“A Mass Spectrometry Method for Water Vapour Transmission Rate (WVTR) testing to $10^{-6}$ gm/m$^2$/day, utilising Deuterium Oxide”

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Most Commonly Used Unit: gm of water per m$^2$ per day (g/m$^2$/day)

Commonly used analogy: Amount of water per football pitch area per day
Barrier Properties

- OTR (Oxygen Transmission Rate) - \( \frac{\text{cm}^3}{\text{m}^2 \cdot \text{bar} \cdot \text{day}} \)
- WVTR (Water Vapour Transmission Rate) - \( \frac{\text{g}}{\text{m}^2 \cdot \text{day}} \)

- OLEDs
- Organic photovoltaic
- Inorganic thin film
- Solar cells
- Food packaging, technical products

- Packaging
- Vapour deposited PET
- aSi PV e-Paper LCD

Target

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Typical WVTR measurement system

- Most WVTR instruments adopt the ASTM F1249 standard or concepts similar to it
- The test membrane is mounted in a cell where one side of the membrane is exposed to a moisture containing test gas and the other side is connected, either directly or indirectly, to a moisture sensor
  - Moisture sensing technology includes coulometric, IR spectroscopic, dew point etc.
  - The use of tritiated water and radionuclide sensing does allow $10^{-6}$ g/m²/day but has the associated hazards!
- The various sources of background moisture and detector type limit the sensitivity
Current methods for high barrier performance

VacuTRAN (VG Scienta)

[Graph showing WVTR vs. time with various methods and their performance levels]
Benefits of Vacuum enabled permeation measurement

- The use of vacuum technology reduces or eliminates the deleterious background effects and enables WVTR measurement to <10^{-6} \text{ g/m}^2/\text{day}.
- Vacuum pumping enables rapid dry down
  - Can achieve a moisture partial pressure of better than 10^{-5} \text{ mb} easily within 1 hour.
  - Equivalent to 10 ppb moisture levels at atmospheric pressure!
- Effects of outgassing mitigated
  - Materials selection and use of UHV best practice
- All metal sealed system
  - Eliminates moisture ingress from the ambient environment
- Guarded ‘O ring’ seals
  - Test gas leaks eliminated via the use of inter-seal purge
- Allows the use of a mass spectrometer detector
  - Ultra-High sensitivity multi-species detection (10^{-15} \text{ mbar partial pressure})
  - Allows use of D2O as water analogue to reduce “background”
Mass spec’ detector enables multi-species detection

- **VacuTRAN™** utilises a quadrupole mass spectrometer detector
  - Extremely high sensitivity – sensitivity only limited by background levels
  - Can detect any species up to 200 amu in mass
  - Enables simultaneous measurement of multiple species
  - Can follow any of the species in the mass spectrum e.g. O₂ and D₂O
Gas permeation through a membrane

Membrane

Concentration C1

Partial pressure $P_1$ (atmosphere side)

Absorption

Diffusion

Desorption

Partial pressure $P_2$ (vacuum side)

Concentration C2

$P_1 > P_2$
Characteristic S-curve permeation

Indicate concentration gradient through the membrane at different points on the S-curve.

Partial pressure

Elapsed time

Breakthrough time

Steady state permeation
Permeation is the process whereby a gas/vapour passes through a solid material, e.g. a plastic membrane.

The flux of a given test gas $Q$ passing through a given membrane of area $A$ and thickness $d$ is given by the following:

$$Q = K \frac{A.\Delta P}{d}$$

where

- $K$ is the permeability constant of the membrane for a given test gas
- $\Delta P$ is the partial pressure difference across the membrane

The permeability $K$ of a membrane may be expressed in terms of the solubility $S$ of the species in the membrane and the diffusivity $D$ of that species through the membrane by the following relationship:

$$K = S \cdot D$$
Breakthrough time $t_b$

- Steady state permeation level of D$_2$O

Partial pressure

- Background level of D$_2$O

Change in signal is a measure of D$_2$O permeation

Elapsed time

Transmission rate $Q = P \cdot S$

1. Determine $Q$
2. Determine $K$
3. Determine $D$
4. Determine $S$

$$Q = K \frac{A \cdot \Delta P}{d}$$

$$t_b = \frac{d^2}{6D}$$

$$K = S \cdot D$$
Run Conditions identical except D2O or H2O used: sample PEN plus Barrier films Sample no 1

RAW DATA
no need to normalise as peak values are the same

Interpretation notes:
1) The breakthrough times are the same
2) The peak transmission rates are the same
3) The lower initial level of D2O demonstrates the increased sensitivity

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VacuTRAN system
Chamber 2 and calibration gas inlet

Calibration gas inlet to chamber 2

Capacitance manometer gauge

Turbo pump (restricted to 50ls⁻¹)

Turbo backing line

Connection to chamber 3 (RGA)
Chamber 3 including RGA

- RGA mass spectrometer
- 400l s⁻¹ turbo pump
- Backing line and N₂ vent

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RGA mass spectrometer

Key features:

- Closed gold plated ion source design coupled directly to chamber 2 and free from chamber 3 background interference signals.
- Operated in the $10^{-5}$-$10^{-4}$ mbar pressure range.
- Mass range 0-200 a.m.u.
- Faraday and SCEM detectors offering detection range of $10^{-4}$ to $10^{-14}$ torr
- Dual burnout-resistant oxide coated iridium filament design
- User-programmable multi-tasking firmware for creation of process-specific control and data acquisition functions

Optimised settings for VacuTRAN:

- Low ionisation energy @ 40eV (negligible Ar$^{++}$ formed that would otherwise be coincident with D$_2$O at 20 a.m.u.)
- Single filament operation (minimises unwanted filament surface reactions)
- Ultra-pure N$_2$ used as “Stabilisation gas” for maintaining elevated pressure operation and to normalise permeate signal to, removing the effects of any slight signal drift due to the RGA.

Chart illustrates the linear relationship between measured partial pressure and RGA signal recorded in the typical operating regime of the machine. $R^2$ fit = 0.9999
2 test gas inlet ports (4% D₂/N₂ and 2% O₂/N₂ mixes)

3 calibration gas inlet ports (more available upon request)

CLC column with heater collar and insulation

Calibration gases:
- 100ppm or 500ppm D₂/N₂
- 2% O₂/N₂
- spare option
Moisture generation panel

Two standard test gases:
- 2% O₂/N₂
- 4% D₂/N₂
Patented Chemical Loop Combustion (CLC) reactor

- The CLC units are used to generate a D₂O/N₂ gas mix by oxidising the D₂ in a D₂/N₂ supply gas.
- A CLC unit operates at 450 °C and converts virtually all D₂ to D₂O, ~ 99.8% as confirmed by the National Physical Laboratory (NPL).
- CLC unit contains a metal oxide media and requires regeneration after a period of running (dependent on D₂ gas concentration and period of usage). A 2% O₂/N₂ gas mix is required for regeneration purposes.
- The CLC unit on the moisture generation panel will require regeneration after each sample test. This automated process takes 6hrs and can be done in the background whilst the system is baking/pumping in preparation for the next sample. It does not impact on sample turnaround time.
- The CLC unit on the calibration panel, using 100ppm D₂/N₂ supply gas, will need regeneration approximately once every two years.
There are two choices of membrane sealing methods available. Both fit in the same worktop access point.

1) **O ring Sealed** *(circular or square)* (for speed and convenience)

2) **Metal Sealed** (for ultimate performance)
Membrane Mounting

In both cases the membrane is gently placed on the holder horizontally.

The upper matching seal is then lowered onto the membrane.....

Bolts are then tightened (green dots).

This action seals
   i) the membrane to the Vacuum and
   ii) the permeant gas from atmosphere.

Removal is simply the reverse process.
Metal seals

When metal seals are used the only polymer component exposed to the vacuum and the mass spectrometer is ........The sample itself........

Both Seals with Upper Seal Holder

Copper : Fully Softened

VG Special profile
Metal Seals Arrangement

Metal Seal
Post Sealing Operations

- Once sealed, the vacuum is engaged and a pump down sequence is started.
- At the same time the interspace seal is purged with an inert gas.
- Also at the same time Pure N\textsubscript{2} gas is then purged at the atmospheric side of the membrane under test.
- The mass spectrometer then measures the chosen gas species during pumpdown until a stable situation is observed.
- During pumpdown and N\textsubscript{2}-flush, residual gases are removed from the membrane; both into the vacuum and into the purging gas, which is exhausted. The time for this purgedown is dependent on the membrane’s properties and importantly, the environmental exposure it has had prior to loading into the tool.
Membrane stresses

- It is known that increases in stress applied to a film can result in an increase in permeation rates
  - Measurements on the oxygen permeation of various plastic films is shown opposite (Ref NPL report)
  - For the technologically important films there is minimal effect for stresses less than 10MPa

- Membrane support structure designed to minimise the applied stress to the membrane sample while maximising the available surface area for permeation
  - Multiphysics modelling with Comsol suggests the membrane stress is ~6MPa
  - With a maximum deformation of ~5μm
Independent heater control for all 4 heating zones

Vacuum control screen

Full manual control of vacuum pumps and valves.

Active interlocks provide system protection against operator errors.
VacuTRAN Calibration

• To ensure accuracy of results a traceable calibration method is employed. This can be used before, during or after a permeation test, and ensures accuracy and repeatability of results.

• This is done by injecting a gas of known concentration, through a special inlet arrangement, to the mass-spectrometer.

• The method uses a patented technique to ensure calibration is independent of drift, which overcomes the common problem when using mass spectrometers.

• The method also uses a unique onboard generation of $\text{D}_2\text{O}$ standards which also eliminates the problems normally associated with use of low-level moisture standards.

• Hence calibration is directly traceable to national standards.
The first step in the calibration chain is to demonstrate that the moisture generator provides an accurate calibration gas.

The Moisture Generation Standard was tested at The National Physical Laboratory: Teddington UK.
Calibration Method: Onboard D2O generation

• **D₂O standards are generated in-situ from a D₂/N₂ mixture**
  – D₂O is generated from the reaction of D₂ with a solid state oxygen carrier
  – Low cost of ownership <$5 per day
  – No critical temperature or flow control required
  – Completely stoichiometric reaction i.e. 500 ppm D₂ generates 500 ppm D₂O independent of flow. (Certified by National Physical Laboratory)
  – Traceability simply achieved via certification of the D₂/N₂ mixture

• **Calibration gas mixtures follow the same flow path as the sample gas**
  – Reduces calibration errors and allows calibration mid run if required
  – Can be diluted to generate a range of calibration gases

• **Can use same method to generate test gas mixtures if required**
  – Dilution with O₂/N₂ mixture produces a test gas for simultaneous WVTR and OTR
The Results of Calibration at NPL are shown below:
This confirms the generation of the correct moisture standard

\[ H_2 \rightarrow H_2O \text{ conversion efficiency} \]

- Conversion efficiency of CLC reactor calculated as:
  \[
  \text{conversion efficiency} = \frac{\text{CLC output}}{\text{gravimetric amount fraction of } H_2 \text{ standard}} \times 100
  \]

![Graph showing FTIR Reading ppm vs. D2O generated amount ppm with a linear fit equation \( y = 1.0129x \) and \( R^2 = 0.9955 \).]
System to standby state

- System baked and UHV levels achieved in both chambers.
- RGA filaments out-gassed.
- Background levels stabilised.

Load sample and test

- Load sample.
- Pump down sample chamber and open to rest of system.
- Set sample and seal purge running with high purity N₂.
- Further bake-out and pump down system to UHV level.
- Achieve stable background levels of D₂O on the RGA.
- Introduce D₂O to atmosphere side of sample and monitor RGA.
- Test completed when steady state permeation signal achieved.

Calibrate system

- Close off sample from rest of system.
- Achieve stable background D₂O level.
- Introduce calibration gas.
- Measure upstream pressures using traceable gauge.
- Monitor D₂O cal signal on RGA and record once stabilised.

Process data

- Apply adjustments to signals due to H/D exchange reactions.
- Use calibration data to convert RGA permeation signals to real partial pressure values.
- Use known pumping speed of vacuum chamber to convert partial pressure of D₂O to a WVTR for the test membrane.
- NOTE: All of the above is performed in an excel spreadsheet using requested data inputs from operator.

Sample measurement and analysis process map
ABSTRACT

A method of measuring a permeation efficiency of a barrier including providing said barrier between a first and a second chamber, placing a test sample in said first chamber, providing a reference gas to said second chamber, wherein said reference gas is unreactive with respect to the test sample, wherein said reference gas has a plurality of stable isotopes, maintaining an equilibrium quantity of particles of said at least one stable isotope in said second chamber such that said quantity is within at least one order of magnitude of an expected number of particles of said test sample present in said second chamber due to permeation through said barrier, obtaining a mass spectrometer reading in relation to said at least one stable isotope, obtaining a mass spectrometer reading in relation to said permeate, and correlating said mass spectrometer readings and said maintained quantity of at least one stable isotope particles to obtain an absolute value for a quantity of said permeate, to establish a quantity of permeate passing through said barrier per unit time.
SUMMARY

- Vacuum enabled membrane WVTR measurement to $10^{-6}$ g/m²/day
- High sensitivity achieved through the use of a mass spectrometer
- High background rejection by replacing H₂O with D₂O in the test gas
- Demonstrated equivalence of H₂O and D₂O permeation
- Low cost of ownership through the in-situ generation of D₂O from D₂ in a patented solid state chemical reactor
- Simultaneous measurement of any other gas species
- Calibration can be traceable to national standards

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Final Thought: Need for standardisation

High-barrier films are objectively enabled to evaluate

Before standardization
- method A/condition X \( \sigma \ g/m^2 \text{ d} \)
- method B/condition Y \( \square \ g/m^2 \text{ d} \)
- method C/condition Z \( \Delta \ g/m^2 \text{ d} \)

Supplier \rightarrow Customer

After standardization
- ISO method \( \bullet \ g/m^2 \text{ d} \)
- ISO method \( \square \ g/m^2 \text{ d} \)
- ISO method \( \Delta \ g/m^2 \text{ d} \)

Supplier \rightarrow Customer

✓ Customer: Re-evaluation is unnecessary
✓ Supplier: Original method/condition development is unnecessary

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