# Pemulen TR2 – The Once and Future King (of Conservation)

All hail Pemulen. The old recipe sheets are dead; long live the new recipe sheet (this one).

In the event you haven't been paying attention, I've been working for years to get recipes for stock Pemulen gels that will allow the conservator to obtain consistent and reliable pH values when preparing said gels.

To that end, I've written three previous articles in the *WAAC Newsletter* and made numerous recipe sheets to be passed out in my MCP workshops as well as the GCI's CAPS workshops. To date they have all been wrong at least to some extent (but at least my heart was in the right place).

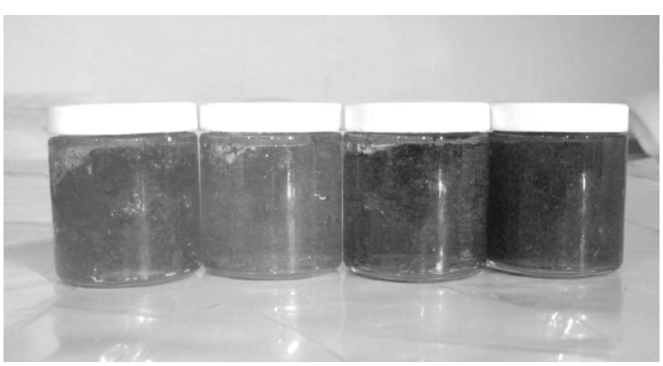
So, why the problem? It turns out measuring the pH of Pemulen gels is surprisingly difficult. My original thought was to dilute the stock gel down to a very thin consistency and measure the pH with a conventional pH meter. While one got very nice and repeatable numbers, they were entirely wrong. (Think measuring 7.2 for a pH 6.5 gel.)

Fearing that the polymer in the Pemulen was clogging the reference electrode (Richard Wolbers' suspicion), I tried "salting" out the Pemulen by adding sodium chloride (table salt) to the dilute Pemulen solution mentioned above. This did precipitate the macromolecules that are Pemulen and allow a reading that would not be compromised by the presence of the Pemulen itself. This also gave erroneous numbers.

pH papers work fairly well, but their precision is limited. It's difficult to tell if a gel is at pH 7.5 when the reference colors are at 7.0 and 8.0. Also, a 1% Pemulen gel will barely wet the pH paper. One is also cautioned by the manufacturers to read the pH sticks within a narrow time window, which makes comparing colors a bit difficult, though not insurmountable.

However, a pH indicator dye is the most accurate means to determine pH of a weakly buffered system. While Pemulen gels aren't exactly "weakly buffered," they are very odd, witness their difficulty in measuring their pH.

Figure 1
The pH indicator dye takes on different colors with the pH of the gel. From left to right: orange (pH 5.0), yellow-green (pH 6.5), green (pH 7.0), and blue/purple (7.5).

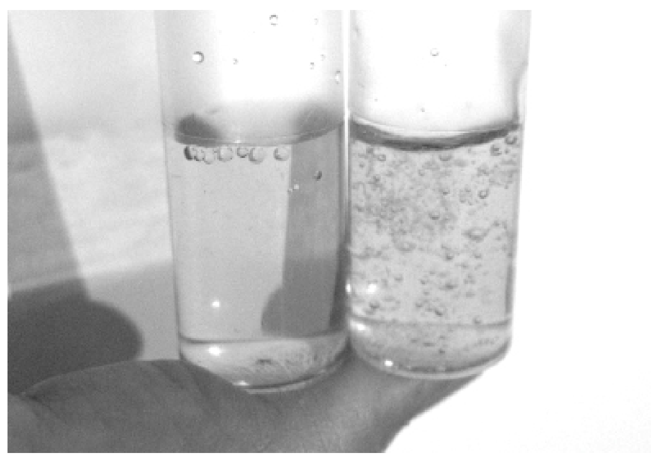


So for calculating this version of the recipes, I've used a pH indicator dye (the dye supplied with the Hach pH Test Kit) added to the Pemulen gels to determine their pH. Using both the color comparator that came with the kit and also comparing the color of the Pemulen gel with the color of a buffer solution at a know pH, I'm pretty sure that the values below are finally correct.

Here is the procedure I've been using to make 200mL of 2% Pemulen gels:

In a wide-mouth screw top jar, weigh out 4.0 grams of Pemulen TR2. Add 100mL of distilled or deionized water, cap the jar, and shake like crazy until the Pemulen powder is well dispersed. Periodically shake the jar. In about a half hour, you should have a cloudy-white, even suspension of swollen Pemulen particles making a grainy, very thick suspension.

Figure 2
pH 6.5, 1% Pemulen gel next to pH 6.5 buffer solution. Both are the same shade of yellow-green.



To the basic suspension add the following amounts of base(s) dissolved in water and shake vigorously. The final volume of the base/water mixture is 100mL, resulting in a final stock gel volume of 200mL. Shake periodically until everything looks pretty homogenous – there will be lots and lots of air bubbles in the gel. Once it's at this point, a good stirring with a spatula wouldn't be a bad idea.

The following table shows the amount of base(s) to add to the Pemulen suspension to get the desired pH gel. While both weight and volume measurements are listed, it is much better to measure triethanolamine (TEA) by weight, as it is so viscous that accurate measurement by volume is difficult.

[In those fun and care-fee days I've spent playing with the pH indicator dyes and Pemulen, I've noticed that the gels are not completely homogeneous until about 24 hours after mixing. The pH 6 gel is even more difficult to get evenly suspended – stir it periodically over a few days breaking up any thicker areas.]

*by Chris Stavroudis*

| Final pH | Grams TEA | Volume TEA | Grams 10% NaOH | Volume 10% NaOH | Volume water (to 100 ml) |
|---|---|---|---|---|---|
| 6.0 | 4.5 g | 4.0 ml | | | 96 ml |
| 6.5 | 5.0 g | 4.5 ml | | | 95 ml |
| 7.0 | 5.5 g | 4.9 ml | | | 95 ml |
| 7.5 | 9.0 g | 8.0 ml | | | 92 ml |
| 8.5 | 9.0 g | 8.0 ml | 6.2 g | 5.6 ml | 86ml |

Remember that the above recipes are for a stock 2% gel. Normally Pemulen gel is used at 1%. Any time you want to make up a Pemulen gel, dilute these stock gels 1:1 with water or other aqueous solutions. They can be diluted with water, pH-adjusted water (at the same pH as the gel), or they can be diluted with MCP components to add chelating agents and additional pH buffering.

So, you might wonder: What's the deal with TEA and why is (dilute) sodium hydroxide being added to the higher pH gels?

An excellent question. Let me explain…

TEA, triethanolamine, is an interesting material. Its pKa is 7.76 making it a buffer for aqueous solutions between pH 6.9 and 8.5. As a weak base, there are always two forms of the TEA floating around when it's mixed with water. There is the neutral triethanolamine molecule and the positively charged triethanolammonium ion (TEA-H+). The relative proportion of the neutral TEA and the TEA-H+ ion are determined by its pKa and the pH of the solution.

Something interesting happens when we use TEA to neutralize an acid like Pemulen (a modified poly(acrylic acid)). Let's look at a mixture of a fixed amount of hydrochloric acid (HCl) neutralized with TEA to different pH values.

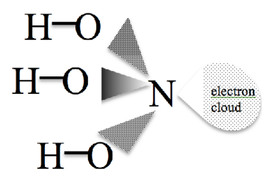
The following table shows the total amount of TEA and the percentages of molecular TEA and the TEA-H+ ion in that solution to adjust the pH of 100mL of a 0.1M solution of HCl  (0.84mL in 100mL water).

| **pH** | 6.0 | 6.5 | 7.0 | 7.5 | 8.0 | 8.5 |
|---|---|---|---|---|---|---|
| **Total TEA** | 1.52 g | 1.58 g | 1.75 g | 2.31 g | 4.09 g | 9.70 g |
| **% TEA** | 2% | 5% | 15% | 35% | 65% | 85% |
| **% TEA-H+** | 98% | 95% | 85% | 65% | 35% | 15% |

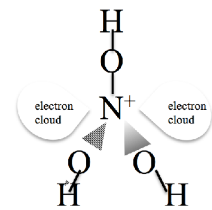
Remember that the amount of acid hasn't changed, but because TEA is a weak base with its pKa near the middle of our pH range, the effect is a bit surprising. So, to make the last solution above, we will have to use nearly 10% TEA to get that small amount of HCl to pH 8.5. And of that 10%, 85% will be in the molecular form.

Let's look at TEA a bit more closely.

TEA – triETHANOLamine. There are three ethanol groups attached to a nitrogen atom. In its molecular form, a good part of this molecule's nature comes from the alcoholic groups, and you will note that they all point in pretty much the same direction. Besides being a base, it has pretty strong similarity to other alcohols and works as a solvent pretty much like an alcohol.




triethanolamine




triethanolammonium ion

When the TEA is in it's ionic form, (TEA-H+), you will notice that the alcohol groups are spread out and pointing in different directions. This effectively reduces the alcoholic behavior, and the ion's interactions are much more strongly based on its charge anyway.

So, the reason I've added sodium hydroxide to the pH 8.0 and 8.5 Pemulen gel recipes is to keep the overall concentration of TEA down, and particularly, to keep the amount of the alcoholic, molecular TEA's concentration lower while retaining it's ability to function as a buffer.

Another nice thing about TEA as opposed to other bases is that it is organic (not the health food store kind) and is soluble in many organic solvents which helps with final clearance if doing a follow-up rinse with an organic solvent. (Remember, Pemulen gels are water-based so the primary rinsing is always with an aqueous system. pH adjusted water – dilute mixtures of acetic acid and ammonium hydroxide – is the rinse of choice, matching the pH of the rinse to the pH of the Pemulen gel.)

pH Test Kit, 4.0 - 10.0 pH, Model 17N
Hach Company
P.O. Box 389
Loveland, CO 80539
www.Hach.com

The calculations above were made in the MCP and checked/verified with: "CurTiPot", an Excel spreadsheet by I. G. R. Gutz, "pH and Acid–Base Titration Curves: Analysis and Simulation freeware," version 4.0 available from http://www2.iq.usp.br/docente/gutz/Curtipot_.html