Gas Recovery & Recycle Limited

Generation of Moisture standards for calibration of RGAs

GR²L is a CleanTech company based in the UK. It operates in the Renewable Energy sector where its unique Chemical Looping Combustion based purification systems reduce cost and increase energy utilisation

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Overview

- **Why do we need transferable "standards" for moisture?**
  - Moisture calibration for outgassing and permeation measurements
- **Methods to generate "standards" in the 50-50,000 ppm range**
  - Need to accurately measure flow, temperature and pressure
- **Introduction to Chemical Looping Combustion, CLC.**
  - Oxygen "free" combustion
- **Simple experimental setup for *in-situ* moisture generation**
  - No requirement to accurately measure flow, temperature or pressure
- **Confirmation of the stoichiometric nature of the CLC reactors**
  - NPL measurements, FTIR measurements, QMS measurements
- **Summary**

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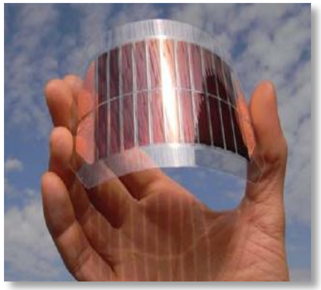
Why do we need transferable "standards"?

- **Permeation of gases and vapours through materials is of vital importance across a number of industries:-**
  - Plastic beverage containers
  - Packing for perishable foods
  - Plastic flexible electronics
  - Organic photovoltaics

- **Measurement of outgassing rates for selection of materials for use in vacuum and vacuum related industries**
  - Vacuum insulated panels
  - Component selection for use in accelerators
  - Design of sealed vacuum systems e.g. therapeutic X-ray sources
- **QMSs can be used accross these applications but for absolute measurements calibration is required**



Current methods used to generate moisture "standards"

- **Conventional methods use a source of liquid water to generate a moisture flux**
    - Either a bubbler or a permeation tube
    - Bubblers for high levels ~10,000 ppm and above
    - Permeation devices for lower levels ~10s to 1,000 ppm
- **By measuring/controlling temperature, matrix gas flow and pressure can then define an amount of moisture**
    - For traceability need to certify sensors for T, F and P
    - Can lead to expensive instrumentation
- **Can add extra dilution stages to achieve lower moisture amounts**
    - Adds to the uncertainty of the "standard"
- **What is required is a simple way to generate moisture "standards" which does not require long periods of stabilization nor expensive certified sensors**

Chemical Looping Combustion, CLC

- **Technology jointly developed with Cambridge University, UK**
  - Originally utilised in the clean combustion of coal for power generation
- **In Chemical Looping Combustion, CLC, metal oxide couples e.g Cu (II) (Copper oxide) → Cu (0) (Copper metal), are used as a solid state oxygen carrier**
  - No gas phase oxygen present during the combustion process
- **H_2 is oxidised stoichiometrically to H_2O at medium temperature (350-450°C) effecting reduction of the metal oxide couple**
- **Metal oxide couple can be regenerated using air**
- **Overall the combustion reaction is equivalent to conventional gas phase oxidation**

$$H_2(g) + MO(s) \rightarrow H_2O(g) + M(s)$$

$$\tfrac{1}{2}O_2(air) + M(s) \rightarrow MO(s)$$

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(g)$$

CLC based Moisture Generator

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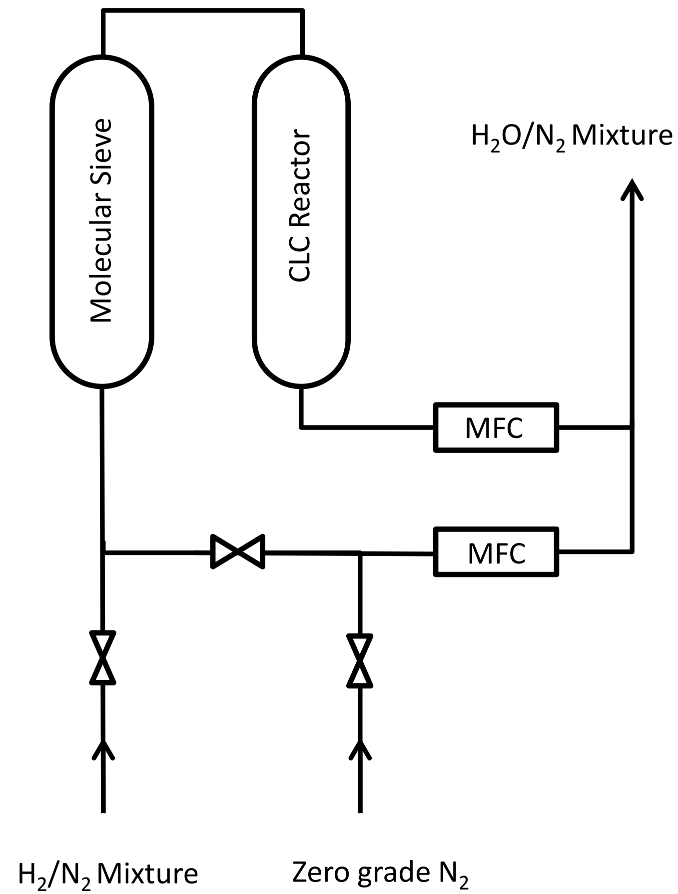
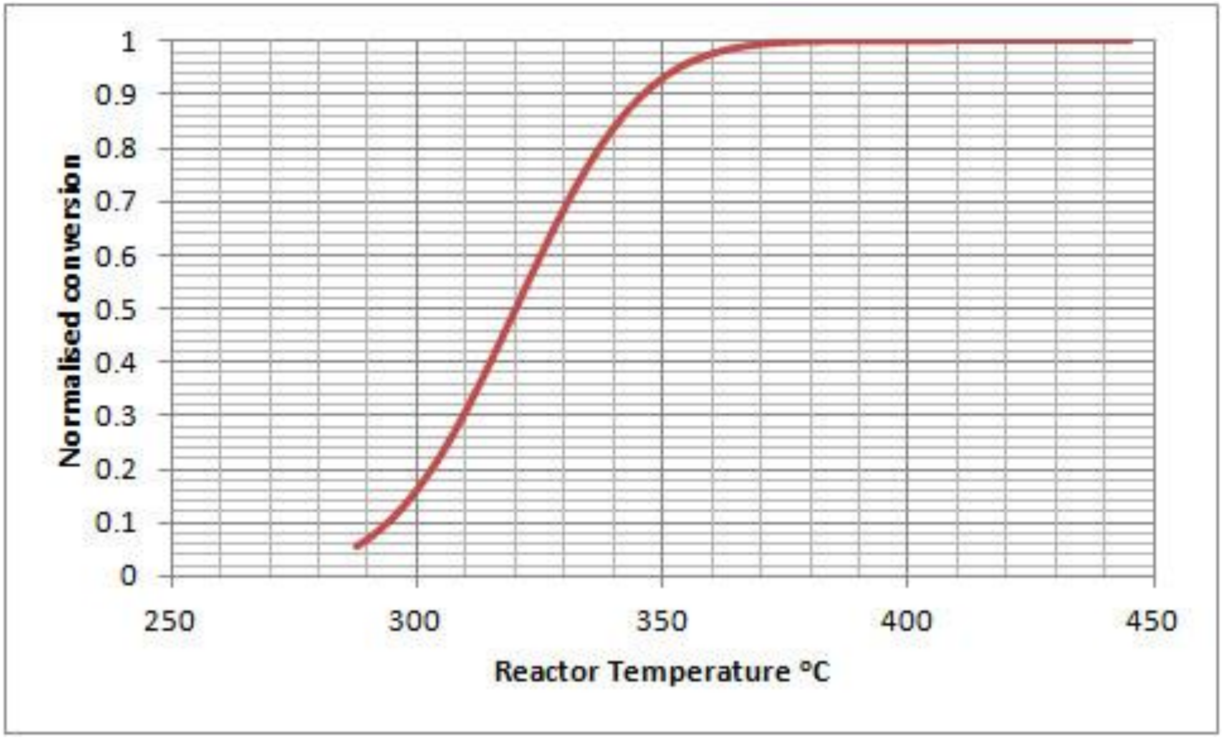
- **Stoichiometric nature of the H_2 oxidation preserves concentration**
  - 500 ppm H_2 in N_2 gives 500 ppm H_2O
- **Conversion independent of pressure and flow within wide parameter range**
  - No high accuracy measurements required
- **H_2O accuracy only governed by accuracy of original H_2 mixture**
  - Typically better than 1%
- **Can blend with zero grade N_2 to create variable mixtures**
- **No cylinder lifetime issues**
  - H_2 mixture maintains accuracy 1-2 years



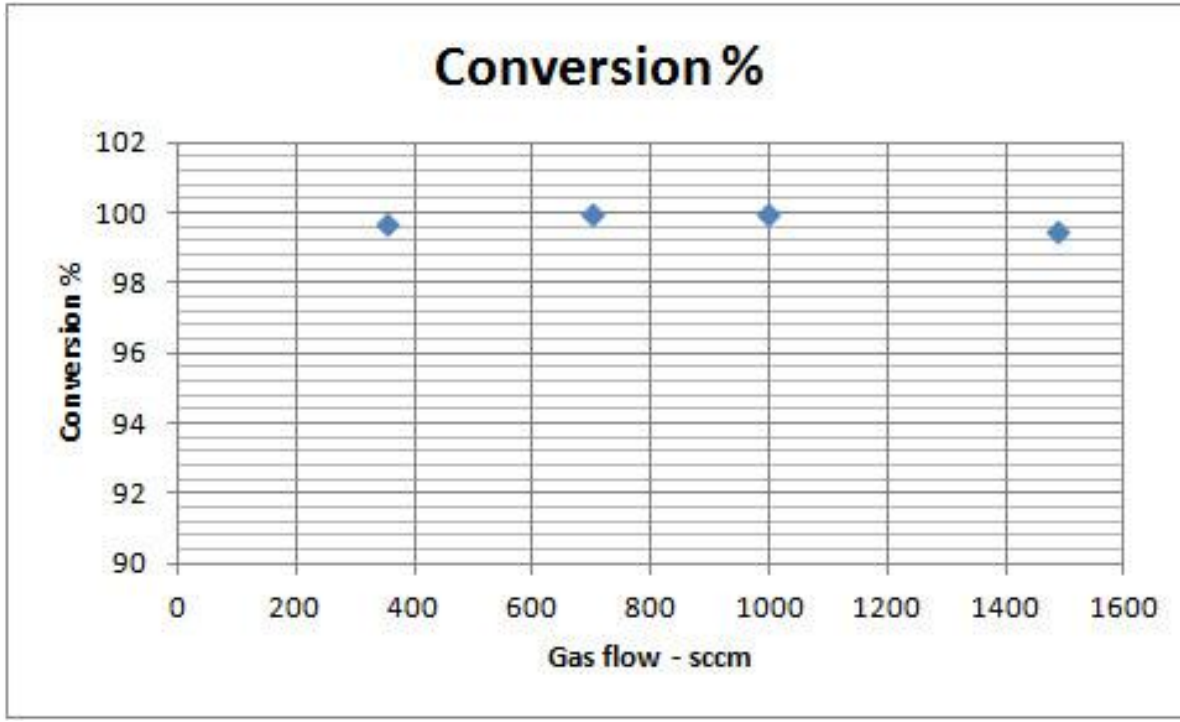
Temperature requirements

- **The CLC reactor has a "lightoff" temperature of ~270°C**
  - Above 380°C the reactions are complete
  - Graph shows normalised mass 18 response as a function of temperature
- **Accurate temperature control is not required – just need to ensure the reactor is above 380°C**
  - Normal operating temperature is 400°C



Conversion efficiency and flow requirements

- **Graph shows the conversion efficiency of the CLC reactor as a function of flow.**
  - 1” diameter vessel
  - 6” active length
- **Conversion measurement uncertainty is ≤1%**
  - Conversion is 100% within experimental error
- **With a 0.1% certified H_2 mixture can generate moisture “standards” to approx. 1% uncertainty**
  - Shelf life of H_2 standard is 12 months plus

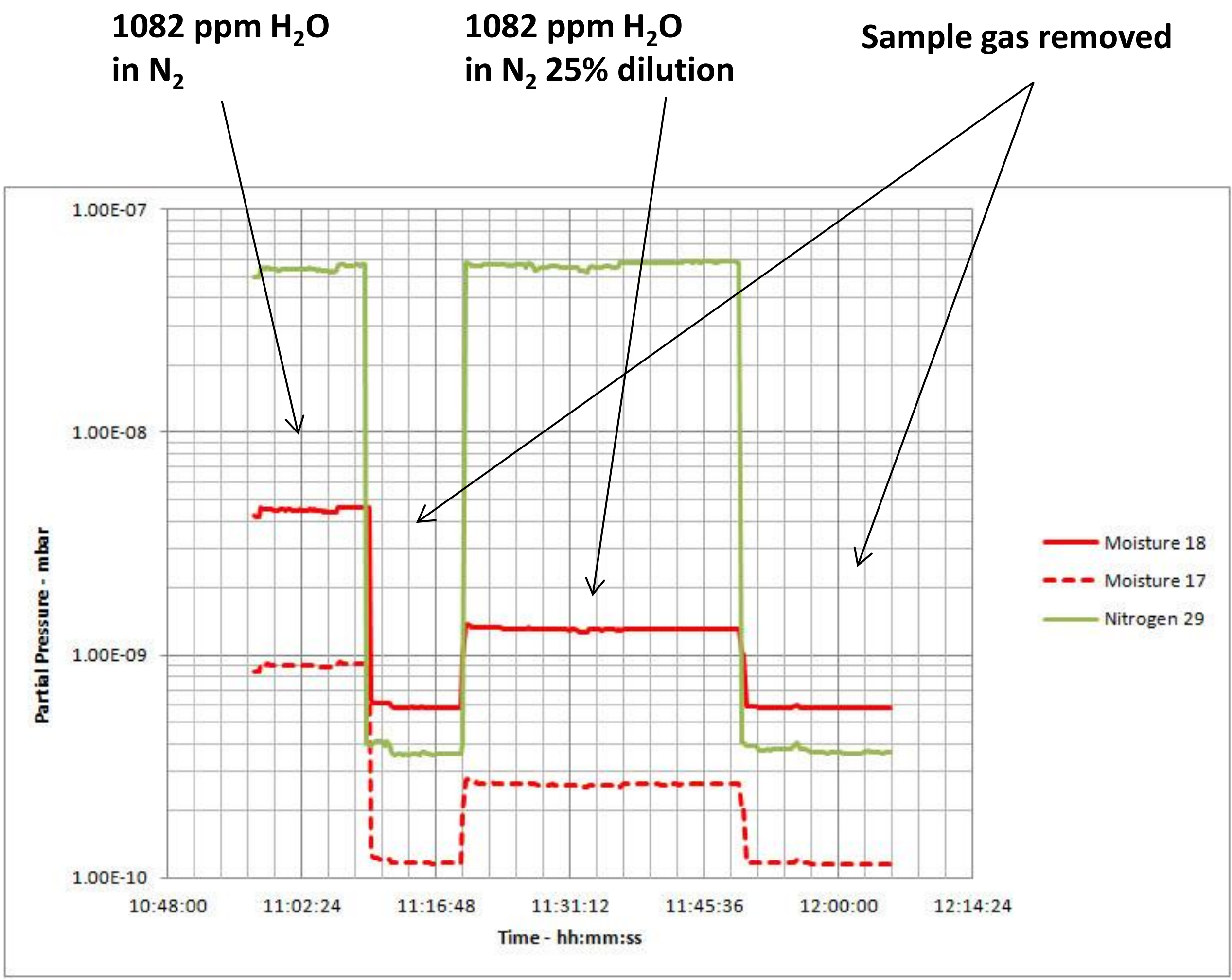


National Physical Laboratory

VG SCIENTA

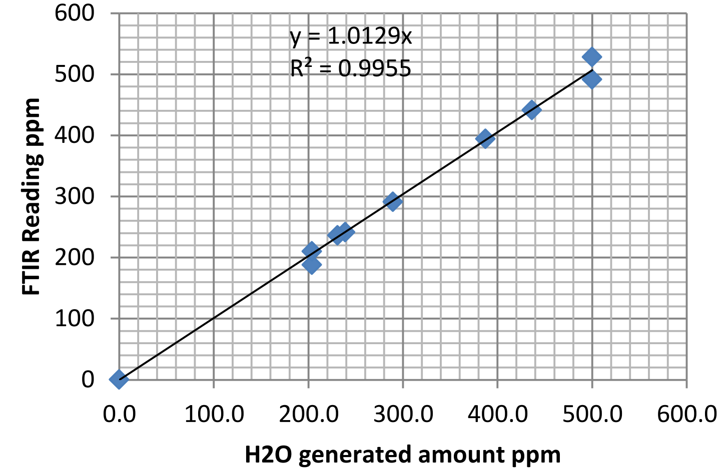
Mass spectrometer results

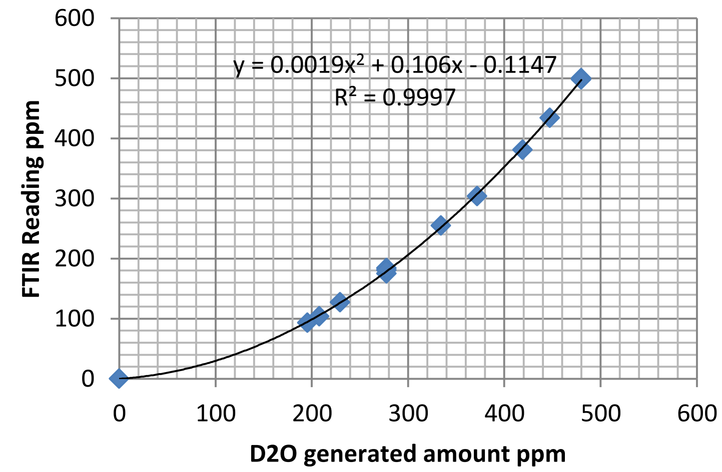
- **Use CLC reactor to generate H_2O levels in an N_2 matrix**
  - H_2 @ 1082 ±5%
- **Sample pressure is 5 10^{-6} mbar**
  - QMS normalised to ion gauge reading
  - Use mass 29 to monitor N_2 – 1% of parent ion
- Simple dilution system to achieve 1:4 dilution
  - i.e. 270.5 ppm



Generation of Heavy water

- **Can easily make isotope species from appropriate gas mixture**
  - D_2O from D_2 in N_2 mixture
  - By regenerating the CLC with $^{18}O_2$ can create heavy heavy water
- **Graphs show actual moisture v calculated moisture blend**
  - Using MKS Multigas FTIR
  - H_2O curve shows linear response from the system
  - No FTIR calibration for D_2O, see the expected "quadratic" response





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CLC based Moisture generator Summary

- **Stoichiometrically generates moisture from a hydrogen isotope mixture**
  - Will deliver from 10 to 10,000 ppm moisture
- **Very stable operation**
  - No critical flow, pressure or temperatures required
- **Moisture generation accuracy only governed by the hydrogen gas mixture**
  - Conversion efficiency 100% within experimental error
- **Stable moisture generation typically within 30 mins**
- **No cylinder lifetime issues**
- **Can generate D_2O standards**
  - More cost effective than using D_2O bubblers etc.
- **Regeneration of CLC with $^{18}O_2$ can generate heavy oxygen moisture variants**
  - $H_2{}^{18}O$, $D_2{}^{18}O$ etc.