (for example, 24 hours) needs to be defined. An example of a continuous emission is a landfill. The emission rate may vary.
Functional element (spatial scale)	A spatially separate entity that performs a specific purpose; on an approximate spatial scale of metres to hundreds-of-metres (for example, a process tank, boiler unit, or storage unit).
Fugitive emission	An unintended (or irregular) release (emission) of a chemical constituent to the atmosphere. Fugitive emissions are typically associated with anthropogenic activity and often considered to be leaks.
LDAR	Leak detection and repair. A process in which a leaking component is identified and assigned a leak rate (often based on a correlation factor), prior to the leak being scheduled for repair EN 15446, European Committee for Standardization (2018).
Method	A generic procedure or a set of instructions (either prescribed or guidance) employed for scientific measurement. In the case of emission monitoring, the method refers to a combination of a measurement technology, a sampling strategy, and an emission rate calculation or model. A method should describe the scope, protocol, and relevant metrological factors to
Term	Definition
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	provide evidence that the method can produce data which can be trusted (for example, evidence of method validation). A method will consist of a measurement instrument, sampling strategy and emissions quantification element (if reporting emissions rate) or suite of complementary method elements.
Method element	A <i>method</i> may contain one or more of the following <i>method elements</i> : measurement instrument, sampling strategy and/or emission quantification.
Monitoring	A generic term used to describe measurement, location and/or detection of emissions
Non-continuous emission	An emission that occurs for less time than a defined threshold (see Continuous emissions), including sources that have a repeating cycle (periodic); for example, a pneumatic valve that emits once every hour for 5 seconds. Non-continuous emission sources may be short-lived, episodic, or periodic.
Open path	Open-path optical spectroscopy is used to measure the concentration of a chemical species across a path length across free space within the atmosphere.
Passive spectroscopy	Optical spectroscopy which uses ambient light (such as sunlight) as a light source.
Periodic	A periodic report with a defined period (or frequency). The intention is that the number of reports are not necessarily limited (most likely more than two).
Point-sensor (Sampling strategy)	A point-sensor must be deployed in the measurement area and typically provides a much smaller coverage area
Remote-sensing (sampling strategy)	Remote-sensing (also referred to as standoff detection) involves the measurement of the properties of an object without making physical contact with that object. In the case of emissions measurement, the object is typically understood to be the emission plume. Therefore, a method which uses remote-sensing does not need to be

Term	Definition
	physically located within the emissions plume (or even in the region where emissions may occur). The opposite of remote-sensing is referred to as a point measurement system (or in-situ sampling), which needs to be physically located within the plume, or within the target region.
Sampling strategy (method element)	Describes how the measurement is collected and represented, and the platform used.
Sampled pump	A device that extracts a portion of the atmosphere (combination of leaked gas and air) to be measured at a known flow rate.
Site (spatial scale)	A spatially separate premises that performs an activity consisting of a number of functions or consists of one or more functional elements; on an approximate spatial scale of hundreds-of-metres to tens-of-kilometres (for example, a landfill site, tank farm, anaerobic digester plant).
Snapshot	A single report representing a state at a given time, or two reports separated by a time period or before and after an event (for example, repair). The intention is that the number of reports are limited (most likely two or less).
Technique	A generic term used to describe a type of measurement instrument, sampling strategy, emissions quantification, or data process.

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