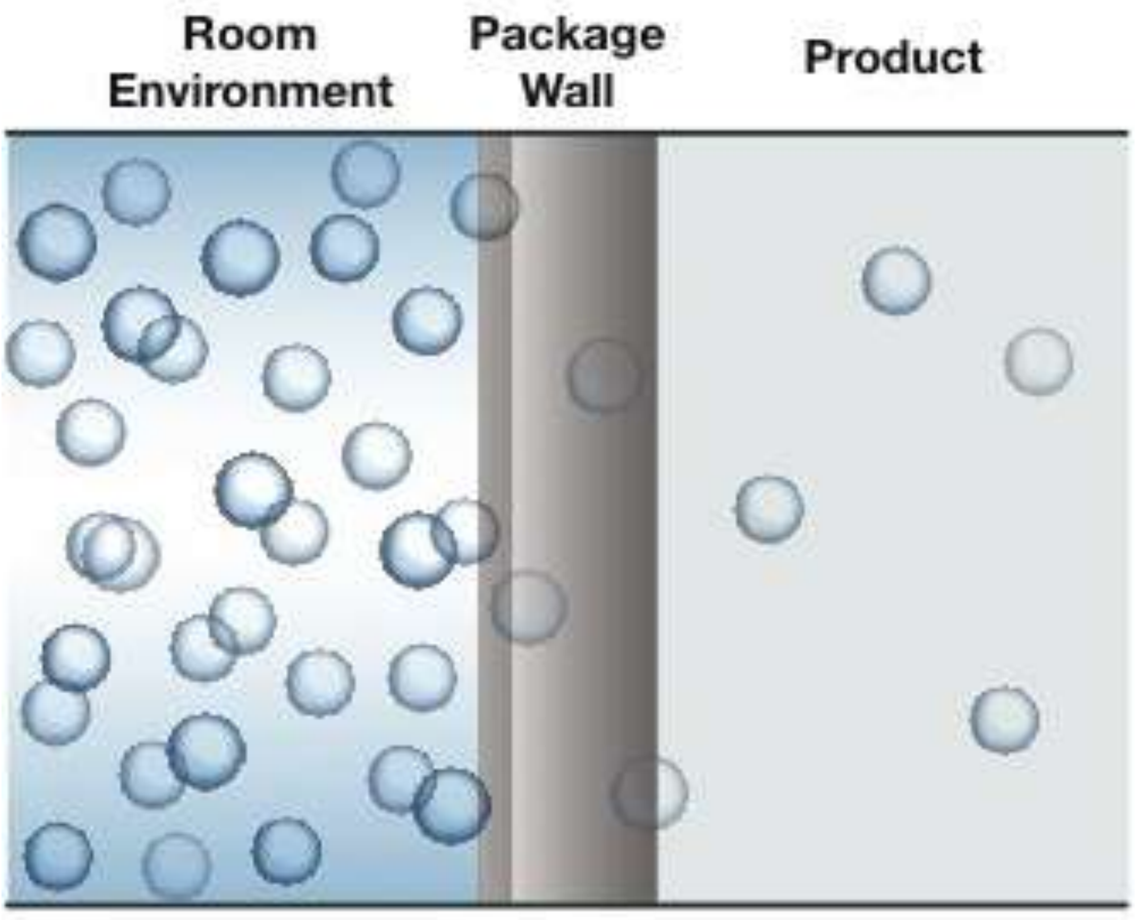
Permeation Measurement Testing Techniques

Michelle Stevens
MOCON, Inc.

Permeation



Permeation

Permeation is simply the flux of molecules through a material normalized to the pressure drop across the film.

Units of permeation "explain" the mechanism:

volume of gas at STP — material thickness

$$\frac{cm^3\left(273.15K;1.013\times10^5\,Pa\right)\times cm}{cm^2\times s\times Pa}$$

area — time — pressure drop, driving force

Permeation

Transmission rate

$$\frac{g}{m^2 \times day}$$

Permeance

$$\frac{g}{m^2 \times day \times atm}$$

Permeability coefficient

$$\frac{g \times mil}{m^2 \times day \times atm}$$

Permeation

Molecules permeate from high concentration to low concentration until equilibrium is established.

Permeation of a compound is dependent on the partial pressure difference of THAT compound

Driving force

CHEMICAL POTENTIAL

Fundamental driving force that prompts a molecule to diffuse within a polymer

Analogous to the electrical potential of a battery

Substances will naturally tend to move from a higher chemical potential to a lower one

FOR MOST PACKAGING APPLICATIONS, THE ACTIVITY CAN BE REDUCED TO <u>CONCENTRATION</u> OR <u>PARTIAL PRESSURE</u>

Diffusion

Diffusion is the process by which matter is transported from one part of a system to another as a result of random molecular motions.

Diffusion refers to the net transport of material within a single phase in the absence of mixing.

In Fickian systems, D is independent of concentration.

Units of D:

$$\frac{cm^2}{\sec}$$

Solubility

Solubility represents the dissolution of permeant into polymer and relates the concentrations within the film to the partial pressure of the permeant.

Solubility is dependent upon permeant concentration or driving force.

Units of S:

$$\frac{cm^3(STP)}{cm^3 - mmHg}$$

Solution-diffusion mechanism (Graham's colloidal diffusion)

The gas is sorbed at the entering face and dissolved

The dissolved penetrant molecules then diffuse through the membrane and

Desorb at the exit face.

Permeability

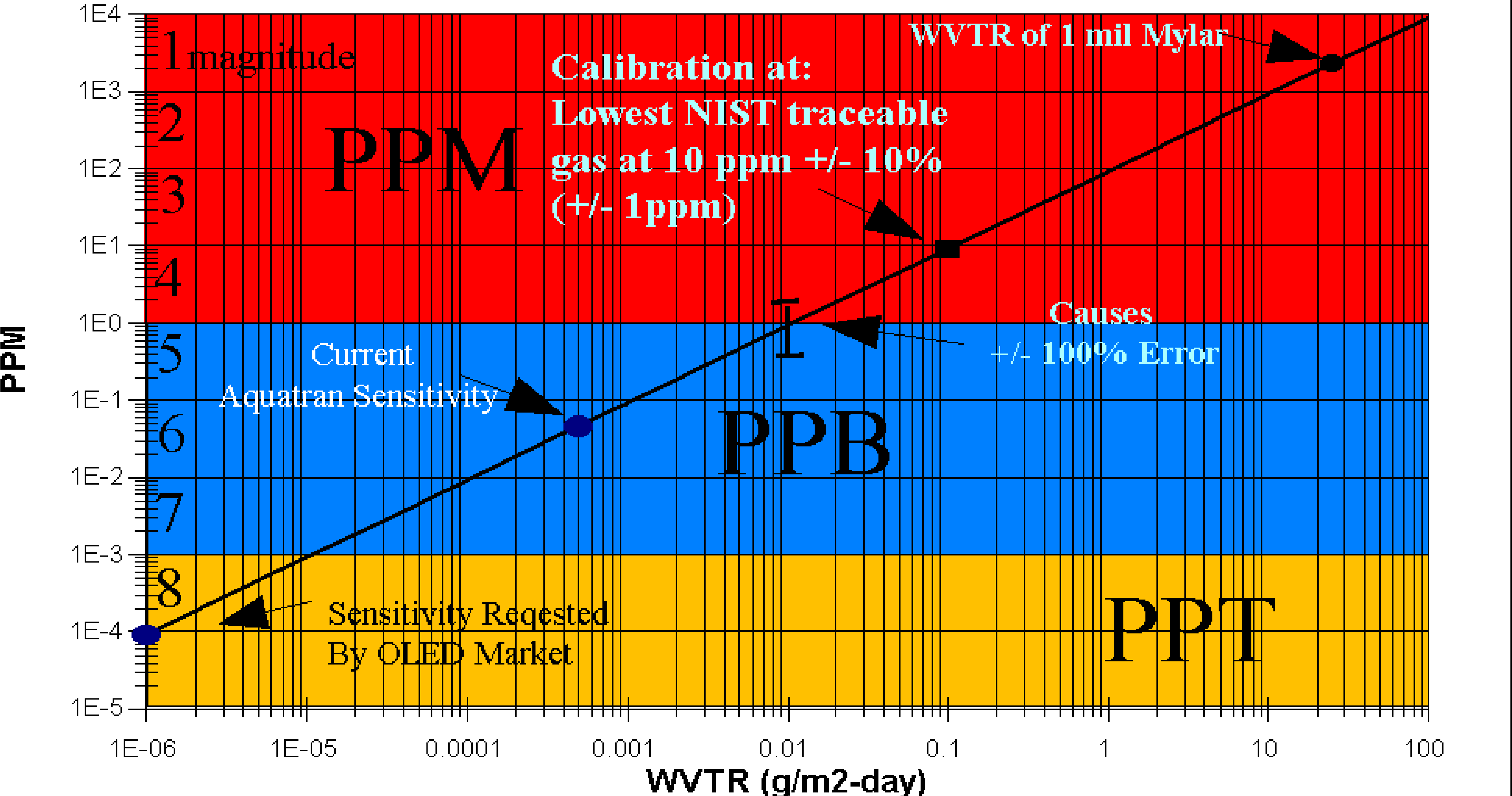
Permeability can be defined as the product of the solubility coefficient and the diffusion coefficient

$$P = S \bullet D$$

Generally, P and S can be directly measured and D can be calculated.

However, there are indirect methods for measuring D as well.

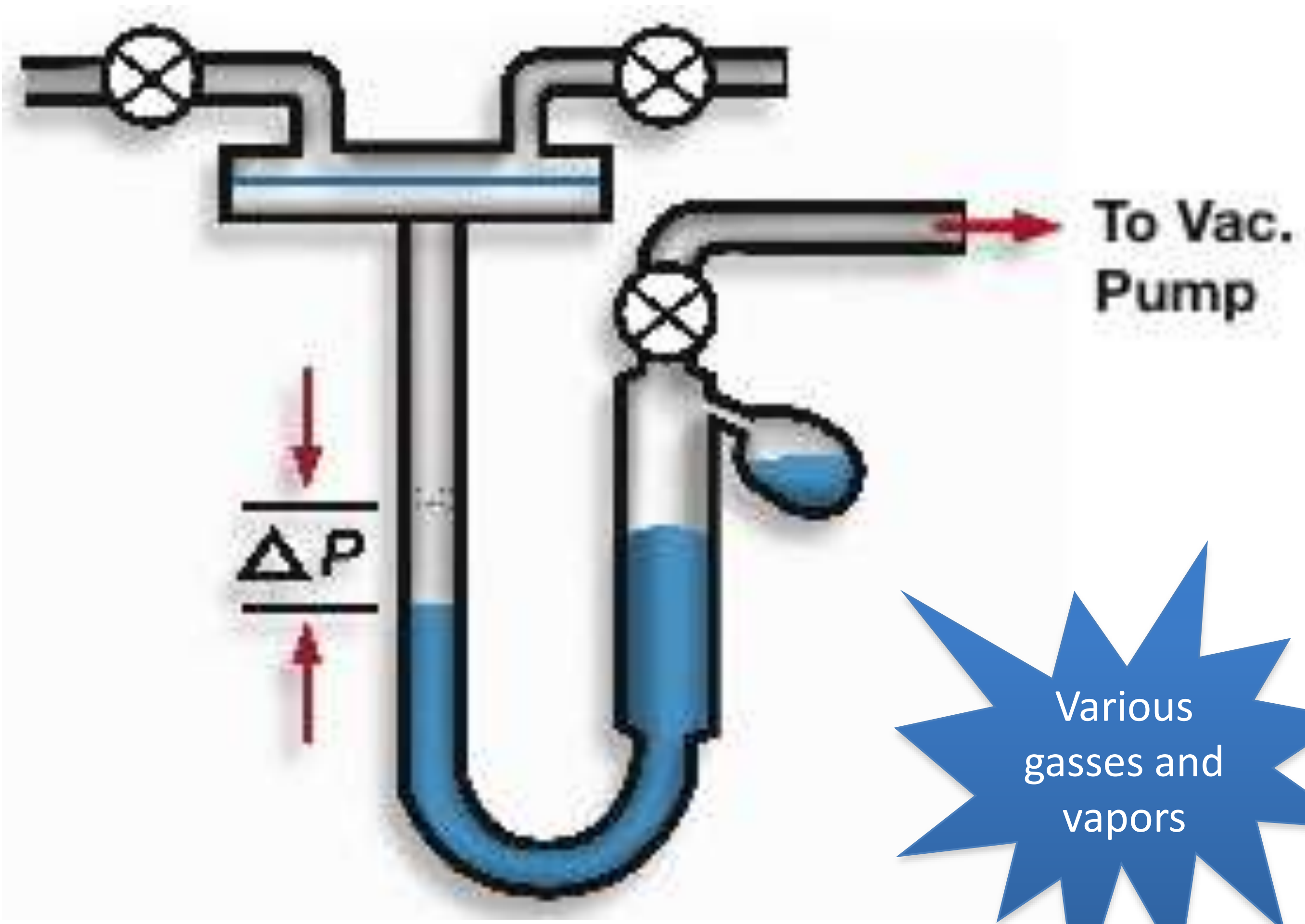
Lowest Available Calibration Gas
NIST traceable WV +/-10% (10ppm)



Basic test methods for measuring permeation

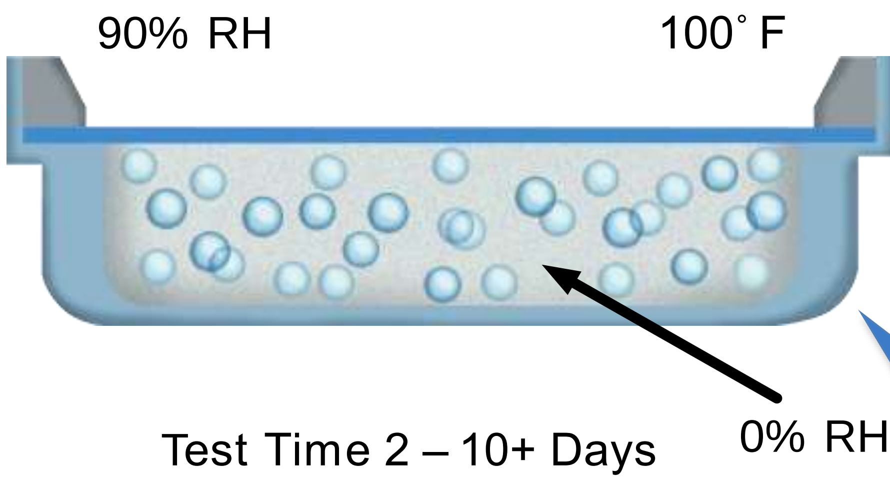
- Manometric
- Gravimetric
- Isostatic
  - Flow-through
  - Accumulation
- Optical / Chemical
- Specialized

Manometric



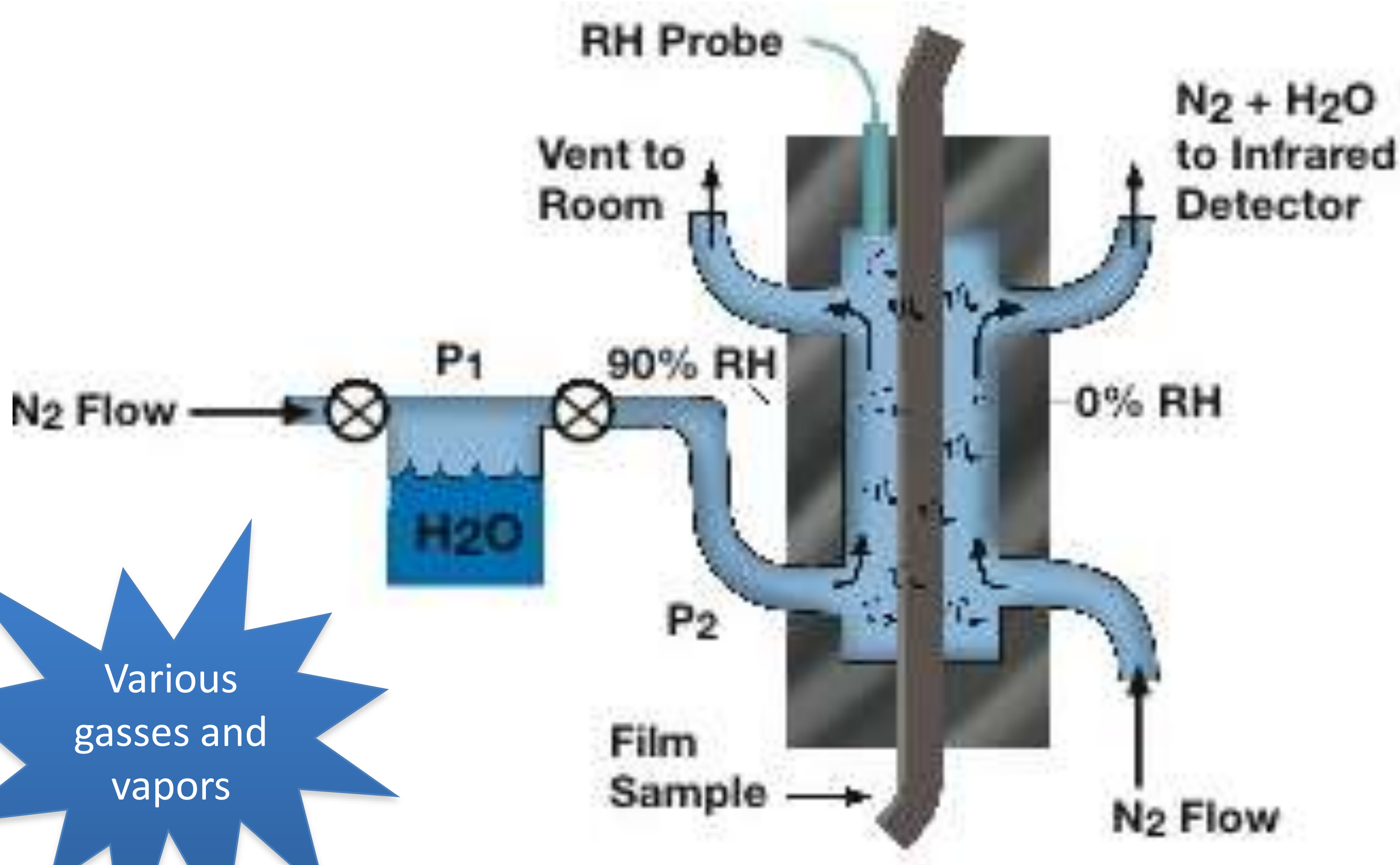
Various gasses and vapors

Gravimetric method
(dry cup - weight gain)



Typically water but can be other liquids

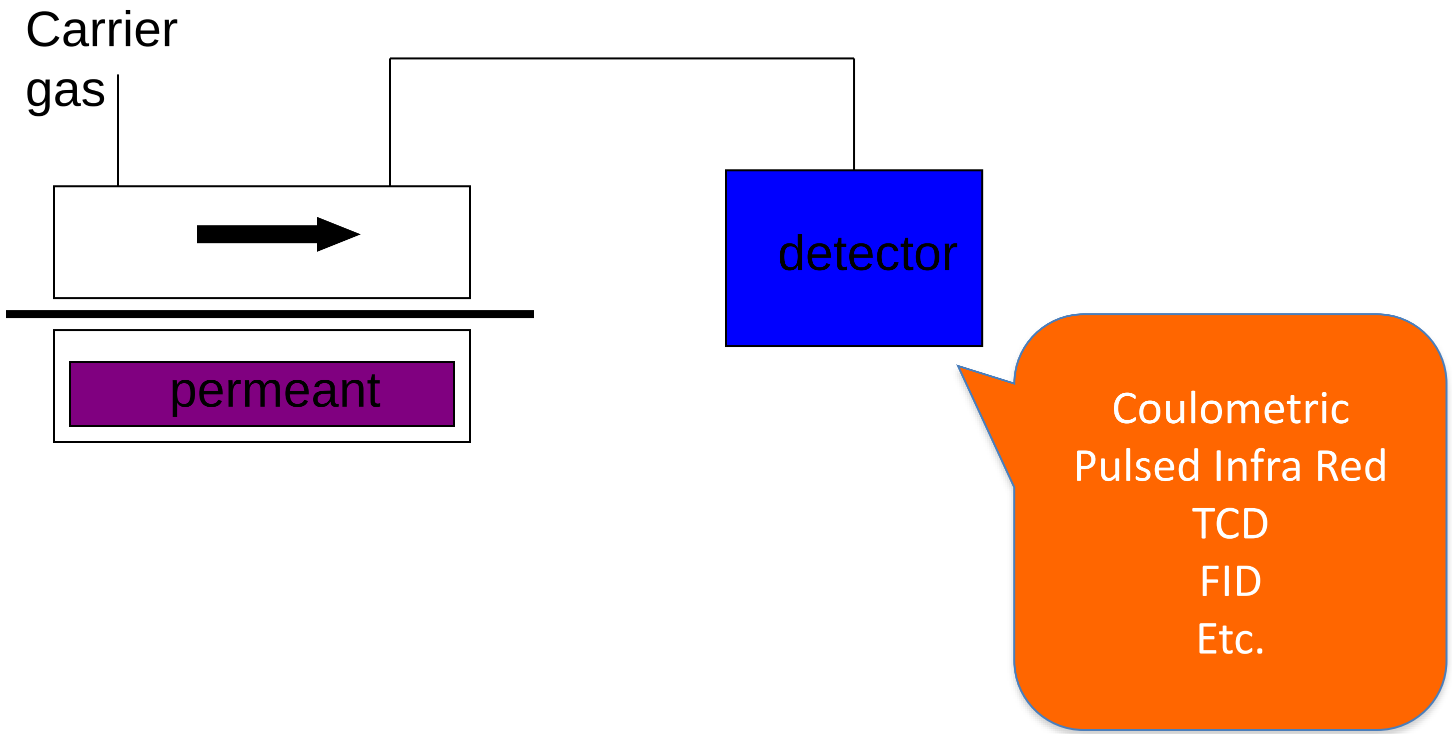
Isostatic Permeation Measurement
Flow-through technique



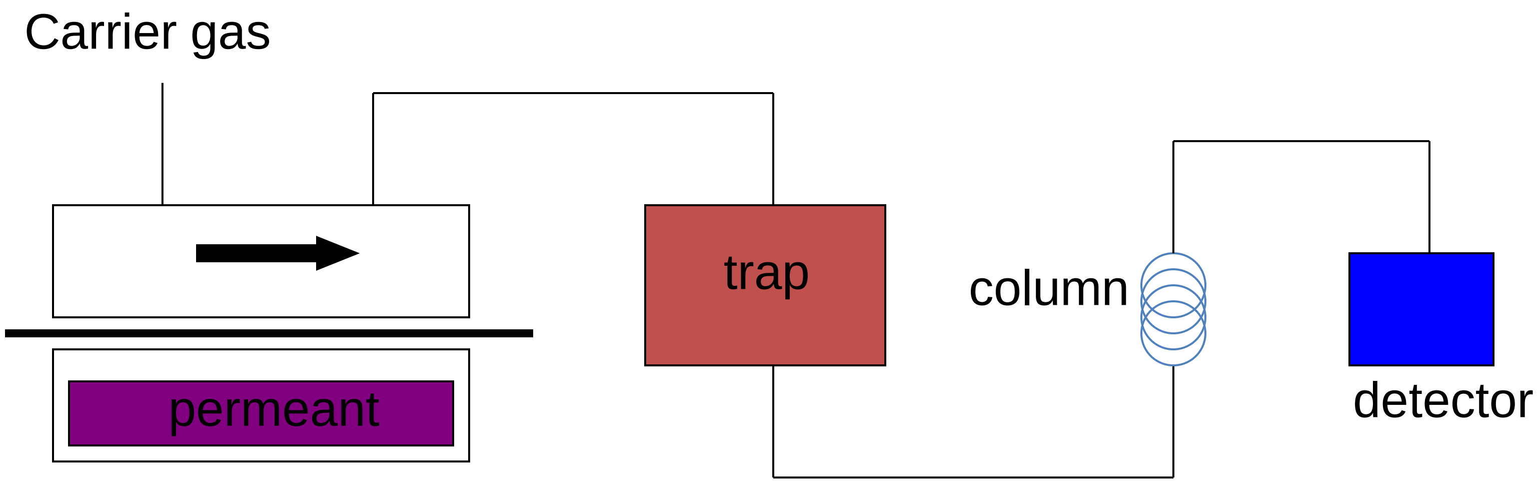
Various gasses and vapors

Isostatic Permeation Measurement

Flow-through technique

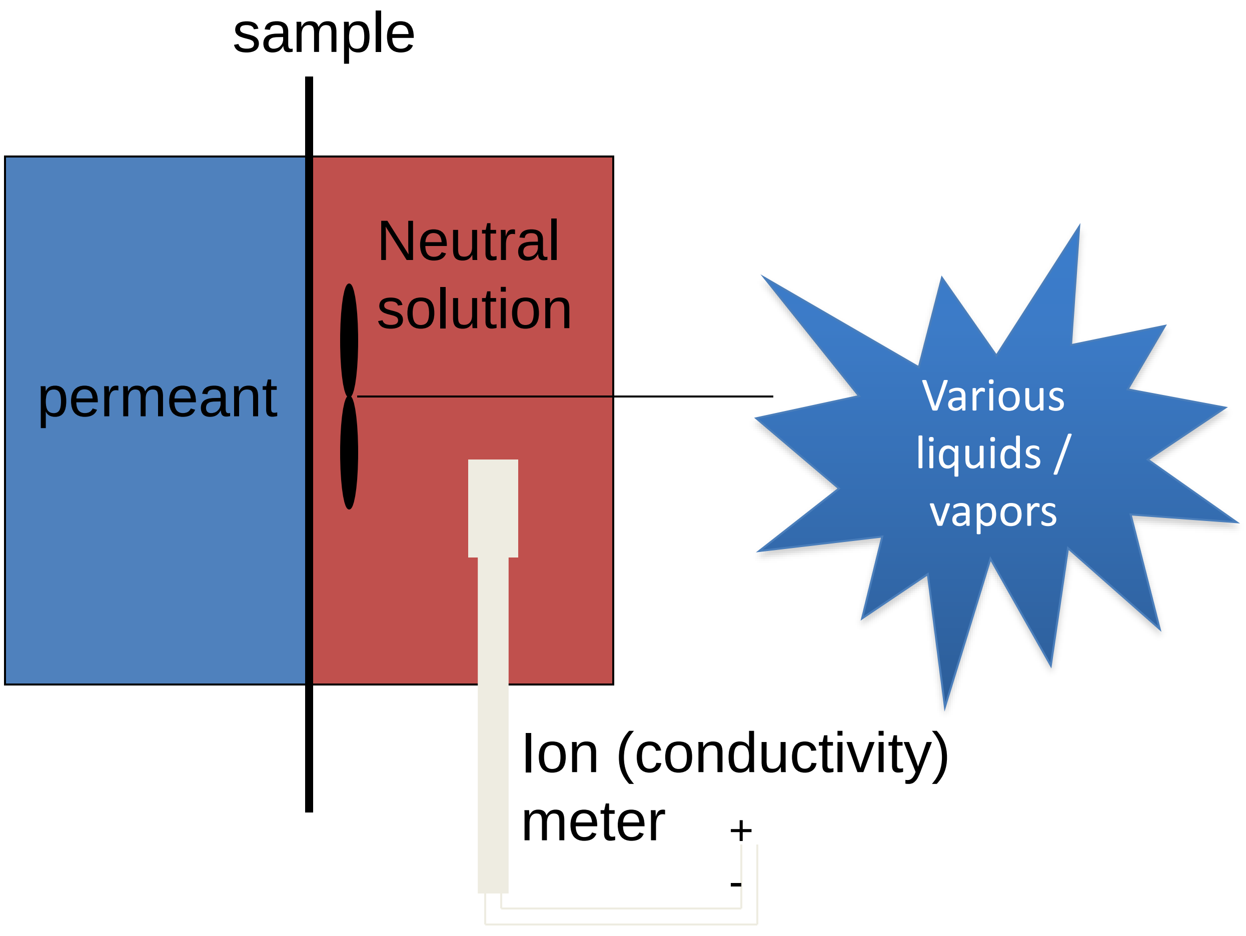


Isostatic Permeation Measurement
Accumulation / separation technique

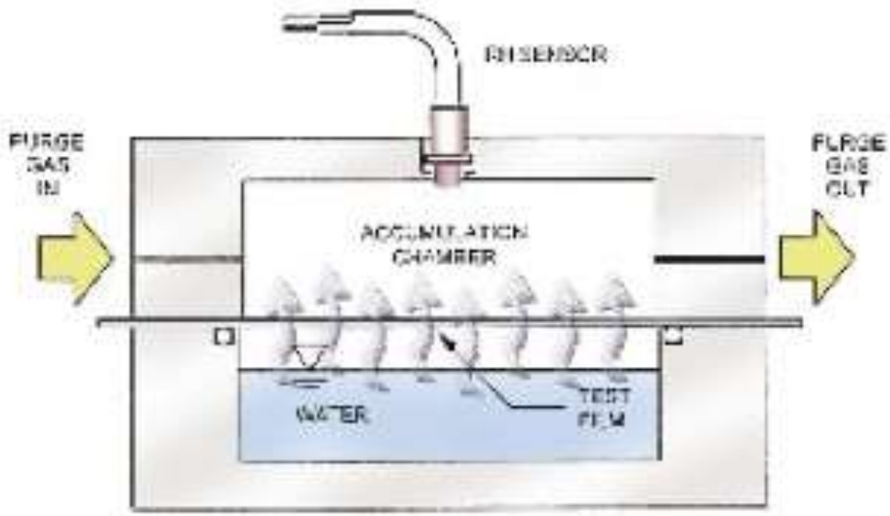


Isostatic Permeation Measurement

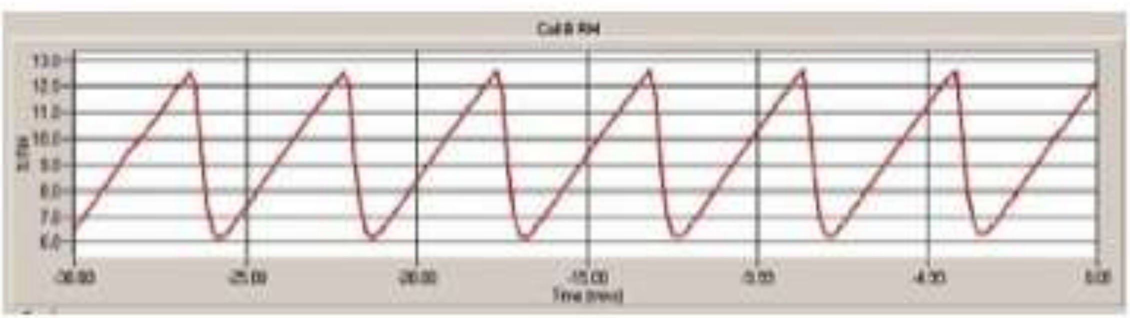
Modified ASTM F-739



Accumulation
old ASTM E398

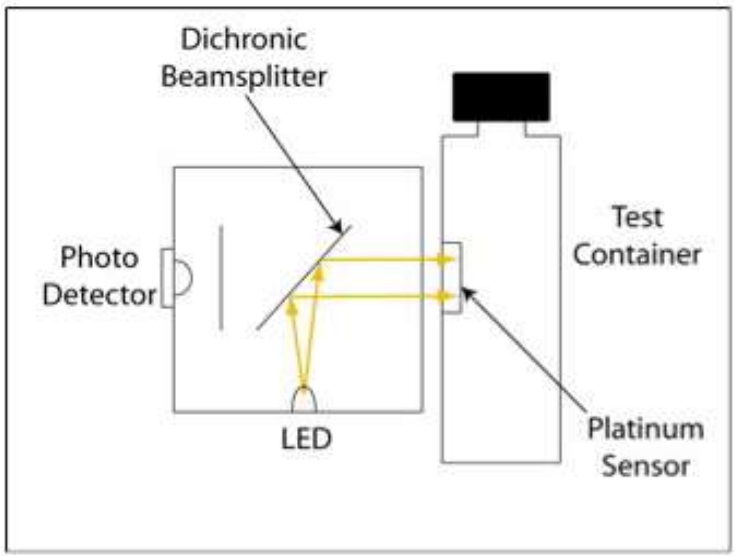


water

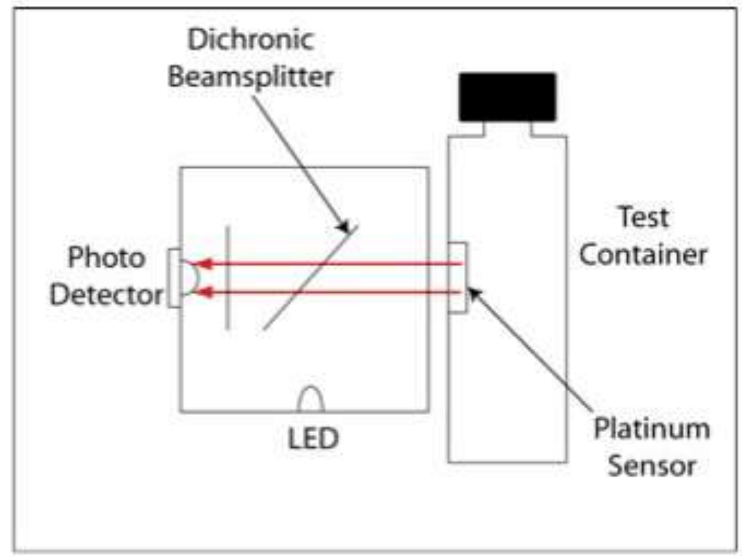


Optical Permeation Measurements

Optical Permeation Measurements



Excitation Pulse



Fluorescence Response

Optical Permeation Measurements

AQUATRAN®

AQUATRACE® sensor

- Phosphorus pentoxide
- Faraday's Law of Electrolysis
  - Water molecules require a known amount of energy to dissociate into hydrogen and oxygen

AQUATRACE® sensor
Theory of operation

- Electrolysis cell in which all entering water is continuously and quantitatively absorbed and electrolyzed into hydrogen and oxygen.
- In accordance with Faraday's Law the electrolysis of 0.5 gram mole of water (9.01 grams) requires 96,500 coulombs.
- The analyzer is designed so that all current which flows electrolyzes water.
- Therefore the observed current and the rate of entrance of the water are related to each other with standard accuracy.

Calcium Test – Method 1

Method relies upon the corrosion of Ca metal forming CaO and CaOH

Ca metal is deposited on the film surface

A glass lid is placed over the deposition

The edges of the lid are sealed w/ epoxy

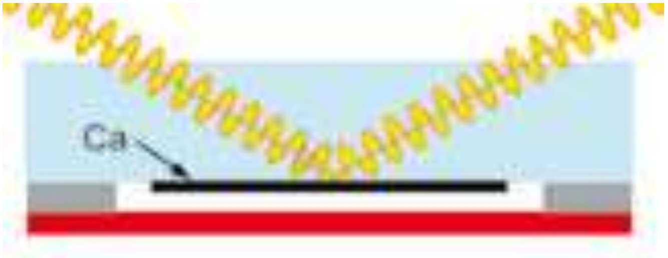
Sample is placed within a high humidity environment

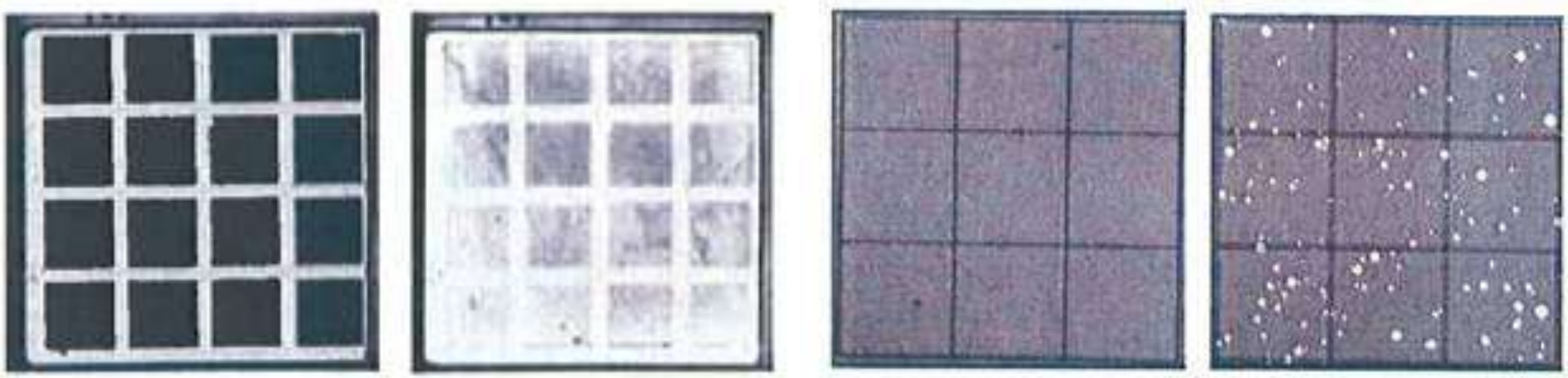
As water reacts with Ca metal, the film becomes transparent

Light measurements are used to monitor Ca oxidation and then the quantity of water absorbed is calculated.

Water
and
oxygen

Calcium Method 1

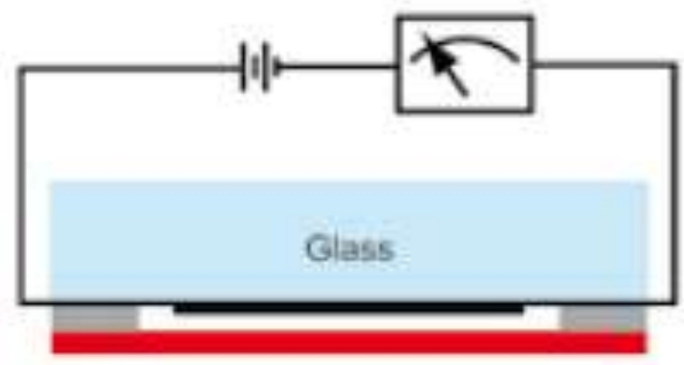




Results reported as low as 5e^{-5} g/(m^{2}xday) – for glass

G.Nisato – Evaluating High Performance Diffusion Barriers: the Calcium Test

Calcium Method 2



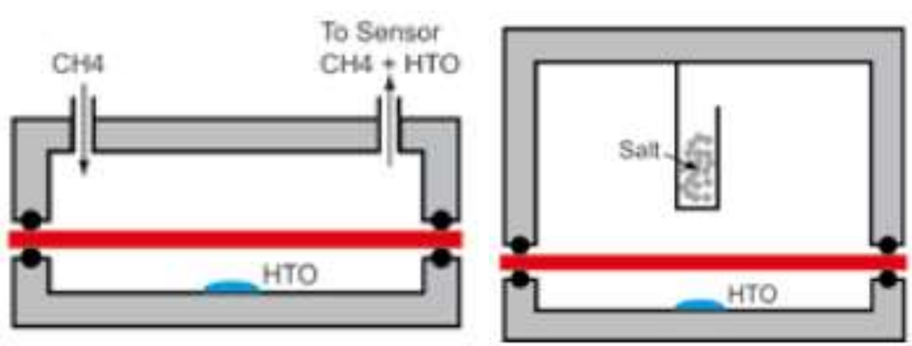
Method also relies upon the corrosion of Ca Metal forming CaO and CaOH, but monitors the electrical properties as the calcium corrodes

Ca metal is deposited on the film surface
Non-corrosive tabs are incorporated at the edges of the Ca Film
A glass lid is placed over the deposition
The edges of the lid are sealed w/ epoxy (tabs through seal)
Sample is placed within high humidity environment
As water reacts w/ Ca metal, the resistance changes
WVTR is calculated from this change in conductance

Tritium Test Method

water

- Water is doped with tritium forming HTO
- The HTO is maintained in one side of a test cell (100% RH)
- The opposite side of the film is analyzed in one of two fashions
  - Real time HTO transmission is monitored via sweeping the permeating HTO vapor with a carrier gas stream (methane) to an ionization chamber, where it is quantified.
  - Transmitting HTO is collected within a hydroscopic salt and then periodically removed and analyzed for its tritium concentration via scintillation methods



- Method reported to provide results below 1e^{-6} g/(m^{2}xday)
- Some questions have been raised if atomic tritium is also permeating*

Arrelaine A. Dameron – Understanding moisture ingress and packaging requirements for photovoltaic modules
*Arrelaine A. Dameron – Gas Diffusion Barriers on Polymers Using Multilayers Fabricated by Al_2O_3 and Rapid SiO2 Atomic Layer Deposition

Mass Spectrometry Test Method

A sample is mounted within a diffusion cell

Both sides of the sample are evacuated

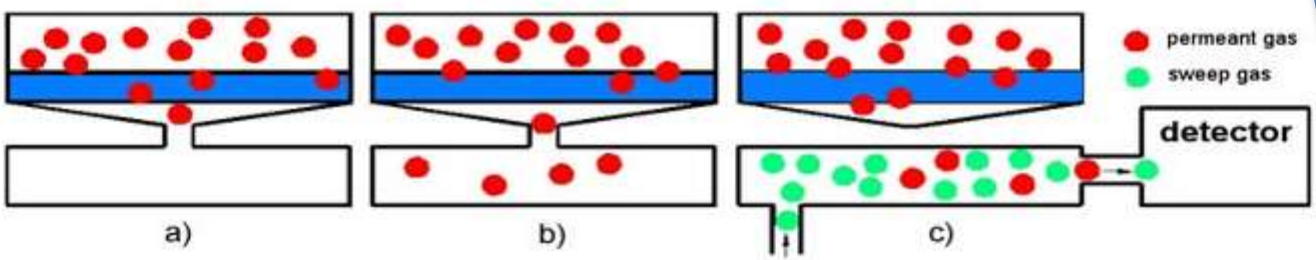
The test side is exposed to a constant pressure of H_2O (A)

The permeating water vapor is allowed to accumulate (B), taking care to keep each sides “total pressure” similar (minimize film stress)

Periodically, the accumulation side is swept to a gas

for water quantification

Various gasses and vapors



Lower detection limits for mass spec should be below 1e^{-6} g/(m^{2}xday)

K.C Obrien – A new technique for the measurement of multicomponent gas transport through polymeric films

Hurdles in Measuring Permeation

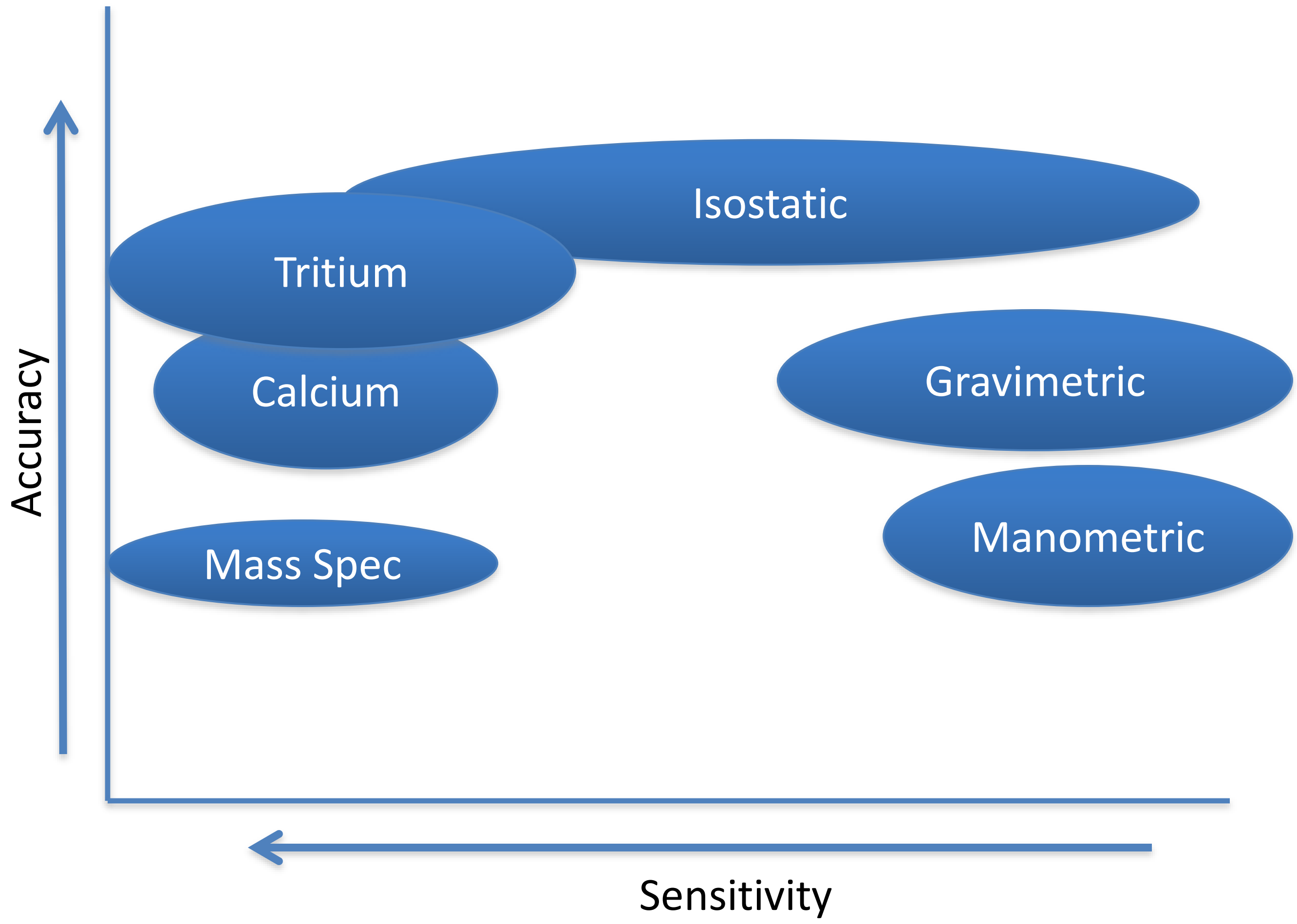
Several obstacles are inherent to permeation testing.

Without proper measurement and/or control of the variables, permeation results can vary drastically.

Because of these obstacles, low-end results from all current methods should be closely examined.

- Temperature
- Leaks
- Calibration
- System noise
- Correlation with established methods / results
- Other (specific to test method)

WVTR Measurement Methods

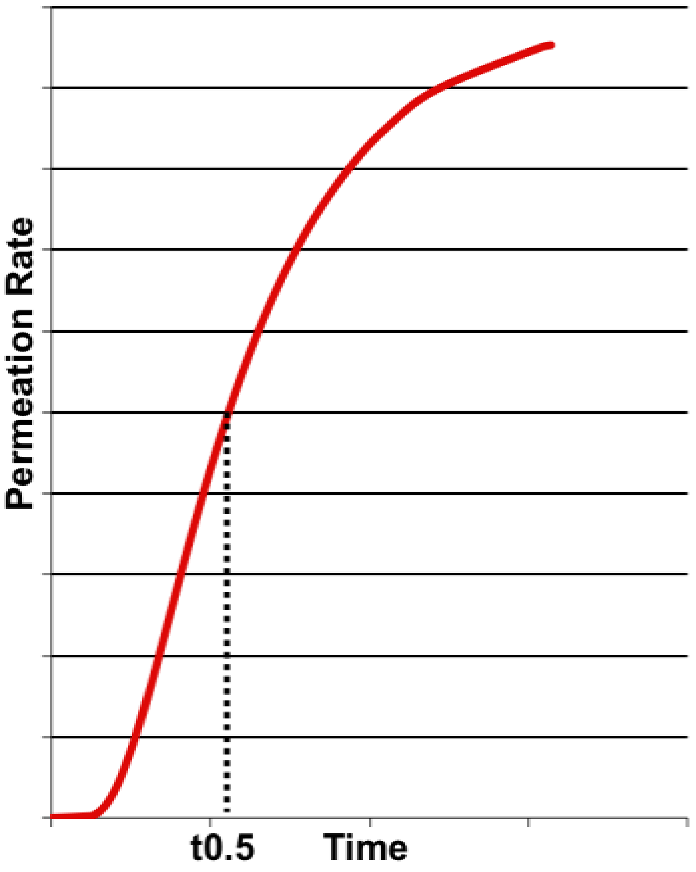


Testing Techniques

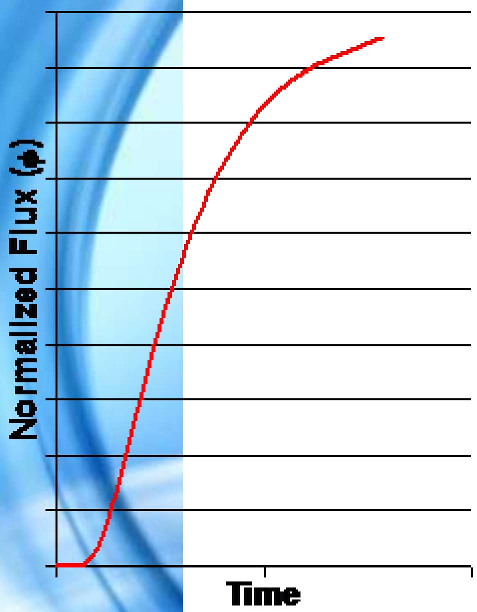
Techniques for measuring S and D

Half-time method

$$D = \frac{\ell^2}{7.199 t_{0.5}}$$

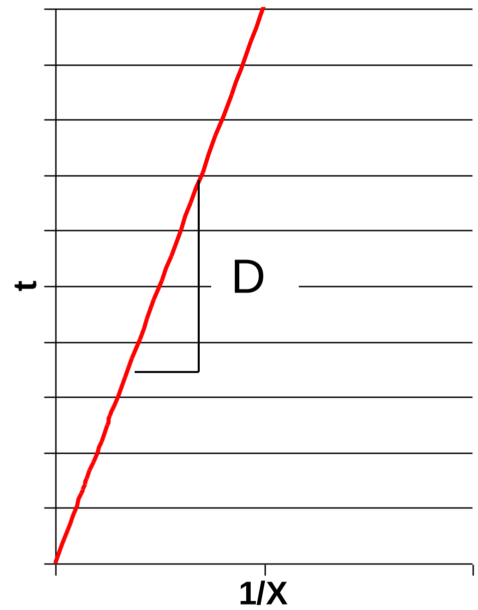


Gavara and Hernandez



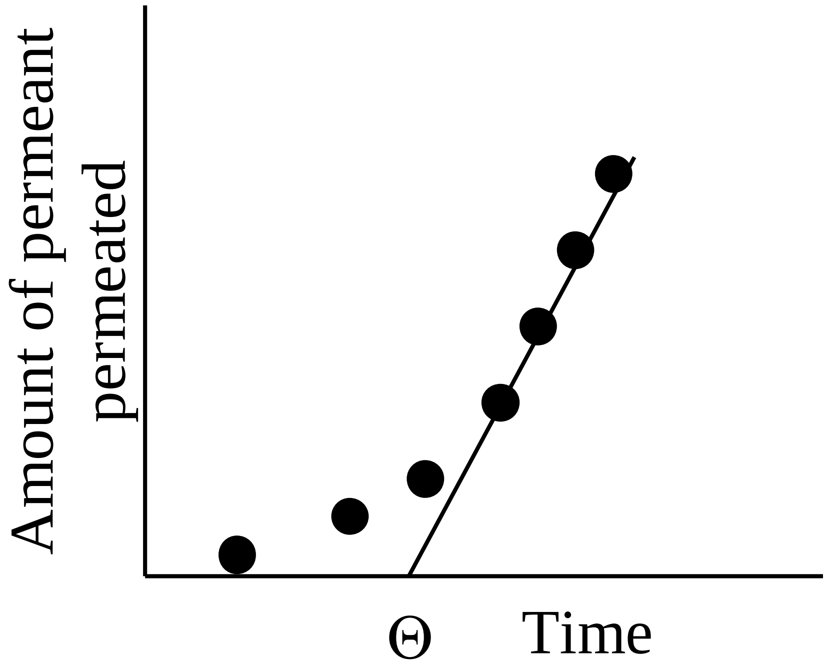
$$\phi = \left(\frac{4}{\sqrt{\pi}}\right) X^{\frac{1}{2}} \exp(-X)$$

(Newton-Raphson)



Time lag method

$$D = \frac{\ell^2}{6\Theta}$$



Thank you for your time!!!

Questions?