

Nitrous Oxide Emissions Associated With 100% Hydrogen Boilers

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Information

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Glossary

CO₂e – carbon dioxide equivalent

daf – dry air-free

kWh – kilowatt hours

mg – milligrams

ppm – parts per million

Nitrous Oxide Emissions Associated With 100% Hydrogen Boilers

Background

The Scottish Government's Directorate for Energy & Climate Change commissioned an analysis of emissions from the combustion of hydrogen in domestic boilers.

The aim of this exercise was to measure the gas composition of flue gas from hydrogen boilers under normal (real world) operating conditions, with a view to establishing what, if any, greenhouse gases are emitted during combustion.

Previous research was conducted by ACE Research and Energy Savings Trust and commissioned by ClimateXChange (CXC) on behalf of the Scottish Government. This aimed to establish the greenhouse gas emissions associated with the most common and readily available zero and low carbon heating technologies.

The findings of the research were inconclusive regarding 100% hydrogen fuelled appliances with the report highlighting that there could be very limited 'trace' amounts of nitrous oxide (N₂O) emissions involved in the combustion of hydrogen within boilers.

As N₂O is treated as a greenhouse gas within section 10 of the Climate Change (Scotland) Act 2000, it was desirable to conduct measurements of N₂O emissions from hydrogen appliances in a realistic domestic environment under typical operating conditions.

Introduction

TÜV SÜD National Engineering Laboratory was commissioned to undertake a series of tests at suitable hydrogen boilers in domestic settings. The primary objective was to determine N₂O emissions, but additional measurements of oxygen and moisture were also required to standardise the data in accordance with the appropriate Standard. Measurements of oxides of nitrogen (NO/NO₂, expressed as NO_x) were also carried out.

Measurements were carried out at a fully functional domestic facility. This facility comprises two homes which are fitted with purpose-built hydrogen gas appliances including cookers and hobs, fires and boilers and a hydrogen meter. The appliances are very similar to today's natural gas appliances and operate in the same way.

The measurements were performed under a variety of conditions intended to reflect real-life domestic operation and the results expressed as an estimated annual emission and as carbon dioxide equivalents.

Only one boiler was available and tested over a range of 6.4 kWh to 29.0 kWh. We were unable to arrange access to a further two boilers at an alternative location due to limited availability and time constraints.

Scope of Work

Measurements were performed using two instrumental continuous analysis systems as described below.

Nitrous Oxide and Water Vapour

These components were determined by a Fourier Transform Infrared (FTIR) analyser. A sample was extracted from the boiler flue via a heated sample transport and conditioning system.

The sample is passed to an Infrared measuring cell in which the absorbance of infrared radiation throughout the IR band is recorded. Fourier transform mathematics is then used to identify and quantify the compound of interest from a reference library which contains the absorbance characteristics of that compound. The instrument output was logged at 20 second intervals resulting in continuous real-time analysis.

Oxides of Nitrogen and Oxygen

Oxides of nitrogen, expressed as NO_x and Oxygen were determined by a multi-gas analyser employing the following measurement techniques:

The sample is extracted from the boiler flue via a heated sample transport and conditioning system.

Oxides of nitrogen: The dried sample is passed to a chemiluminescence analyser which measures the light produced during the oxidation of NO to NO₂. Any NO₂ in the initial sample is first reduced to NO prior to analysis. The analyser therefore measures total NO + NO₂ as NO_x. The instrument output was logged at 15 second intervals resulting in continuous real-time analysis.

Oxygen: The dried sample is passed to a zirconium oxide cell heated to approximately 650°C. The movement of oxygen ions across the zirconium oxide produces a voltage between the two electrodes which is proportional to the oxygen concentration. The instrument output was logged at 15 second intervals resulting in continuous real-time analysis.

Samples were taken during three modes of boiler operation.

1. Modulation – Similar to normal day to day domestic operation.
2. Low Fire – Central heating on.
3. High Fire – Central heating high, hot water running constantly.

The low fire rate is approximately equivalent to 6.40 kWh and the high fire rate approximately equivalent to 29.00 kWh.

The recorded sample data are expressed as average values for each test period.

Summary of Results

The N₂O results are presented in Table 1 below. The full set of test data is shown in Appendix 1 along with trend data obtained during the test period.

The measured N₂O emission concentrations in the exhaust flue were at the detection limits for the low and modulation firing modes. The high fire mode resulted in measured values above the detection limit and these peaks can be seen in the real-time trend data in Appendix 1.

The increase in N₂O emission concentrations during the high fire period are consistent with the emissions data from the NO_x and oxygen measurements (increased NO_x, reduced oxygen).

Table 1. - Summary of Results (N₂O)

Time	Operational Mode	Average N ₂ O Result	
		N ₂ O (mg/kWh)	CO ₂ e kg/kWh
10:30 – 10:51	Modulation	0.00	0.00000
11:07 – 11:31	Low Fire	0.00	0.00000
11:36 – 12:05	Low Fire	0.00	0.00000
12:22 – 12:32	Low Fire	0.00	0.00000
12:42 – 12:55	High Fire	0.50	0.00013
13:04 – 13:22	High Fire	0.74	0.00020

Table 2. - Estimated Annual Emission (N₂O)

Weighted average:	0.272 N ₂ O (mg/kWh)
Weighted CO ₂ equivalent:	0.00007 CO ₂ e kg/kWh

Conclusions

1. Emission concentrations of N₂O were at the detection limit for all periods except those when the boiler was operating at the high fire mode.
2. The estimated weighted average annual emission of N₂O was 0.272 mg/kWh.
3. The estimated weighted CO₂ equivalent was determined as 0.00007 kg/kWh.
4. The peak values measured during high fire operation were consistent with the other flue gas components measured.

Further Measurements

The measurements were conducted at one boiler only during typical operating conditions in a domestic setting. An alternative approach would be to conduct a series of measurements with the boiler in maintenance mode, with the assistance of the boiler engineer, allowing a series of forced step changes in operation. This data would provide an emissions gradient throughout the full range of boiler operation.

Calculations (Emission Factor)

N₂O measurements should be expressed as dry air-free (daf) at 0% O₂.

The actual measurement results are for a wet gas at the measured oxygen value so it is necessary to convert these values first.

Firstly convert to the dry condition.

$$N_2O \text{ (dry)} = N_2O, \text{ ppm (wet)} \times 100 / 100 - H_2O\%$$

Convert to air-free

$$N_2O \text{ (daf)} = N_2O \text{ (dry)} \times 21 / 21 - \%O_2 \text{ (dry)}$$

Calculate result expressed as N₂O, CO₂e kg/kWh

$$N_2O, CO_2e \text{ kg/kWh} = N_2O \text{ (daf)} \times 44/22.4 \times 0.632 \times 265/1,000,000$$

- Where CO₂e = CO₂ equivalent value, 1 mg N₂O = 265 mg CO₂
- 44 = Molecular weight of N₂O
- 22.4 = Molar gas constant at standard temperature and pressure
- 0.632 = volume(m³) of dry stoichiometric combustion products per kWh
- 265 = CO₂e
- Divide by 1,000,000 to convert from mg to kg

Calculation of Annual Emission

The annual emission figure is based on the emission concentrations recorded and the boiler operation. Since the demand on the boiler varies over the course of a year due to changing temperatures, an estimation of the boiler operation as a percentage of high firing is made in accordance with the guidance in: BS EN 15502-1:2021, Gas-fired Heating Boilers – General Requirements and Tests.

This method applies a weighted average based on the typical percentage of time spent at e.g. low moderation (summer) or high-modulation (winter). So the table below shows that for 60% of the year, the boiler is typically operating at 20 or 40% of its maximum and only at 70% capacity for 15% of its annual operation.

Output (%):	20	40	60	70	100
Weighting (-):	0.30	0.30	0.25	0.15	0.00

Results, Hydrogen Boiler Test

Boiler	Boiler 1.
Property	2 bed semi-detached, 1 ½ bathrooms
Radiators	2 - Living room 1 – Kitchen ½ - Downstairs hall ½ - Downstairs bathroom 2 – Bedroom 1 – Towel rail upstairs bathroom

Summary of Results

Table 1. – Test Data and Intermediate Values – Oxides of Nitrogen, Nitrous Oxide, Oxygen and Moisture from Domestic Hydrogen Fueled Boiler. 31 March 2023

Time	Operational Mode	As Measured				@21 % O ₂	Calculated			@21 % O ₂	Calculated	
		NO, ppm Dry	N ₂ O, ppm Wet	O ₂ , % Dry	H ₂ O, %	NO, ppm Dry	NO _x , daf (mg/kWh)	N ₂ O, ppm Dry	N ₂ O, ppm Dry	N ₂ O, daf (mg/kWh)	CO ₂ e kg/kWh	
10:30 – 10:51	Modulation	1.4	0.00	11.3	25.3	3.0	3.9	0.00	0.00	0.00	0.00000	
11:07 – 11:31	Low Fire	1.0	0.00	11.5	24.8	2.2	2.9	0.00	0.00	0.00	0.00000	
11:36 – 12:05	Low Fire	0.9	0.00	11.6	25.0	2.0	2.6	0.00	0.00	0.00	0.00000	
12:22 – 12:32	Low Fire	1.1	0.00	11.4	26.5	2.4	3.1	0.00	0.00	0.00	0.00000	
12:42 – 12:55	High Fire	17.3	0.20	6.8	27.2	25.6	33.2	0.27	0.41	0.50	0.00013	
13:04 – 13:22	High Fire	17.4	0.30	6.8	26.0	25.7	33.4	0.41	0.60	0.74	0.00020	

N₂O, CO₂e kg/kWh value calculated using data from the IPCC Fifth Assessment Report “Global Warming Potential Values”.

1 tonne N₂O = 265 tonnes CO₂

NO_x and N₂O values measured or calculated on a dry air-free basis (daf)

Table 2. – Estimated Annual Emission (N₂O)

Weighting according to EN 15502

Output (%):	21.3	20	40	60	70	100
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Weighting (-):		0.30	0.30	0.25	0.15	0.00
N ₂ O, daf(mg/kWh)	0.00	0.12	0.25	0.37	0.44	0.62

Weighted average:	0.272	N ₂ O, daf(mg/kWh)
Weighted CO ₂ equivalent:	0.00007	CO ₂ e kg/kWh

Notes:

Weighted against the operating load. Typically, a domestic boiler is rarely at a high fire rate.

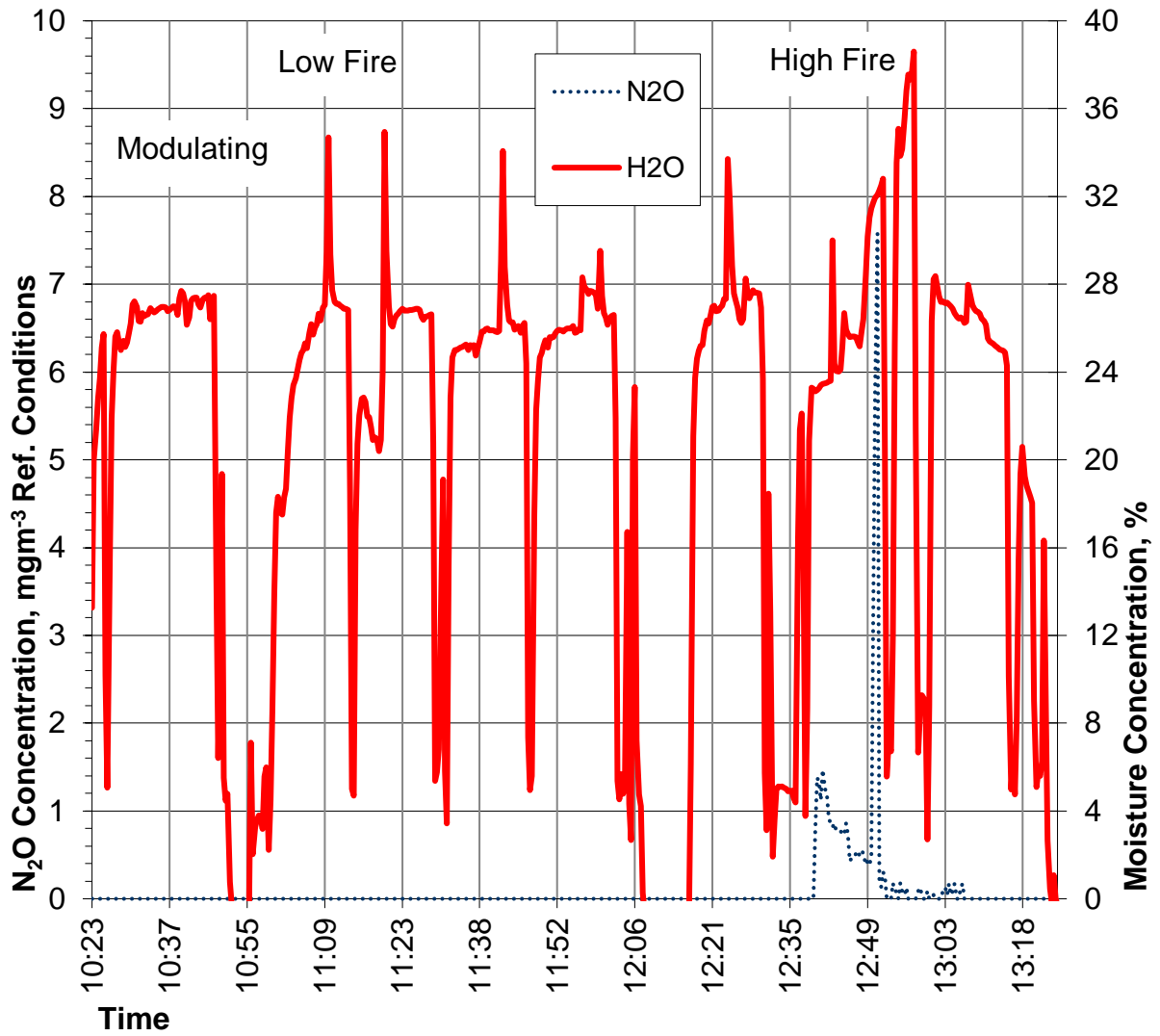
Modulation – This mode is similar to normal operation of the boiler in a domestic setting with the central heating at a comfortable level and hot water not in use.

Low fire – Chimney sweep mode was set to force the boiler into low fire mode, central heating turned up slightly.

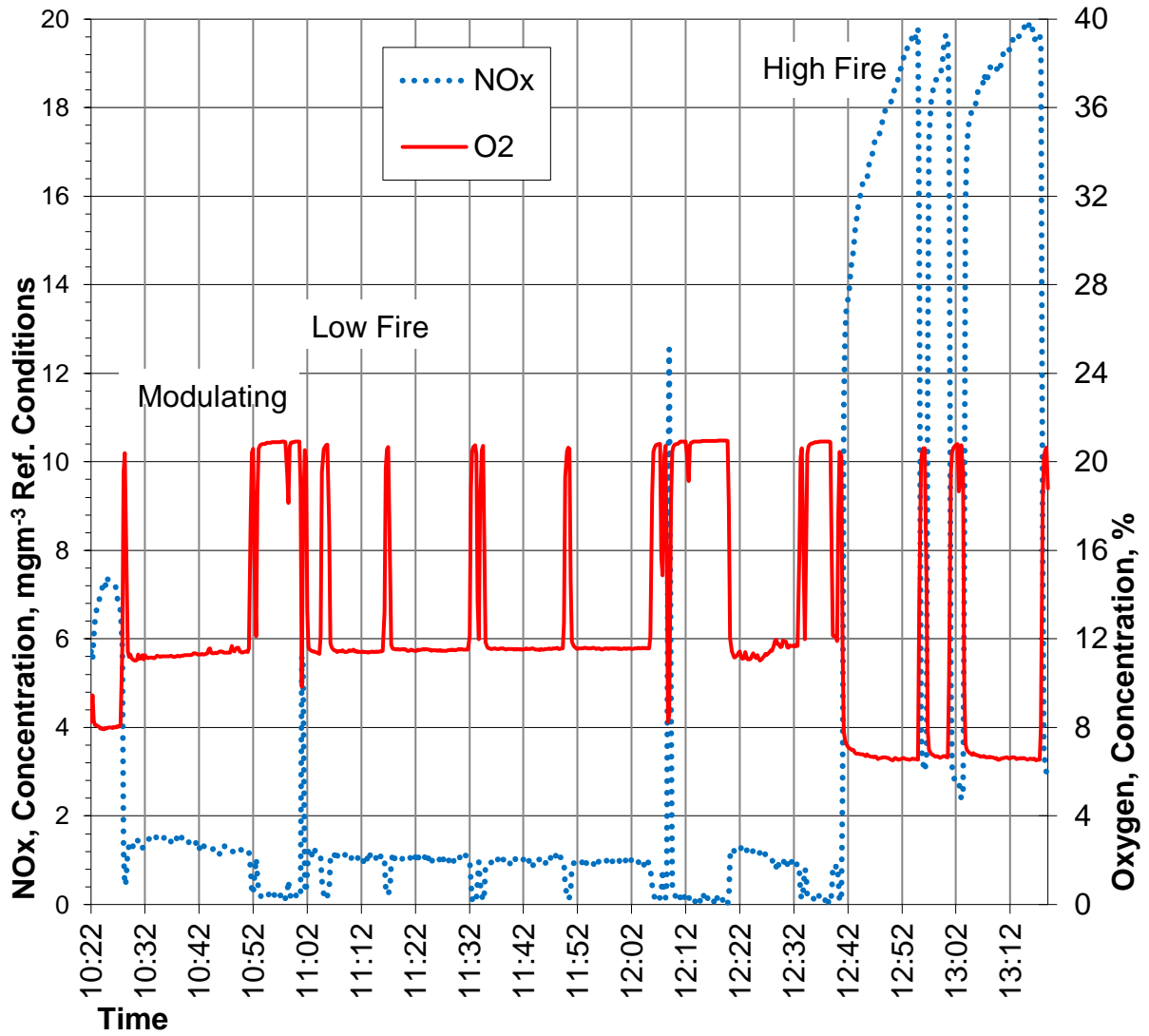
High Fire – Chimney sweep mode was set to force the boiler into high fire mode, central heating turned up high, hot water taps running.

The tests were limited to typical domestic usage. Future tests should be carried out in maintenance mode, which allows the boiler engineer greater control, e.g. prolonged sampling with step changes in boiler modes.

31 Mar 2023 - Nitrous Oxide and Water Vapour



31 Mar 2023 - Oxides of Nitrogen and Oxygen





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