# MOISTURE PENETRATION INTO AMORPHOUS SUGAR MATRICES

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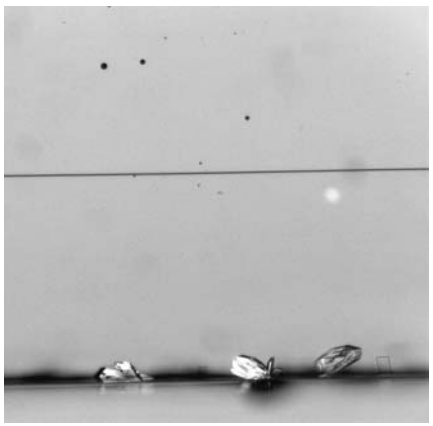
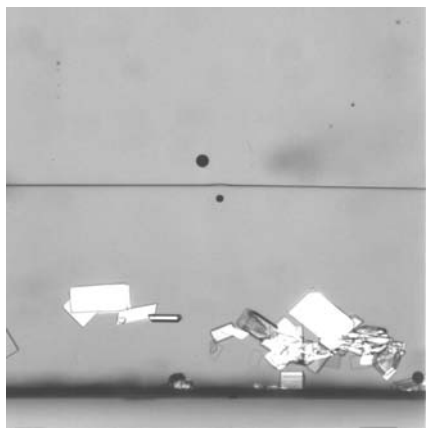


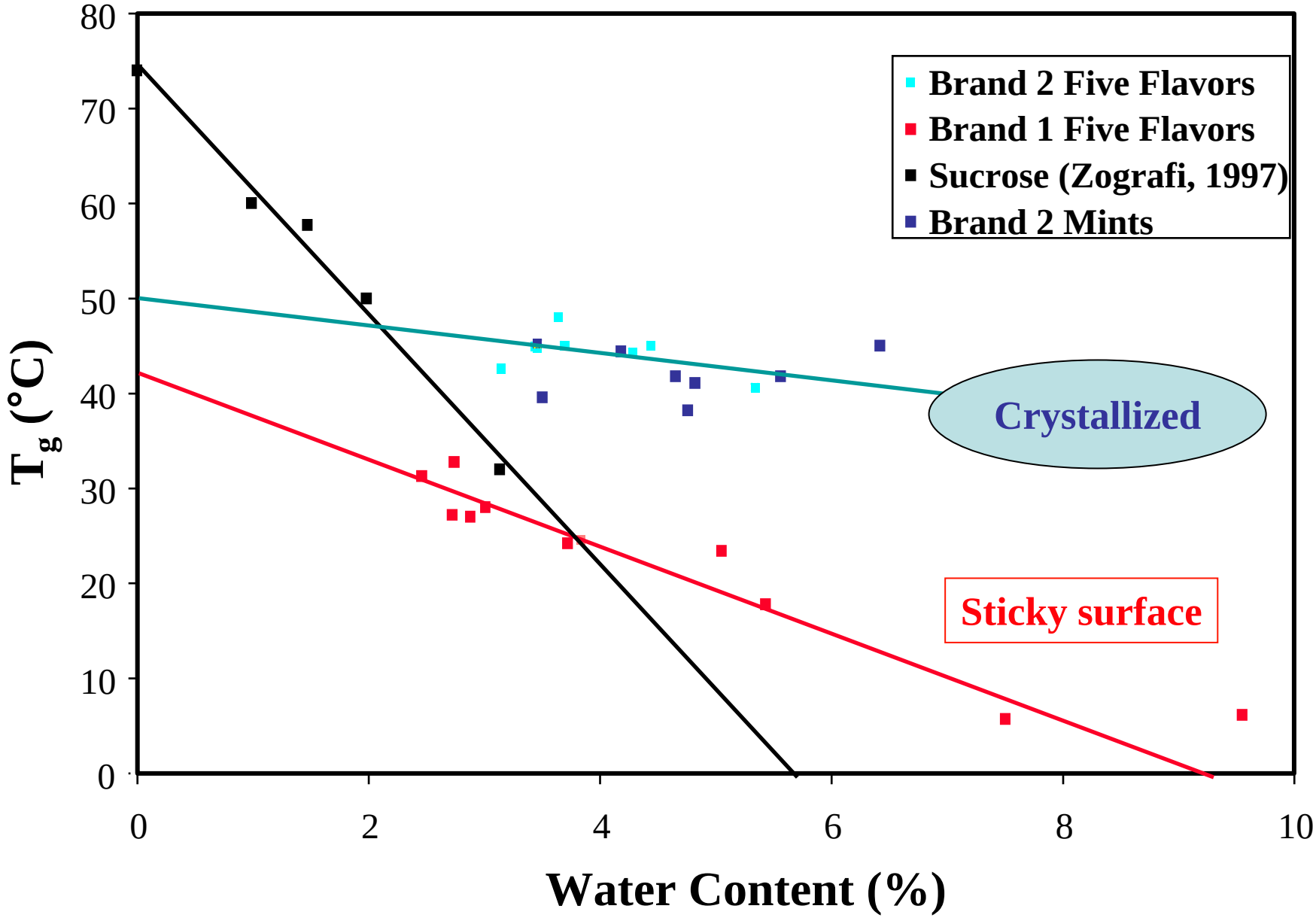


# Hard Candy

- Sugar glass
  - Formed by boiling sugar syrup to high temperature (295 -305°F; 148 - 152°C) and then cooling rapidly below glass transition temperature ($T_g$)
    - Added ingredients, final water content, reactions during processing can all impact moisture uptake, $T_g$ and crystallization

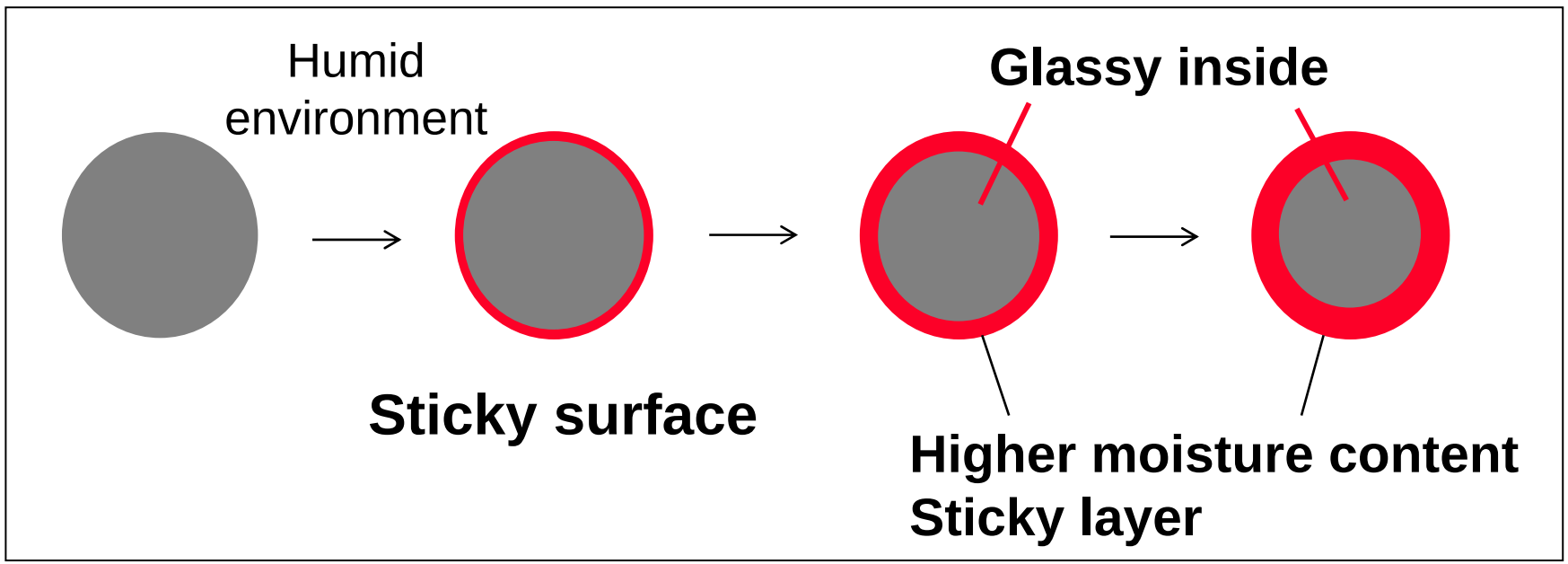
# Commercial Hard Candies

| Sample | Moisture (%) | $T_g$ (°C) |
|---|---|---|
| Brand 1 (5 flavors) | 4.1 ± 1.0 | 26.6 ± 2.2 |
| Brand 2 (5 flavors) | 3.5 ± 1.0 | 40.3 ± 4.4 |
| Brand 2 Sour Balls | 2.8 ± 0.5 | 41.2 ± 1.6 |
| Brand 2 Blue Mints | 4.8 ± 0.9 | 33.2 ± 0.5 |
| Brand 3 Wild Cherry | 3.8 | 37.1 |
| Brand 4 Cherry | 1.7 | 40.2 |
| Brand 5 Throat Lozenges | 3.8 ± 2.5 | 36.3 ± 0.4 |


Brand 2 Five Flavors
Brand 1 Five Flavors
Sucrose (Zografi, 1997)
Brand 2 Mints
Crystallized
Sticky surface
$T_g$ (°C)
Water Content (%)
0
10
20
30
40
50
60
70
80
0
2
4
6
8
10

# Moisture Sorption

- The process of moisture sorption:
  - Surface adsorption
    - Water molecules adhere to polar sites at the surface
  - Diffusion into interior
    - Water molecules diffuse into the interior

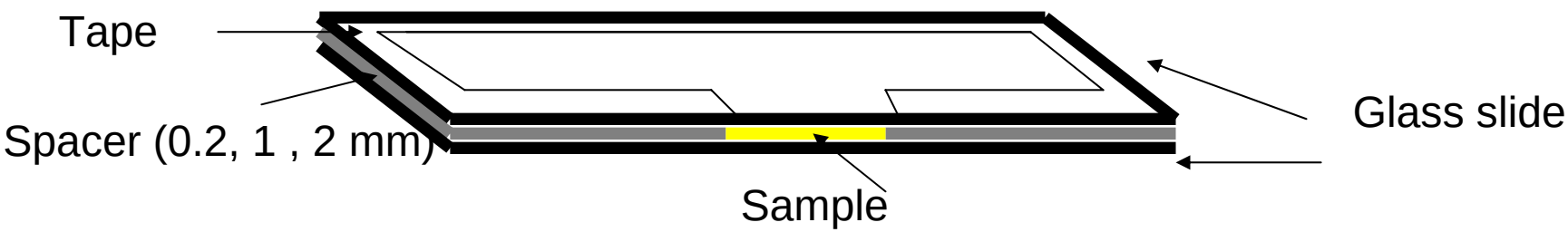


# Objectives

- Quantify moisture penetration into sugar glasses using Raman micro-spectroscopy
  - Important in both foods (candies, dried powders, etc.) and pharmaceuticals
- Measure diffusion coefficients near Tg
- Model penetration curves

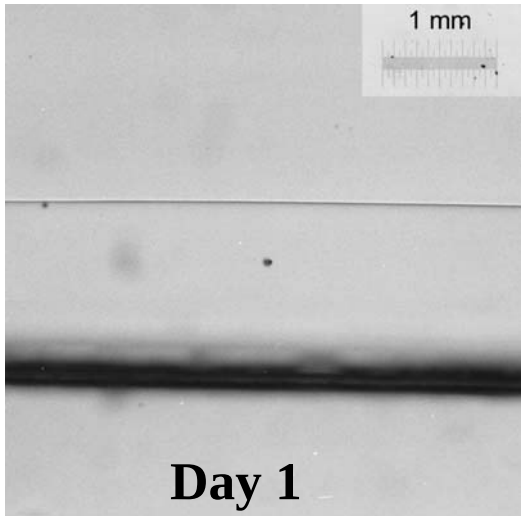
# Sorption Experiments

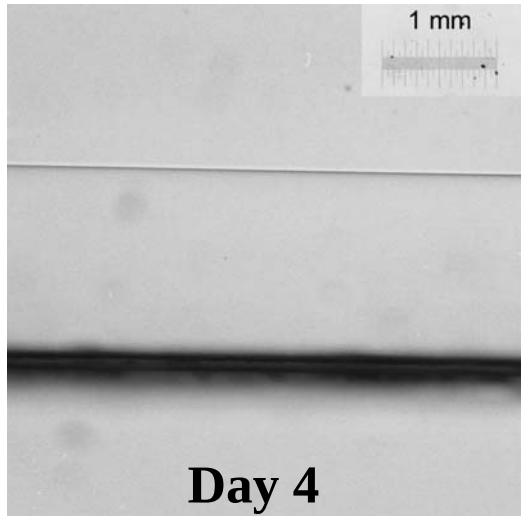
- Form thin layers of sugar glasses
  - Ratio of sucrose to corn syrup
  - Type of corn syrup
- Expose one edge to air at different RH

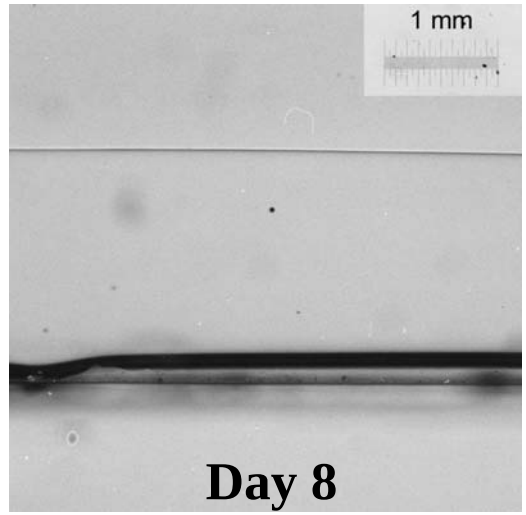


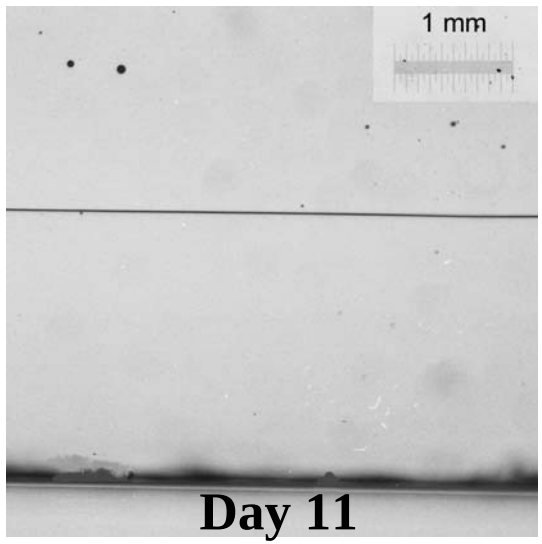
# Moisture Penetration

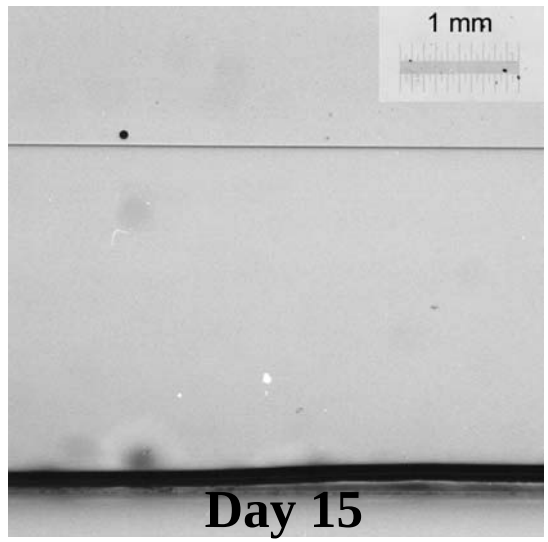
## 50:50 Sucrose/43 DE Corn syrup
## 75%RH and 22°C



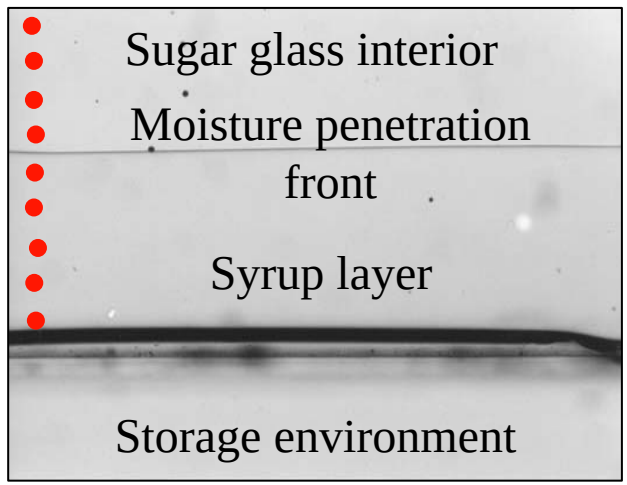



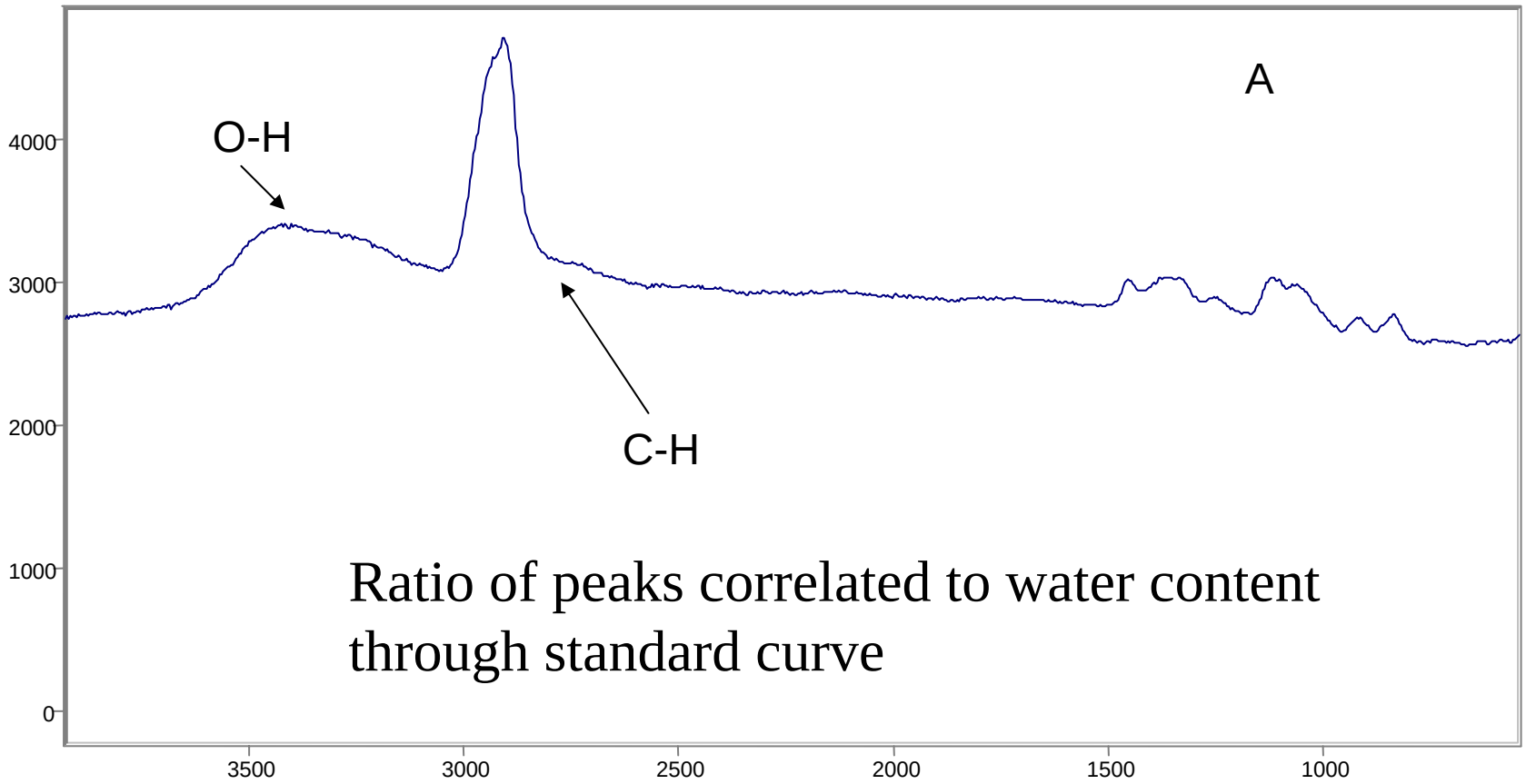



# Micro-Spectroscopy

- Laser spot (≈ 1 - 20 μm) excites vibrational motion in molecules in small area
- Absorbance correlated to water content through standard curve
  - Measure water content at any point in from edge as function of time from when the sample was exposed to humid air



# Preliminary Raman Laser Study

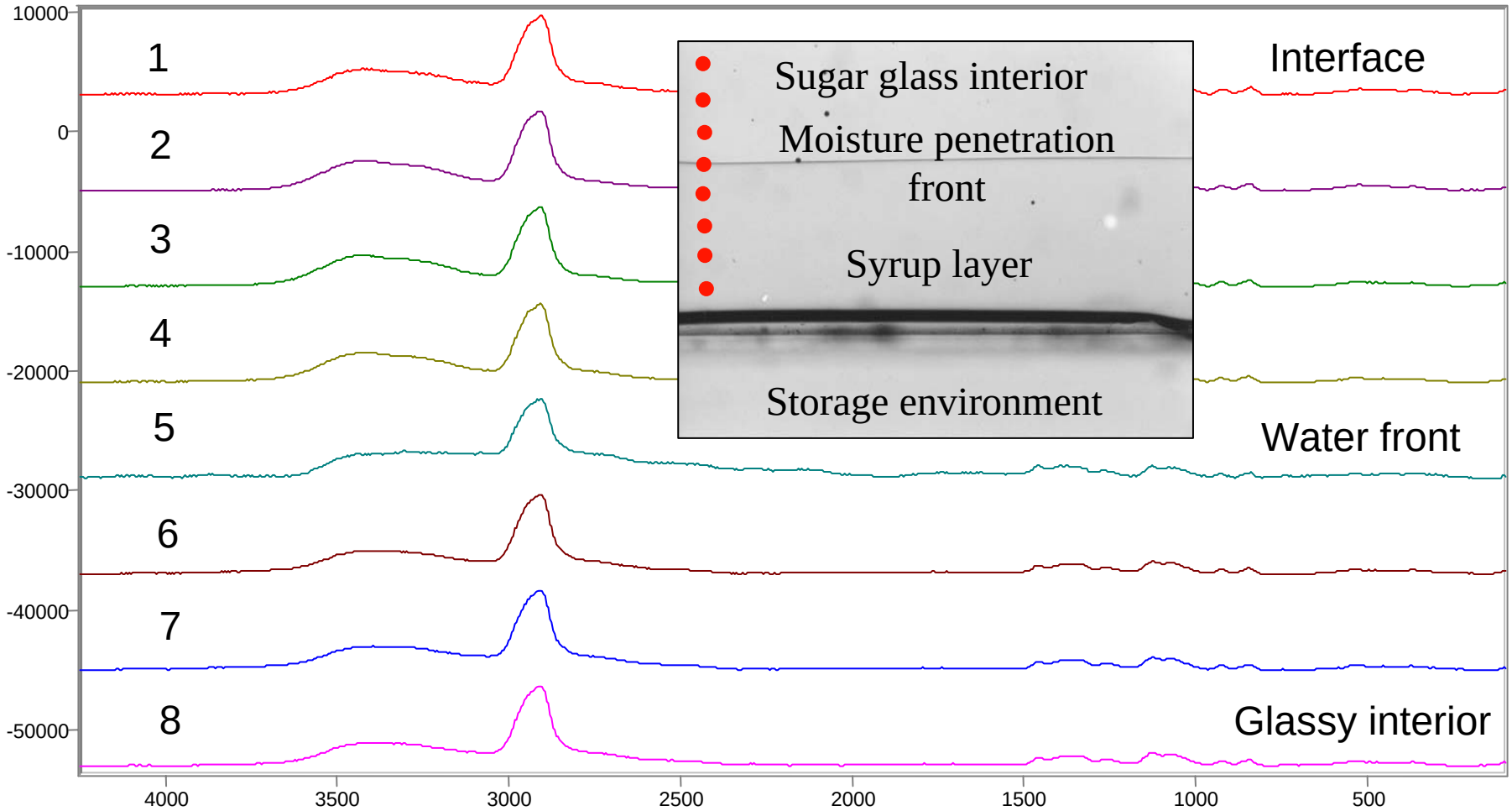



Ratio of peaks correlated to water content through standard curve

532 nm laser with ~20 mW, 5 s. and 20x magnification

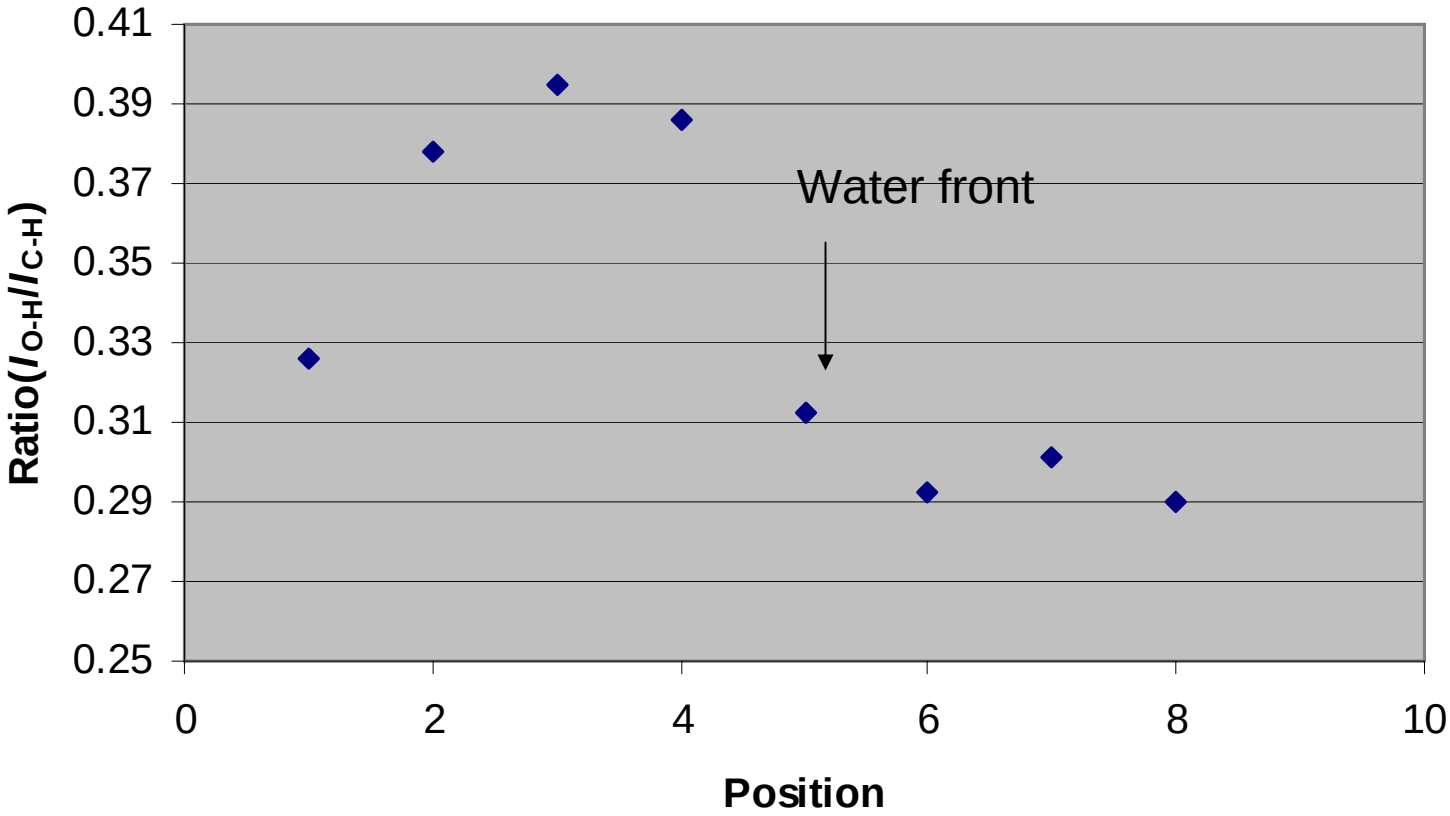
# Raman Spectra

## 50% sucrose/50% 42 DE corn syrup
## 22°C and 75% RH



# Moisture Penetration Profile

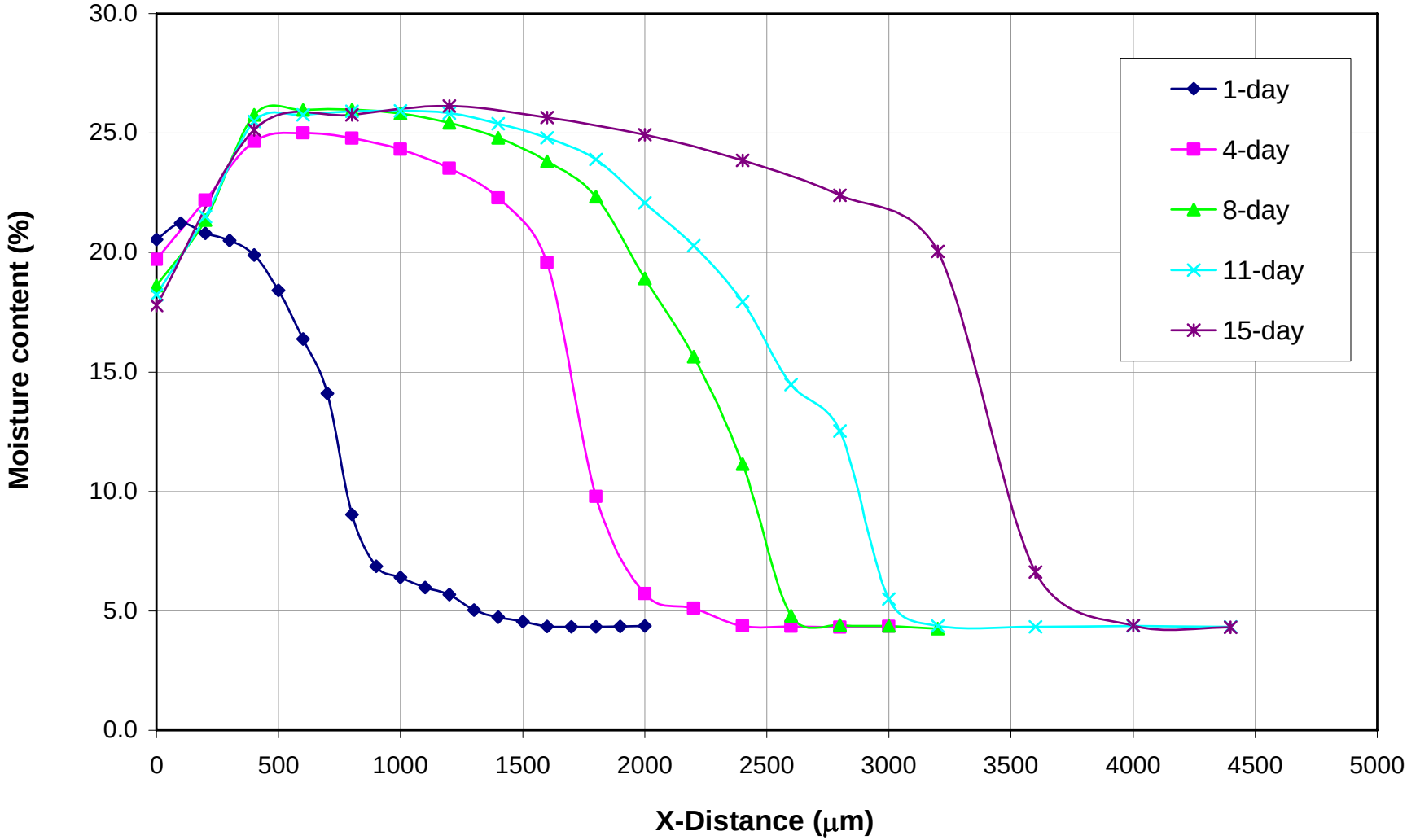
50% sucrose/50% 42 DE corn syrup
22°C and 75% RH




**Peak height ratio $\alpha$ water content**

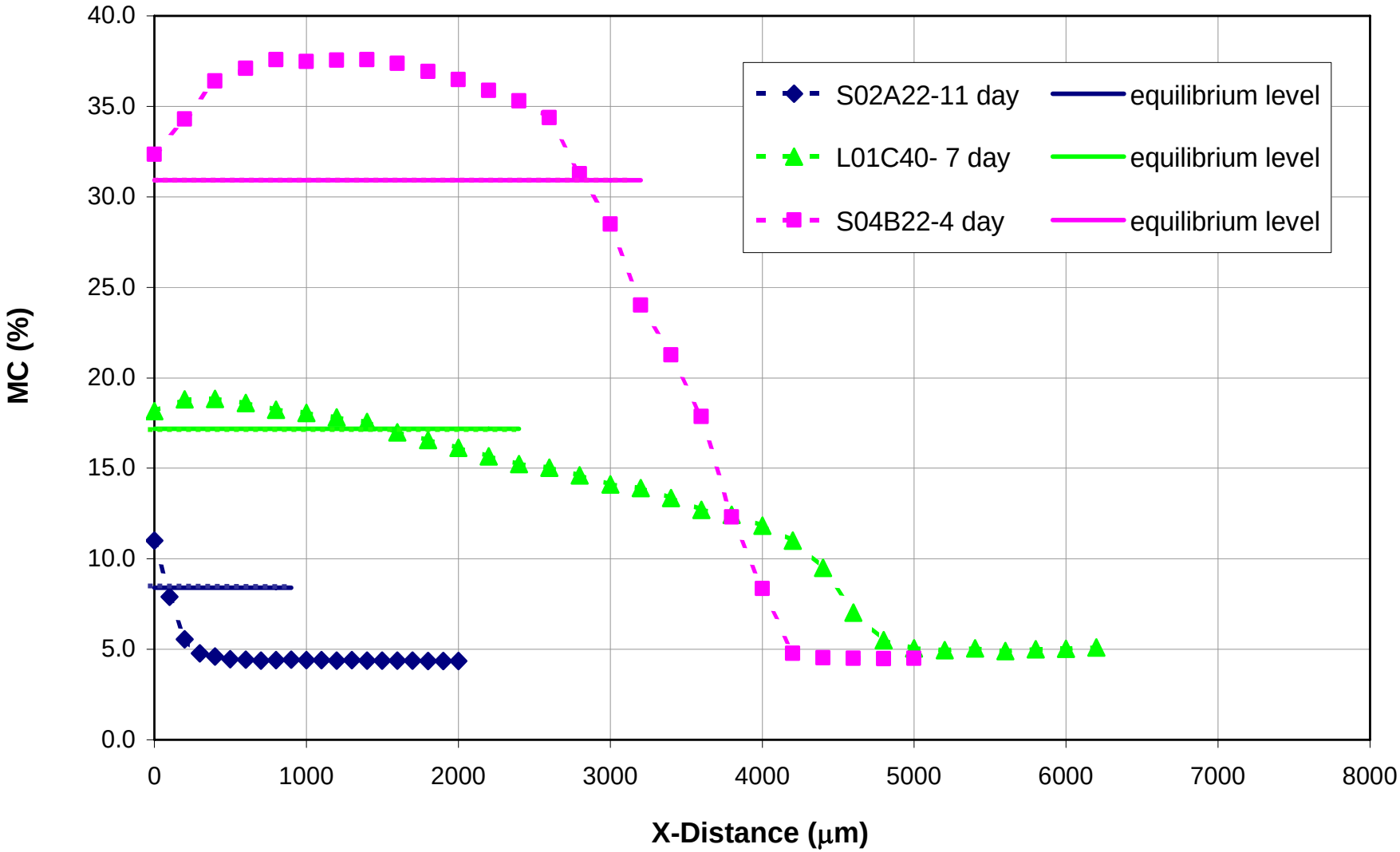
# FT-NIR Measurement

**Moisture content profile during storage of sugar glass**
**(S04C22, sucrose/43CS=50/50, 22°C, 75%RH)**



# Comparison to Equilibrium $H_2O$

**Examples showing moisture content at or near sugar glass edge higher than the corresponding equilibrium level**



# Anomalous Moisture

- Effect of capillary forces on thin film?
  - Results so far on different thicknesses, up to 2 mm, still seem to show this effect
  - Difficulty with films flowing when placed horizontally on the microscope
- Spectra measurement is influenced by the glass slide?
  - Both Raman and FT-NIR?

# Modeling Sorption Behavior

- Need to know diffusivity, D, of water as function of moisture content, both in glassy and amorphous state
- Measurements:
  - Measure D in a range of water content
    - Raman laser micro-spectroscopy with Deuterium-labeled glass
      - Problems with the interfacial boundary
    - Gravimetric analysis
    - Pulse gradient spin-echo NMR at higher water contents

# Summary Status

- Moisture penetration studies underway on a variety of sugar-based and polyol-based systems
  - Development of standard curve for $H_2O$ content
- Continued development of diffusivity measurement methods
- Modeling awaits sufficient penetration and diffusivity data

# “Extra” Results

- Methods to stabilize pharmaceutical glasses
  - Nano-coating of gold or polyelectrolytes over the surface prevents anomalous crystallization of indomethacin glasses
  - Glasses made by vapor deposition method show exceptional stability

Swallen et al., Science*express* (2007)

QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.