TRITIUM – TO ACIDIFY OR NOT TO ACIDIFY; DOES IT MATTER? - Revisited

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EPA Method 906.0, "Tritium in Drinking Water," 1980

- Section 3., Sample Handling and Preservation, states:
  - "The drinking water sample should be collected in its natural state, and should not be acidified."
  - "Since tritium in drinking water is very much apt to be in the form of T_2O or HTO there is no need for special handling or preservation."
- The statement above has been interpreted by most programs to be a requirement of the method to not acidify tritium water samples and has been included in many Sampling and Analysis Plans over the years.
- This has required that separate sampling containers be used for tritium analyses.

HTO = single tritiated water; T_2O = double tritiated water

Technical Notes for EPA Method 906.0, 2009

- Section 3., Sample Handling and Preservation, states:
  - "The method identifies that the sample for tritium should be taken in its "natural state," and not acidified."
  - "This is because there is no need to stabilize the tritium in the sample analogous to the acid preservation applicable for other radionuclides that precipitate at elevated pH.
  - "…preserving samples with acid will not interfere with the technique and acid preserved samples that are analyzed following the method *will* produce valid results."
    - "…acid present in the sample will be neutralized by addition of excess NaOH prior to distillation."
    - "…the amount of hydrogen added is so small relative to the total amount of hydrogen present that it does not significantly change its concentration in the sample by more than about 0.2%."

Proposed Additional Question for Consideration: Effect of Acidification on Mobility of the T^+ Ion Into Plastic

- Plastic sample containers are often used for water sampling.
- Tritium absorbs into hydrogenous material and easily permeates through the material by the mechanism of hydrogen exchanges as evidenced by the following quote from the DOE Primer on Tritium Safe Handling Practices.[1]
  - "If adsorbed onto hydrogenous material, the tritium will easily permeate into the material. The HTO will move much more rapidly into the bulk material than will HT. The permeation rate varies with the type of material and is accelerated by increasing the temperature. As a result of this movement, plastics and rubbers exposed to tritium (especially as HTO) are readily contaminated deep into the bulk material and are impossible to decontaminate completely. …the tritium exchanges with bulk hydrogen…"

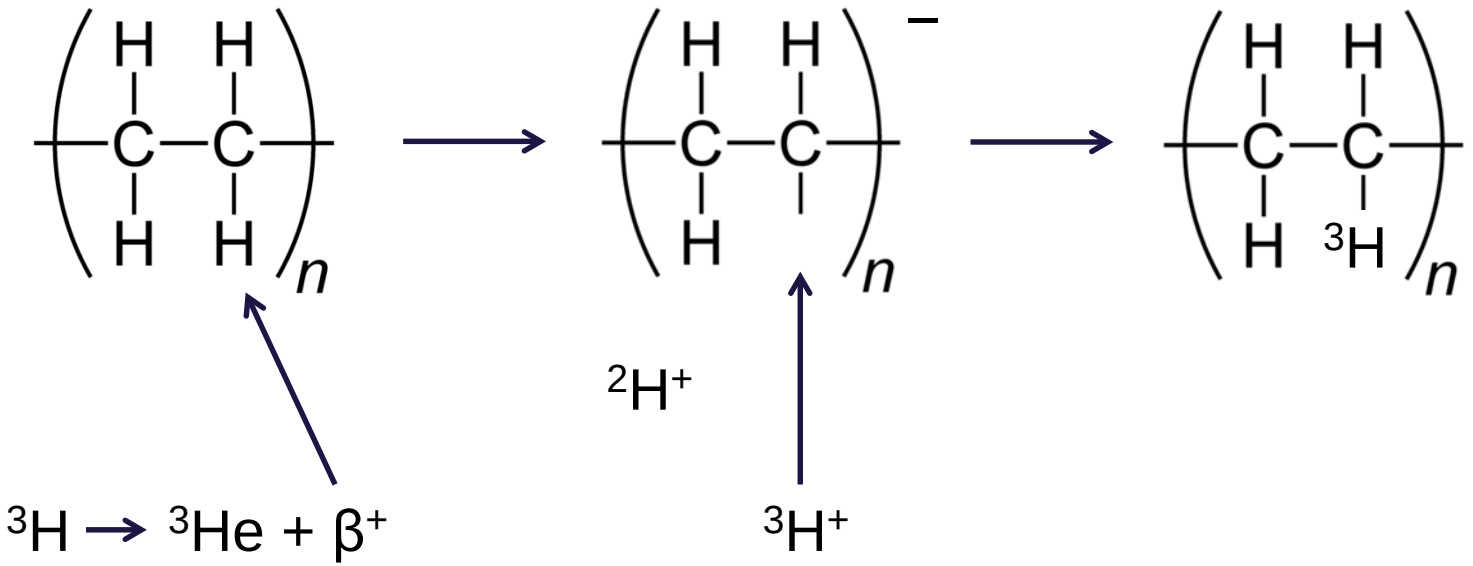
[1]Primer on Tritium Safe Handling Practices, DOE Handbook, DOE-HDBK-1079-94, December 1994.

Mechanisms for ^{3}H Mobility into/through Plastic: Three Pathways[1]

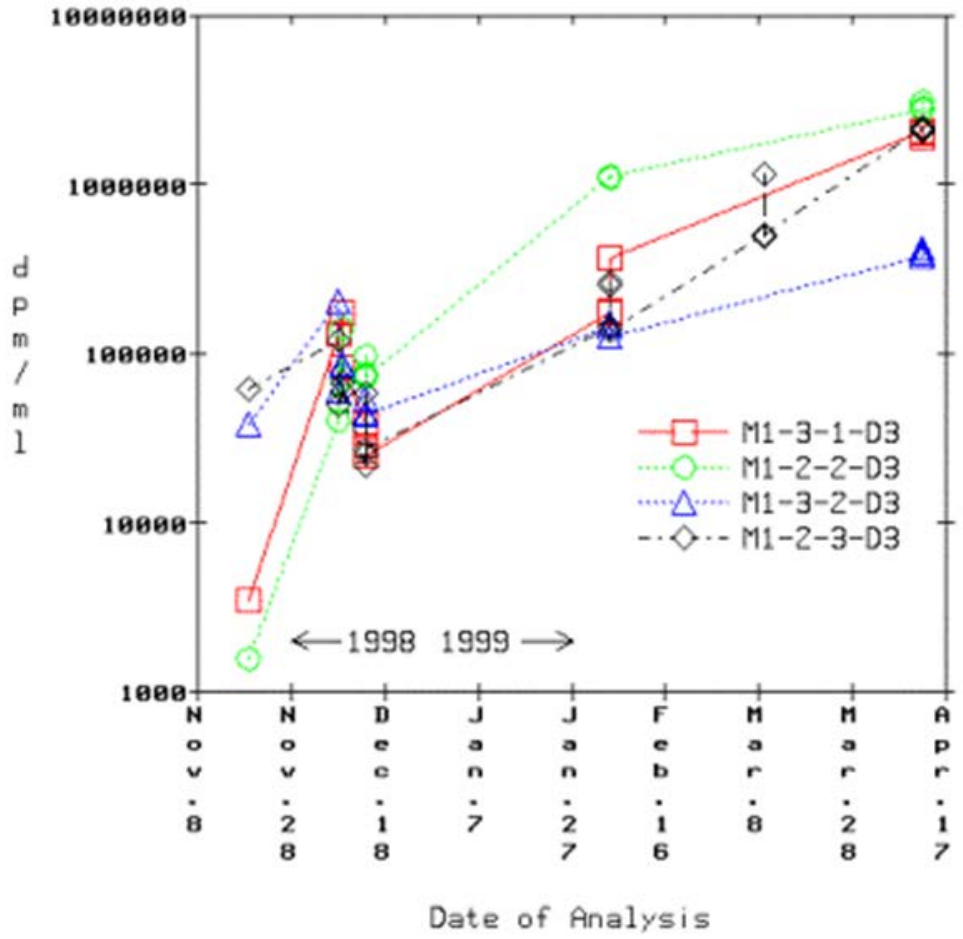
- By simple dissolution of elemental (ionic) tritium into the plastic - Elemental tritium would be quite labile but an equilibrium would be established.
- By absorption of tritiated water into the plastic - Tritiated water slowly diffuses through the plastic and causes slow off-gassing as the water reached the surface and evaporated.
- By direct incorporation in the -CH2- polymeric backbone - The energetic beta decay particles could create free radicals in the polymeric backbone that would then react with either elemental T forms or with tritiated water. In addition, when one T atom of a T_2O molecule decays, it will leave behind a free OT^- radical, which can directly incorporate into the plastic.

[1]Kirk L. Shanahan, Robert J. Reed, Charles J. Coleman, "Tritium Effects on Plastics. Studies at the Savannah River," Westinghouse Savannah River Corporation, WSRC-MS-99-00143.

Mechanisms for ^{3}H Mobility into/through Plastic: Direct incorporation in the -CH2- backbone



Time Evolution of T Concentration in Volumetric Flasks[1]



[1]Kirk L. Shanahan, Robert J. Reed, Charles J. Coleman, "Tritium Effects on Plastics. Studies at the Savannah River," Westinghouse Savannah River Corporation, WSRC-MS-99-00143.

“Where do the elemental (ionic) Tritium forms come from?

- Auto-electrolysis of Water

$$H_2O \leftrightarrow H^+ + OH^-$$

$$K_W = [H^+][OH^-] = 1x10^{-14}$$

- The kinetics of ionization are very rapid.
- This means that ionically bound tritium is very labile and is being exchanged constantly with different water molecules and with other hydrogenous material.
- HT does not form H^+ or T^+ ions and does not exchange with the hydrogen atoms in hydrogenous material as readily.

HT = tritiated hydrogen gas; H^+ = hydrogen ion; T^+ = tritium ion; K_W = dissociation equilibrium constant

Hypothesis: The hydrogen exchange rate with hydrogenous material is proportional to the H^+ concentration in the solution

- Natural water $[H^+] \sim 10^{-7}$
- At pH of 2 $[H^+] = 10^{-2}$ 5 orders of magnitude higher
- $[T^+]$ is proportional to the $[H^+]$ due to the rapid exchange rate between the two.
- If the above hypothesis is true, the exchange rate with hydrogenous material and its migration into the plastic containers will be 5 orders of magnitude faster for acidified samples than for non-acidified samples.
- However, the $[H^+]$ also is elevated and competes with the T^+ for reacting with free radicals and incorporation into plastic.

$[H^+]$ = hydrogen ion concentration; $[T^+]$ = tritium ion concentration

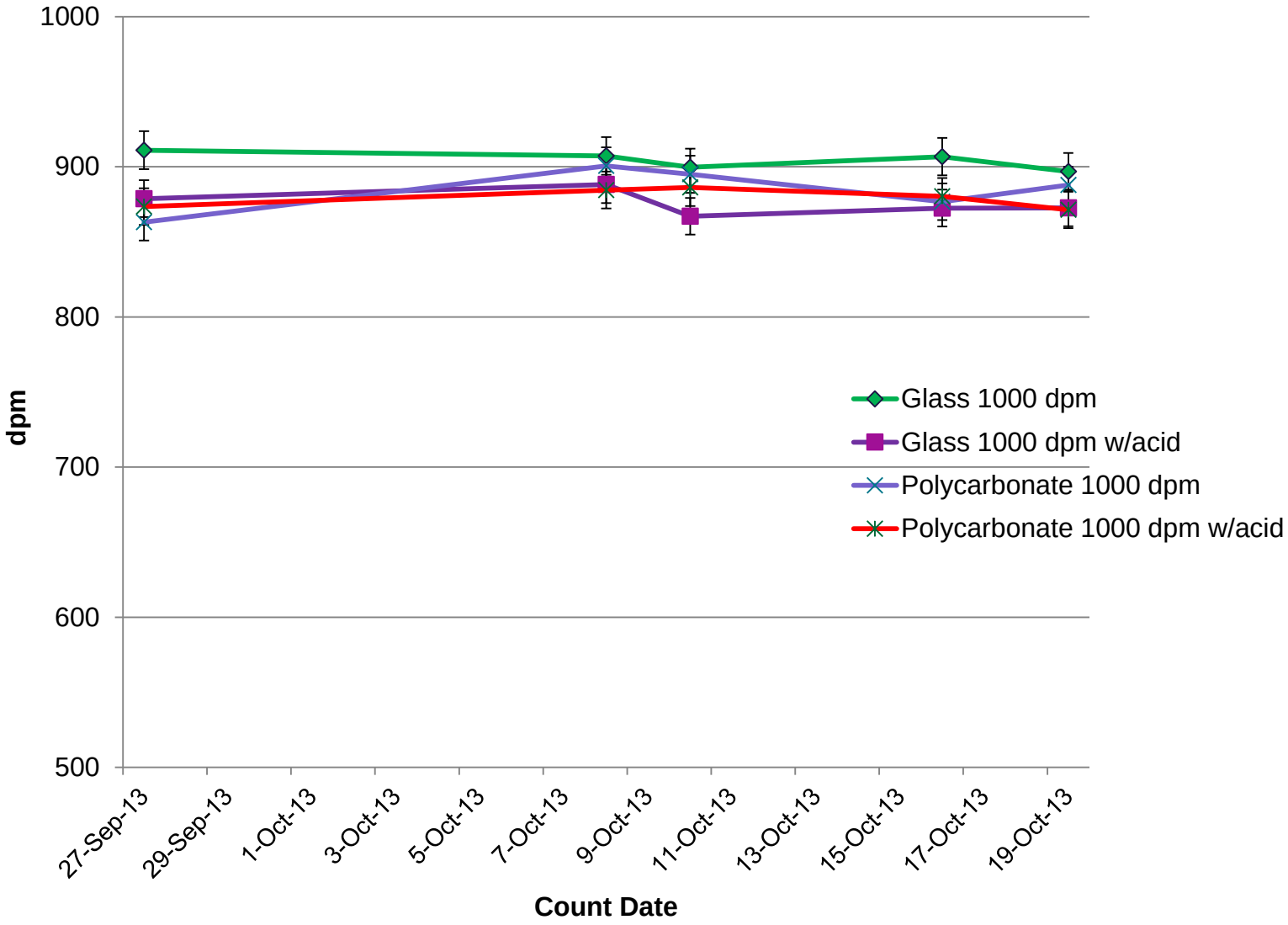
What is the migration rate of T^+ through plastic containers?

- Tritium samples prepared with scintillation cocktail and contained in sealed plastic scintillator vials have been observed to have a significant decrease in countrate when counted repetitively over a few weeks.
- This should be taken into consideration when choosing sample containers and holding times, especially if a 180 day holding time is used.
- We hypothesized this may be a good reason not to acidify water samples to be analyzed for tritium.
- The ‘proof is in the pudding’ – test the hypothesis!

Initial Experimental Design

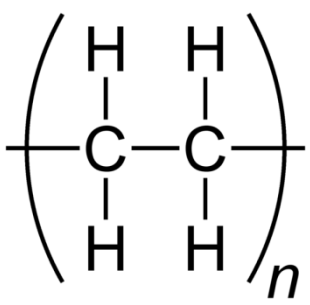
- A series of 1000 dpm/ml standard solutions were set up
  - both acidified and not acidified
  - both in glass, polycarbonate 50 ml vials
- The concentrations were to be measured weekly/monthly for more than 180 days

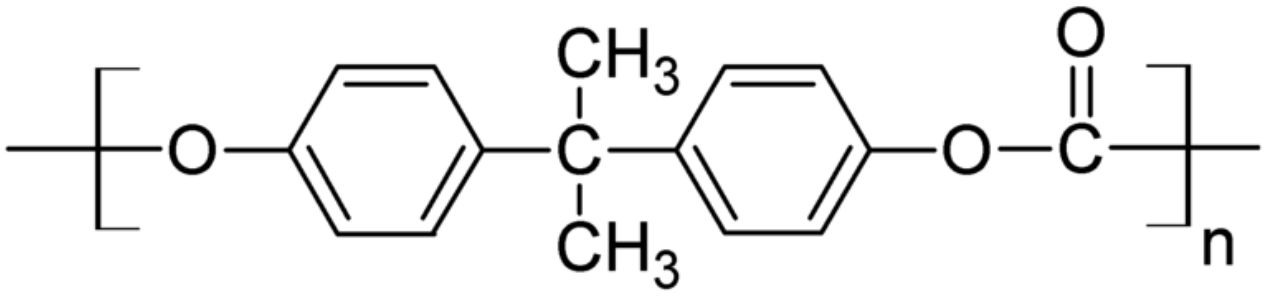
1000 dpm Results



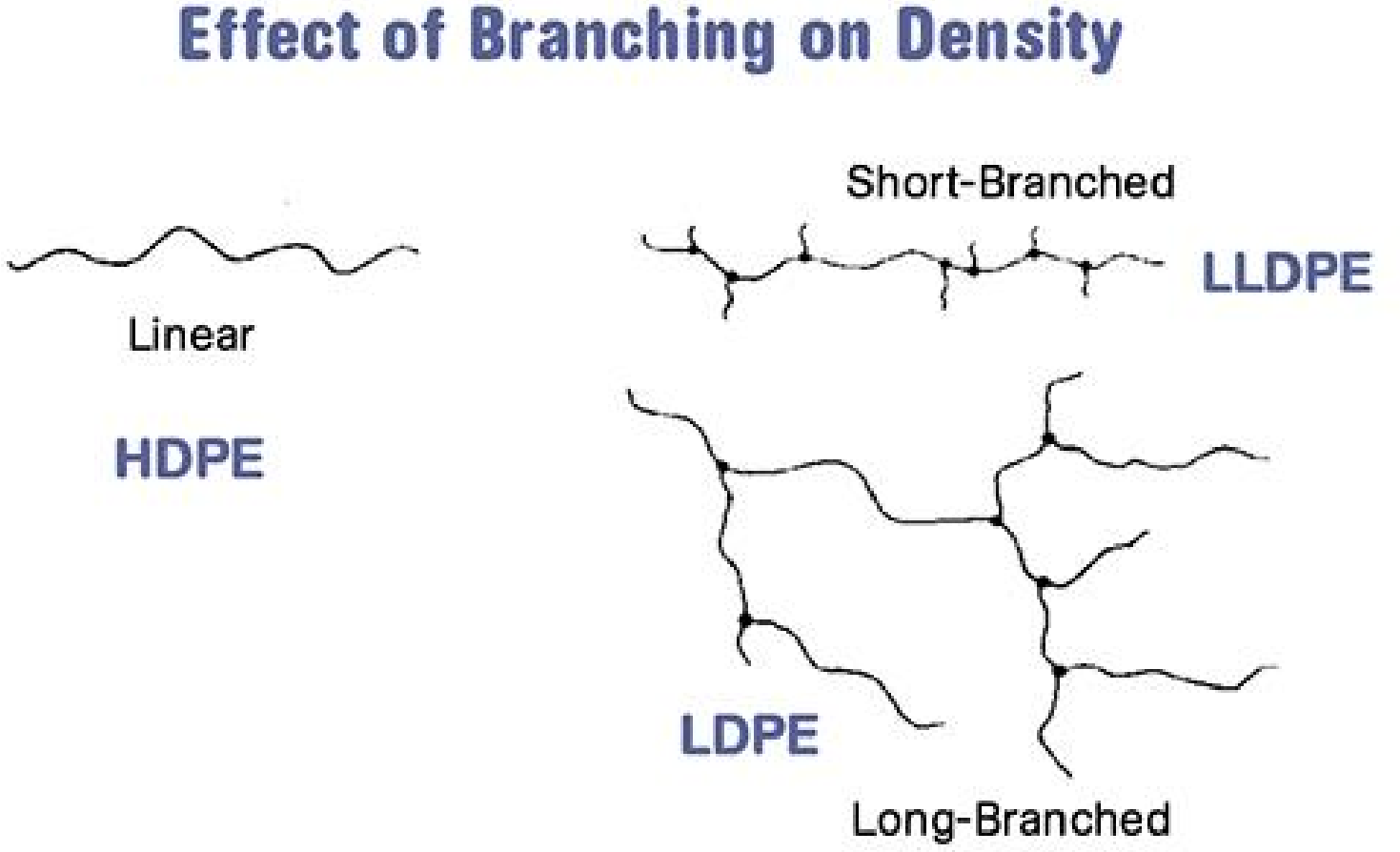
Original Recommendations for Further Work

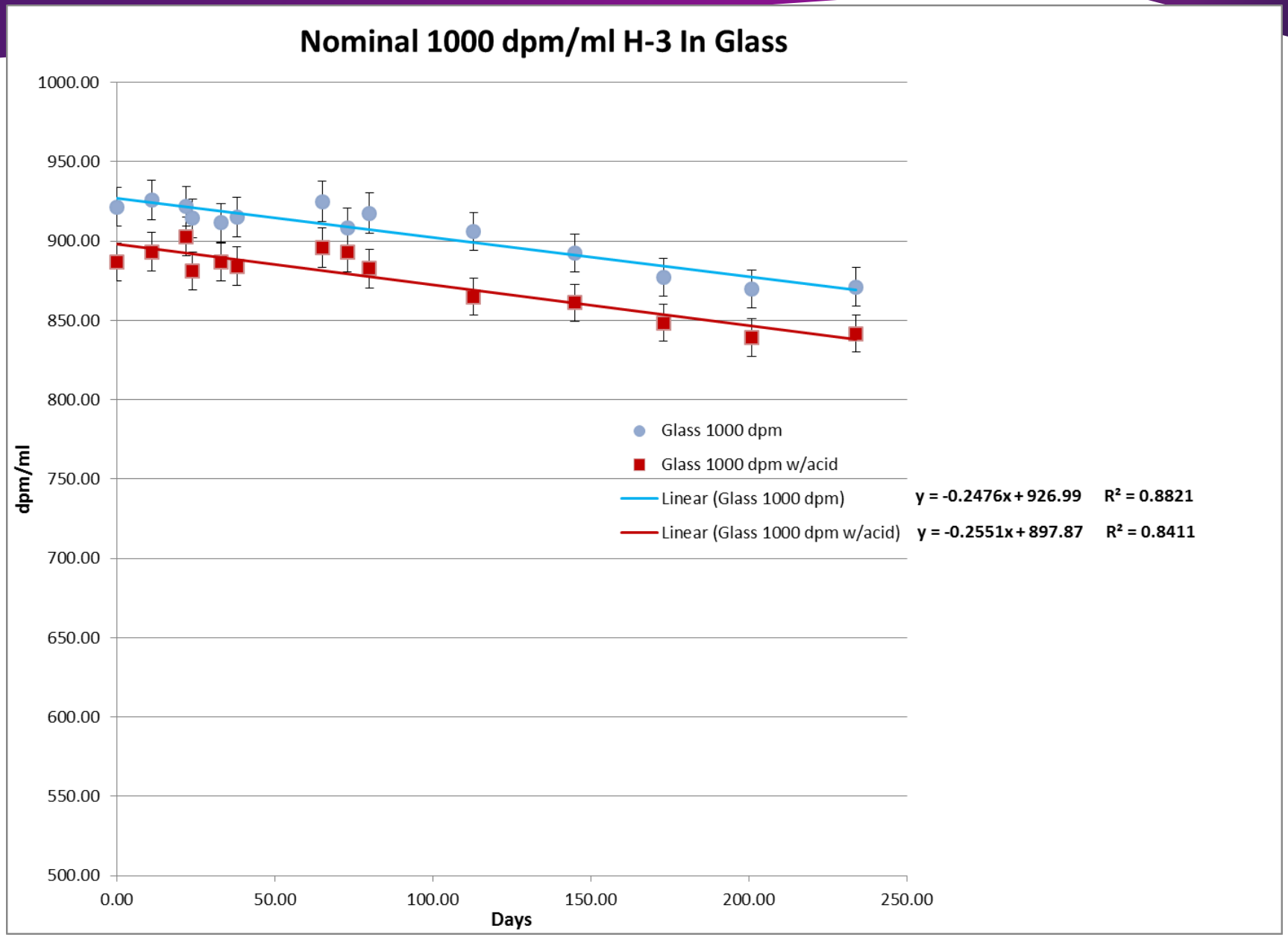
- Continue counting once per month through 180 days
- Repeat experiment with Nalgene (HDPE) plastic bottles and larger volumes (1000 ml)
- Encourage others to try similar experiments



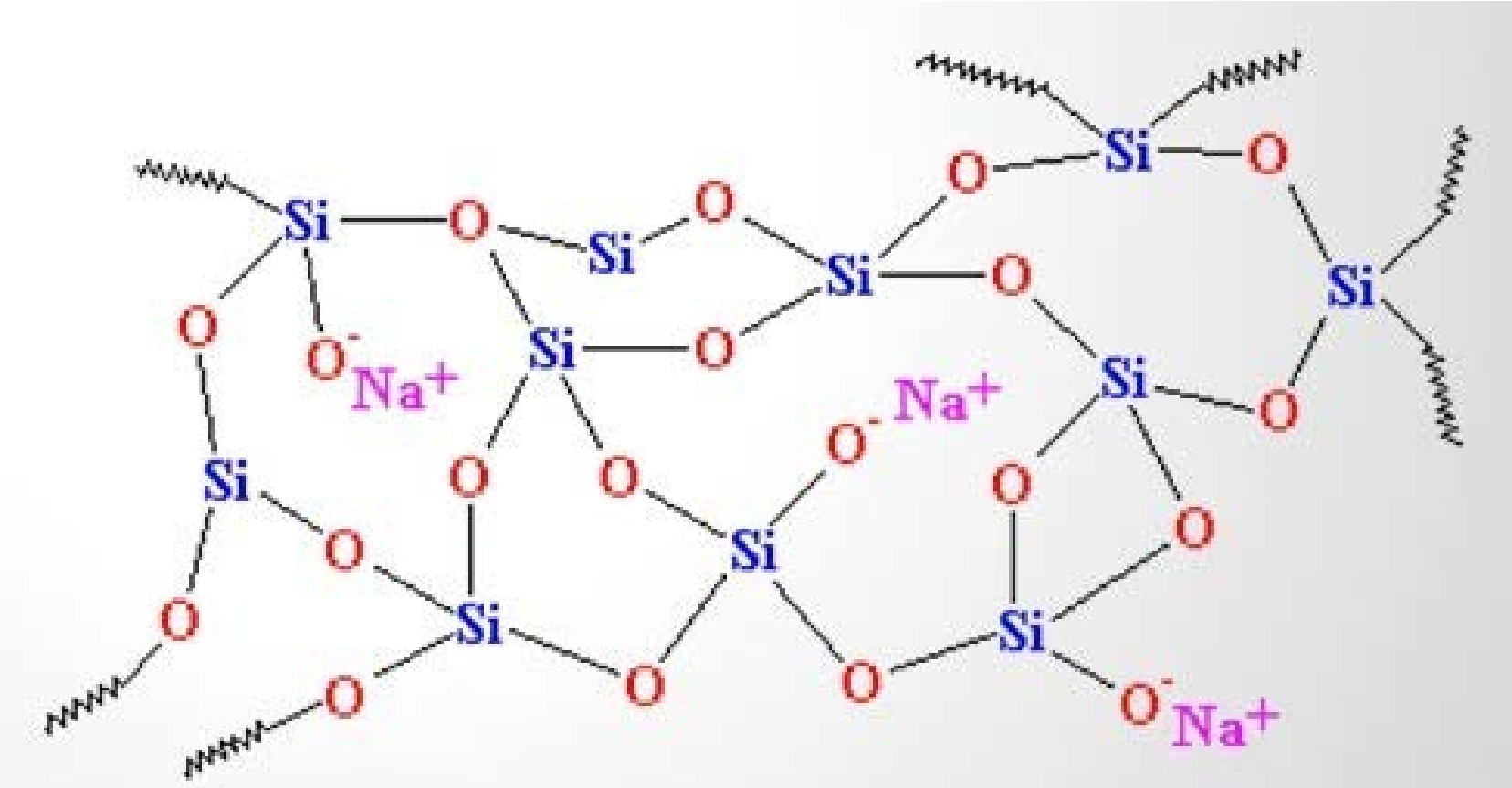


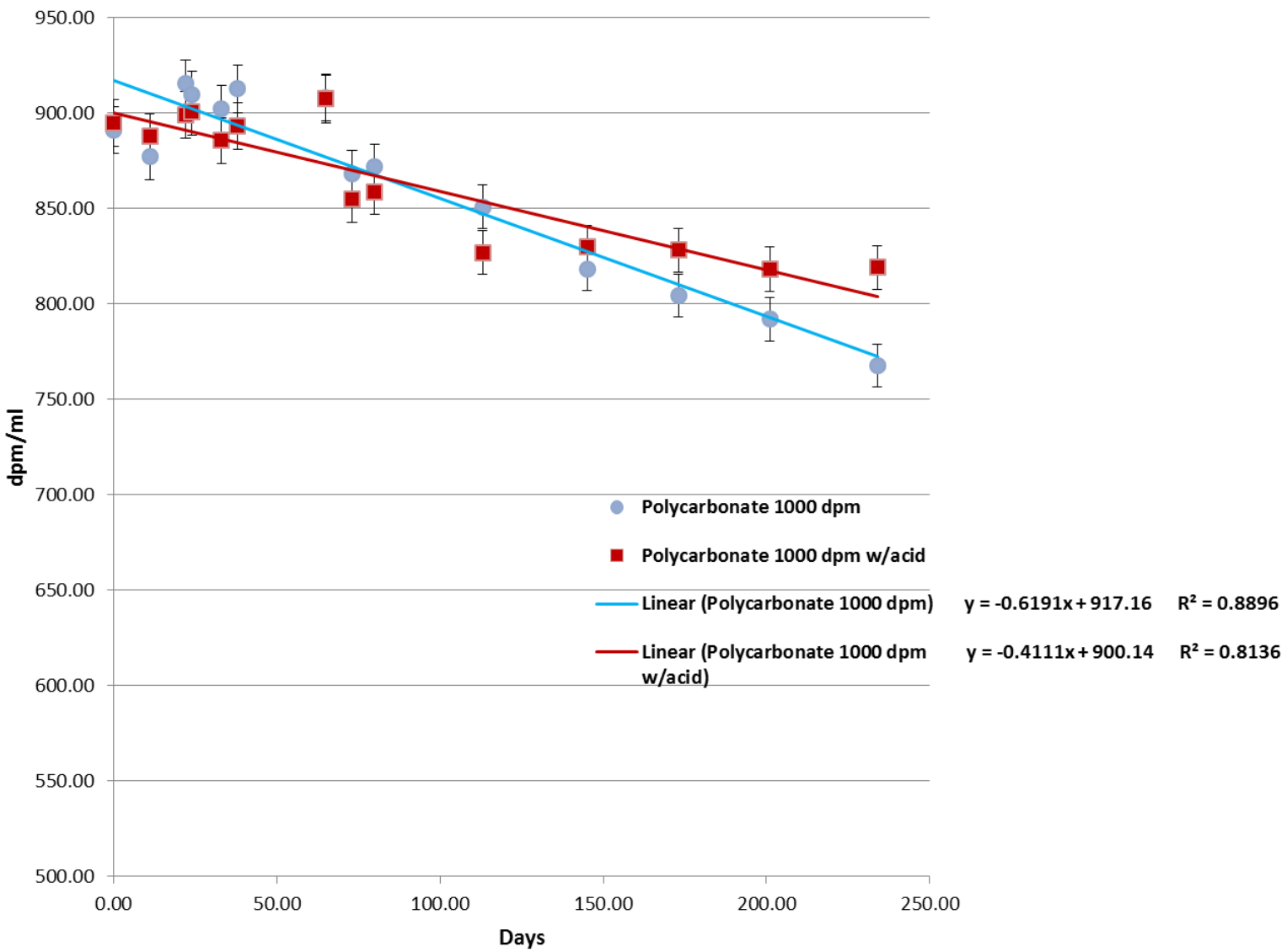
High Density versus Low Density Polyethylene

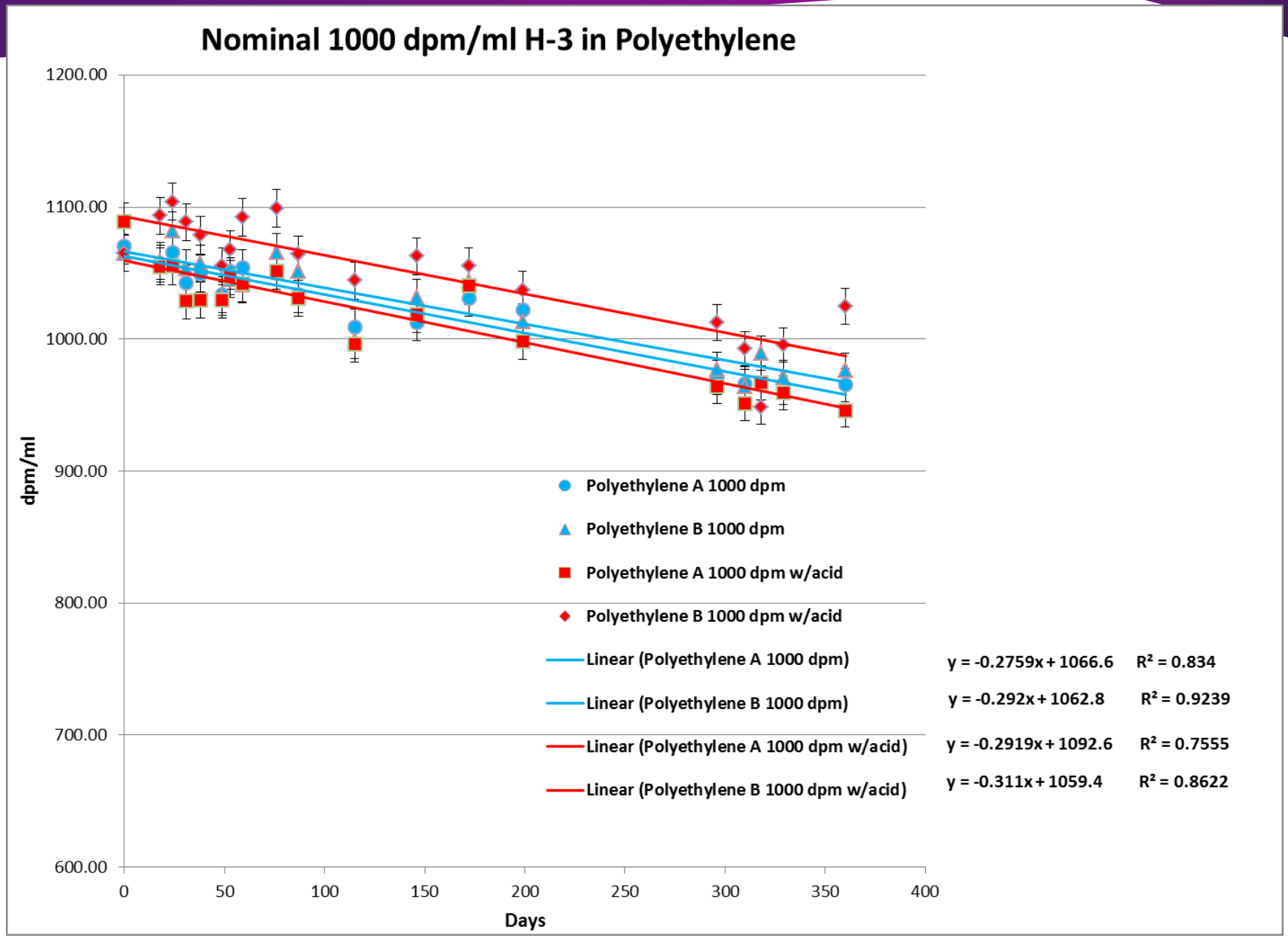


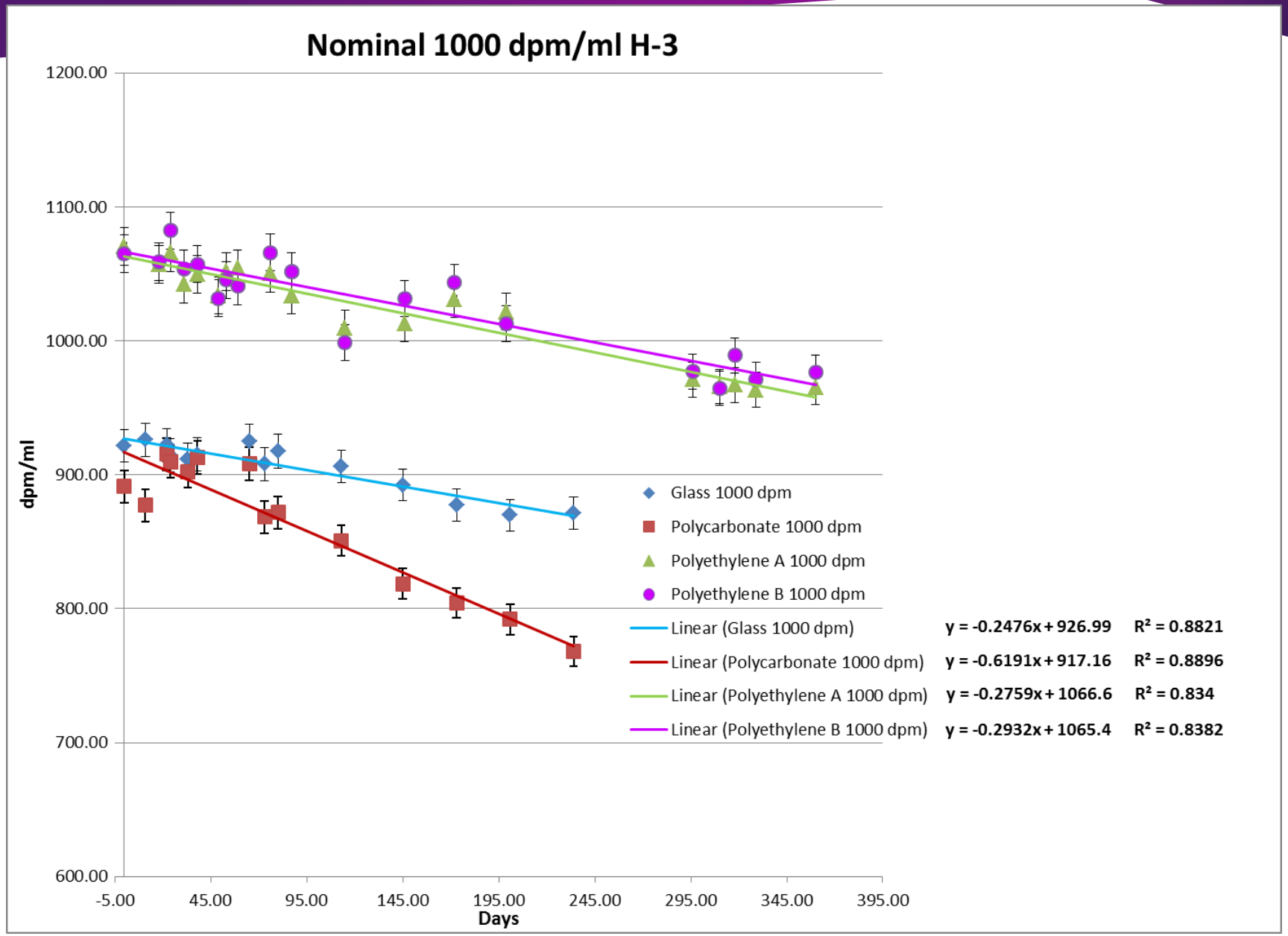


Basic Glass Structure









Conclusions and Lessons Learned

- Tritium loss from storage containers can occur by multiple mechanisms
  - Loss by dissolution and absorption in plastic are likely slow and minimal
  - Loss by direct incorporation in the polymeric backbone can be significant and dependent of the type of container material.
  - Loss by escape of vapor when bottles are opened can be significant and dependent on head space fraction.
- Impact of acidification is minimal
  - While the T^+ concentration in solution is increased at lower pH, the H^+ concentration is also increased and competes with the T^+ for incorporation in the polymeric backbone.
- Tritium should be stored in glass containers with minimal headspace if to be stored for extended times, with multiple openings or environmental levels.

Points of Contact

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