Application note

Process Mass Spectrometers

The pathway to net zero: how clean burning hydrogen can help to hold climate change at bay

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Introduction

The United Nations (UN) has restated the need to accelerate planned reductions in emissions from the utilisation of fossil fuels. In a recent report the UN shows that, while the curve of global emissions is shifting, it is not on target to limit the global temperature rise to 1.5 °C. Indeed, rather than seeing a reduction of emissions by 45% by 2030, these emissions are forecast to rise by 11%.[1]

Clearly a failure to hit interim targets risks missing the goal of reaching net zero emissions by 2050, a goal that for many countries is a legally binding commitment. The International Energy Agency describes an inflection point that will accelerate a shift away from fossil fuels in favour of cleaner alternatives.

Emissions trading programs

The world's largest economies have programs in place to incentivise participants to reduce their emissions with many of these programs based on a 'cap and trade' approach. An explanation of the European Union's (EU) Emissions Trading System (ETS) is given by the European Commission (EC); *"A cap is set on the total amount of certain greenhouse gases that can be emitted by the operators covered by the system. The cap is reduced over time so that total emissions fall.*

Within the cap, operators buy or receive emissions allowances, which they can trade with one another as needed. The limit on the total number of allowances available ensures that they have a value. The price signal incentivises emission reductions and promotes investment in innovative, low-carbon technologies, whilst trading brings flexibility that ensures emissions are cut where it costs least to do so.

After each year, an operator must surrender enough allowances to cover fully its emissions, otherwise heavy fines are imposed. If an installation reduces its emissions, it can keep the spare allowances to cover its future needs or else sell them to another operator that is short of allowances." [2]

Though no longer a member of the EU, the UK ETS continues to follow the same rules as the EU ETS. The USA also has a 'cap and trade' program to incentivise greenhouse gas reductions. Sectors that must comply with limits on CO_2 emissions include energy intensive industries such as oil refining, metals and power generation (electricity and heat). There are penalties for non-compliance, in the EU and UK these are currently set to £100 and €100 euros per tonne respectively.

The hydrogen element

Hydrogen produced from "clean" renewable energy can assist in making the switch away from fossil fuels more achievable. The principal emission from burning hydrogen is water, and while the burning of hydrogen produces emissions of NOx which is of concern this combustion does not produce carbon emissions. In the UK, the Energy Networks Association (ENA) published *Britain's Hydrogen Blending Delivery Plan* which states that the gas grid companies will meet government target to blend 20% hydrogen into the natural gas that is delivered to British homes and businesses. Adding this 20% of hydrogen into the gas grid will reduce carbon annual emissions by an amount equivalent to taking 2.5 million cars off the road, according to the ENA.[3]

The EC released a study by its Joint Research Centre (JRC) entitled *Blending hydrogen from electrolysis into the European Gas Grid*. Among the findings was that up to 5 to 10% by volume of hydrogen could be injected into the natural gas grid without the need for end users to modify installations and without the need for major modifications to the transmission structures. Power generation by solar and wind can reduce the use of fossil fuels for this hydrogen generation, the JRC goes on to say that additional renewables and storage will be required to mitigate dependence on fossil fuel based electricity and that JRC modelling suggests that storage of just a few hours of supply can reduce carbon intensity of hydrogen produced by electrolysis by as much as 40%.[4]

In support of the initiatives described above, the UK and EU are building the infrastructure to produce and utilize increasing amounts of hydrogen. In the north of the UK one such project entitled "HyNet" [5] is designed to capture and lock away CO_2 and to produce, transport and store hydrogen. This project is already underway, captured CO_2 will be stored in almost empty gas fields under the sea at Liverpool Bay, low carbon and flexible hydrogen production will support the supply of cleaner hydrogen which can be used by nearby industries and ultimately blended into the gas grid for homes and businesses. A buffer supply of hydrogen will be stored in former salt caverns which currently store natural gas, these repurposed caverns will store 35,000 tonnes of hydrogen to manage the peaks and troughs in energy demand. The structure of HyNet Northwest can be seen in Figure 1.

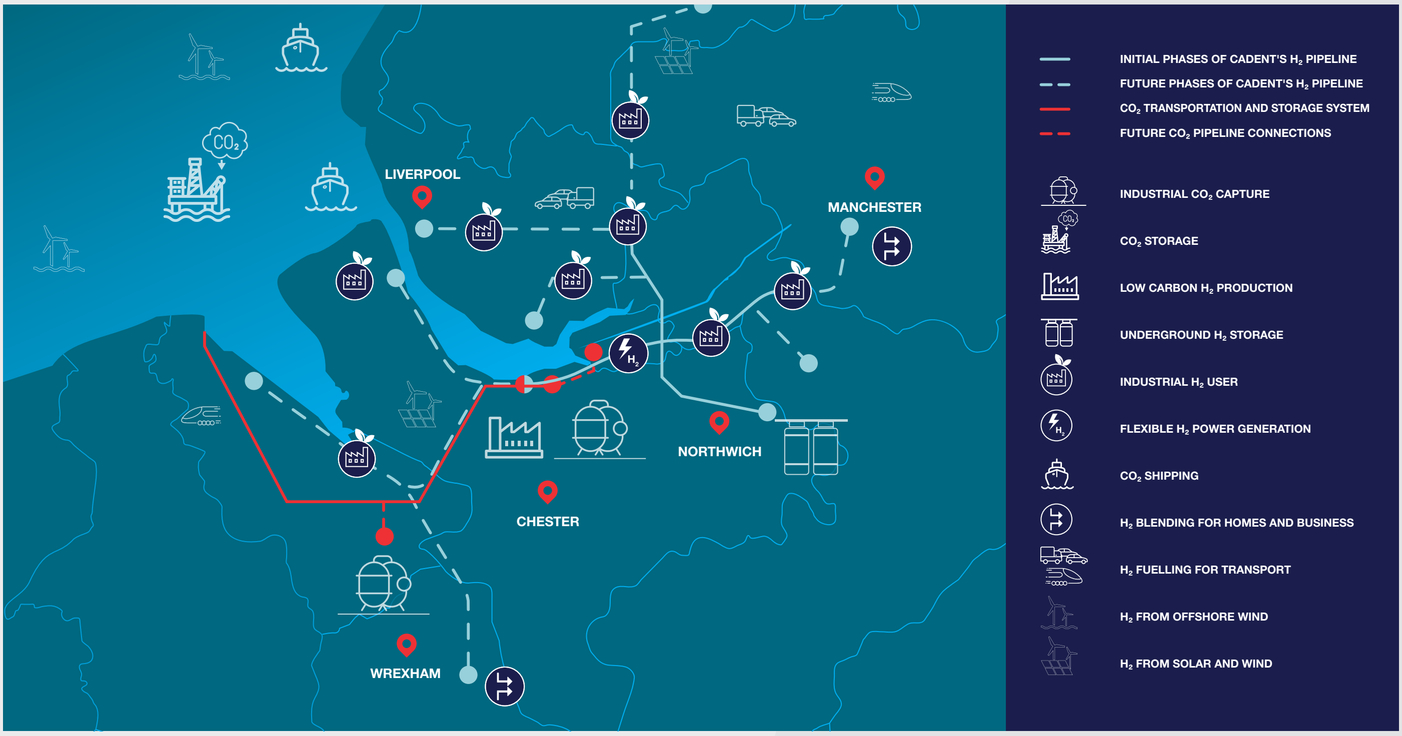

Figure 1: HyNet Northwest structure.

A similar initiative in Europe is underway, entitled the European Hydrogen Backbone (EHB); this program, supported by 31 energy infrastructure companies from 28 countries, has the vision to establish a pan Europe hydrogen pipeline infrastructure necessary to ensure security of demand and supply as recognised by the EC's hydrogen and decarbonised gas package, published in December 2021.[6]

The ambition of the EC is for the development of a 20.6 Mt renewable and low-carbon hydrogen market by 2023 and EHB supports this with the development of "five pan-Europe hydrogen supply and import corridors connecting industrial clusters, ports and hydrogen valleys to regions of abundant hydrogen supply".

Analytical requirements at power generation plants

Operators of power generation plants have several reasons to monitor the composition of the fuel gas that is burnt in the process of generating electricity via gas turbines; the efficient burning of hydrocarbons requires the optimization of fuel to air ratio, natural gas carries a high cost so minimising consumption is attractive, and then there are the environmental concerns; maintaining low firing temperatures holds down NOx emissions and it is essential to have a continuous and accurate analysis of the composition of the fuel to calculate the physical properties of the fuel gas and the CO_2 emissions for the trading of carbon and avoidance of non-compliance fines.

Up to now the preferred method for the analysis of fuel gas at power plants has been gas chromatography (GC). This well proven technique is used across many industries and offers accurate and reliable composition data. GCs are also well known to plant maintenance staff and hence come with a high level of trust. GCs are not without their limitations though—analysis methods are designed by the arrangement of injection valves, columns and detectors, as well as the choice of carrier gas. Accordingly, analytical method changes typically require changes to analyzer hardware and this problem looms large for the power industry when hydrogen is streamed into the natural gas feed as, in many instances, the installed GCs will no longer be able to make this essential measurement.

A further constraint of GC analysis applies to some types of gas turbine that are sensitive to gas composition variations, even when the gas complies with gas quality standards. Auto-ignition problems can arise with some gas turbine combustion systems when the fuel gas contains elevated levels of heavier hydrocarbons. Control systems are in place to address this concern, but they depend on analysis cycle times that the GC cannot meet, requiring the installation of additional (typically infra-red) analyzers measuring C_2+ content.

The solution to these challenges comes from another well proven technique: Mass Spectrometry (MS). These analyzers tend to have the same hardware configuration irrespective of the application, with only software optimisation required to suit different measurement challenges. This makes MS a very flexible tool indeed, able to cope with different analysis methods within a single analyzer and equally at home across the full range of hydrogen content in natural gas—from zero to any concentration up to 100%.

There are other good reasons for using MS as they do not require any carrier or detector gases, resulting in significant long-term cost of ownership savings and they have analytical speeds up to 30x faster than a typical process GC. MS is not new to the analysis of fuel gases since, since the 1980's, MS has been used in the iron & steel industry to monitor the composition of valuable and highly calorific furnace waste gases that are utilised for heating furnaces and the energy hungry ovens that heat steel prior to rolling and shaping. Measuring the composition of these fuels to determine properties including Calorific Value, Wobbe Index and Combustion Air Requirement has long been a proven application for MS, and more recently those same steel producers have discovered that the versatile MS can also provide this composition analysis for process exhaust gases being utilized for downstream power generation. These iron & steel making processes contain varying amounts of hydrogen and have vastly differing heat values, ranging from a few hundred to several thousands of kcal/nm_3, MS can report the properties of these process gas streams using a single analyzer.

The choice of MS technology is important as there are many different types and they each have their unique characteristics. The type that has been proven over many decades to have superior analytical performance, as well as longer periods between calibration and maintenance, is the scanning magnetic sector MS. The scanning magnetic sector MS separates positively charged ions generated from the sample gas molecules in a variable magnetic field prior to measuring the current generated by ions of each mass at a Faraday detector. The spectral peaks produced in the magnetic field have a very symmetrical shape with a flat top, the height of a peak is directly proportional to component concentration and its flat top ensures consistent height measurement while being very tolerant to small variations in peak position. Figure 2 shows the design of a scanning magnetic sector MS.

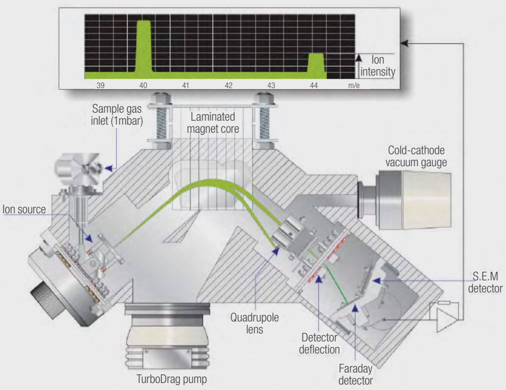

Figure 2: Scanning Magnetic Sector analyzer of the Thermo Scientific Prima PRO MS.

Fiscal metering

Another essential requirement for power generation plants is the need to accurately meter the value of the fuel gas being supplied. In addition to temperature and pressure correction, the compressibility factor at pipeline (metering) conditions is usually required to account for non-ideal gas behaviour of the hydrocarbon mixture. Both the compressibility calculation and the calculation of the lower (net) heating value of the fuel requires the composition of the fuel gas. The combination of the volume flow rate and the heating value gives the thermal input of the plant.

For power generation applications, the plant operator's fiscal metering instrumentation may be used for billing purposes in addition to reporting to the carbon Emissions Trading System, subject to commercial agreement between the supplier and the plant operator. Process MS can satisfy these requirements, reporting accurate and reliable gas composition data for fiscal metering with cycle times shorter than any of the existing GCs currently available while also satisfying the measurement uncertainty requirements of both the ETS and custody transfer arrangements.

Measurement quality standard for fuel gases

A standard for determining whether an analytical method is suitable for the analysis of natural gas is ISO 10723.[7] This standard is one of the 'European Norms' referenced in the Monitoring and Reporting Regulations of the EU Emissions Trading System. This standard can determine the range of composition to which the method can be applied while satisfying defined maximum errors and uncertainties, or it may be used to determine the range of errors and uncertainties for the analysis of gases within a defined range of composition.[7] This standard is applicable to the composition measurement and/or the properties calculated from composition.

A Thermo Scientific™ Prima PRO MS (Figure 3) has been independently evaluated by EffecTech UK, an independent specialist company providing accredited calibration and testing services to the energy and power industries for gas quality, flow and total energy metering. EffecTech is accredited to the internationally recognized ISO/IEC 17025:2005 standard which specifies the general requirements for the competence to carry out tests and/or calibrations, including sampling. It covers testing and calibration performed using standard methods, non-standard methods, and laboratory-developed methods. It is applicable to all organizations performing tests and/or calibrations.

EffecTech applied ISO 10723 to assess the performance of the Prima PRO for the nine components listed in Table 1. The gas matrix contains a wide range of inorganic and organic components including hydrogen, nitrogen, carbon monoxide, carbon dioxide and saturated and un-saturated hydrocarbons. Each reference gas used in the conduct of the test was analysed for 30 cycles over 5 minutes (10 second cycle time).

Figure 4 shows the linearity plots generated by the tests conducted by EffecTech. They demonstrate better linearity than that of a thermal conductivity detector fitted to a GC and prove that the Prima PRO MS can generate accurate, reliable composition data from complex and variable gas mixtures.

Component	Calibration gas (% mol/mol)	Sample composition range (% mol/mol)	
		Minimum	Maximim
Nitrogen	9.000 ± 0.015	0.10	9.94
Carbon Dioxide	5.000 ± 0.015	0.05	2.50
Methane	9.000 ± 0.020	9.84	65.03
Ethane	5.000 ± 0.013	0.50	24.75
Propane	10.000 ± 0.025	0.11	19.74
Ethene	5.000 ± 0.0015	0.099	10.06
Propene	5.000 ± 0.013	0.098	4.91
Hydrogen	43.000 ± 0.070	10.005	69.88
Carbon Monoxide	9.000 ± 0.015	0.098	6.79

Table 1: Calibration gas standard and reference gas ranges.

Figure 3: Prima PRO 710

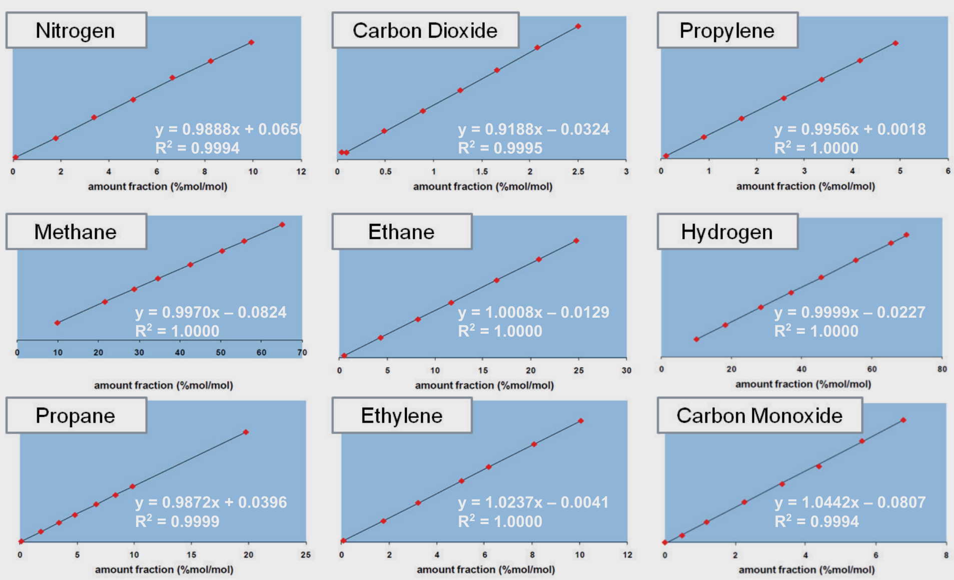

Figure 4: Prima PRO MS linearity data

The tests were conducted using the Prima PRO mass spectrometer.

Furthermore, from the EffecTech test report, Prima PRO MS bias errors on normalised amount fraction were determined by a mathematical model known as a Monte-Carlo simulation. A data set of 5,000 hypothetical random compositions was constructed where each gas component amount fraction lay within the range of gases expected through a typical natural gas metering point. The minimum and maximum amount fraction for each component is shown in table 1 reference gases.

For each of the 5,000 simulated compositions, the expanded uncertainty on the measured physical properties was calculated using the input parameters described above and using a coverage factor (k=2) providing a level of confidence of approximately 95%.

Table 2 below shows the minimum, mean and maximum uncertainties in these properties obtained during the simulation and the range of properties over which the simulation ran.

Summary

The world's largest economies are committed to net zero strategies; the targets are ambitious and slow progress continues to make it more difficult to hit that end goal. The United Nations has highlighted the need to accelerate the transition away from fossil fuels and the International Energy Agency marks the present time as an inflection point where this acceleration can take place.

The utilisation of cleaner burning hydrogen, so long as it is produced sustainably, can help this transition, but large-scale changes to our infrastructure and end use facilities present challenges to overcome; actions being taken by national governments and the EU for the generation, storage, transportation, and use of clean hydrogen are evidence that this transition to hydrogen is taken seriously and investment is already underway.

Some of the challenges are at the point of fuel gas combustion where the adoption of mass spectrometry can overcome the analytical hurdles associated with variable fuel gas hydrogen content and this technology has already proven to be an effective technique, evaluated by an accredited test laboratory and field proven in many previous installations in the iron & steel sector. MS offers full composition and physical property analysis of natural gas, containing varying amounts of hydrogen with measurement cycle times of just a few seconds. MS is extremely linear, very stable, with modest utilities consumption, and offers long periods between calibration and maintenance.

MS is ready to play an increasing part in making the world a healthier, cleaner and safer place.

Property		Minimum	Mean	Maximum
Real superior calorific value ($MJ.m^{-3}$) Gross CV (GCV)	$U(CV_{sup})$ $\%U(CV_{sup})$	0.016 0.051%	0.029 0.078%	0.042 0.121%
	CV_{sup}	19.9	37.1	53.0
Real inferior calorific value ($MJ.m^{-3}$) Net CV (NCV)	$U(CV_{INF})$ $\%U(CV_{INF})$	0.014 0.051%	0.026 0.079%	0.039 0.124%
	CV_{INF}	17.6	33.7	48.6
Carbon dioxide emission factor (gross) CEFG ($t(CO_2).TJ^{-1}$)	U(CEFG) %U(CEFG)	0.009 0.017%	0.018 0.036%	0.040 0.112%
	CEFG	35.8	51.2	57.9
Carbon dioxide emission factor (net) CEFN ($t(CO_2).TJ^{-1}$)	U(CEFN) %U(CEFN)	0.010 0.016%	0.018 0.034%	0.043 0.108%
	CEEN	40.3	56.4	63.1
Carbon dioxide emission factor (quantity) CEFQ ($g(CO_2).m^{-3}$)	U(CEFQ) %U(CEFQ)	0.9 0.048%	1.7 0.093%	2.6 0.173%
	CEFQ	710	1918	3028
Case density ($kg.m^{-3}$)	U(d) %U(d)	0.00031 0.039%	0.00055 0.074%	0 00084 0.150%
	d	0.384	0.776	1.152
Relative density	U(RD) %U(RD)	0.00025 0.039%	0.00045 0 074%	0.00069 0.150%
	RD	0.313	0.633	0.940
Real Wobbe number ($MJ.m^{-3}$)	U(WN) %U(WN)	0.028 0.054%	0.033 0.071%	0.041 0.106%
	WN	32.1	46.6	57.0
Molecular mass ($kg.kmol^{-1}$)	U(M) %U(M)	0.007 0.039%	0.013 0.074%	0.020 0.150%
	M	9.1	18.3	27.1

Table 2: Uncertainty estimates—physical properties.

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