A Tale of Two Citrates (actually four) *by Chris Stavroudis*

This has bugged me for some time: conservators buying triammonium citrate (or diammonium citrate or ammonium citrate) rather than purchasing citric acid and adjusting the pH by themselves.

Please read this carefully: ammonium hydroxide can be added to citric acid to get the **exact same materials in solution** as any of the other more expensive ammonium citrates. Once again: ammonium hydroxide can be added to citric acid to get the **exact same materials in solution** as any of the other more expensive ammonium citrates.

To control the ionic species in a citrate solution, one simply sets the solution pH. Using a calibrated pH meter is best, but in this case, pH papers will work well enough.

With citric acid one also has the option of using sodium hydroxide rather than ammonium hydroxide to get equivalent solutions, the difference being the counter ion – ammonium versus sodium ions. If the citric acid is adjusted to a given pH with sodium hydroxide or ammonium hydroxide, the two solutions will have the same combinations of citrate ions in solution at that given pH.

For example, when we dump triammonium citrate into water at, say 2%, the solution will have a pH around 7.4 or 7.5. (The MCP says the pH will be 7.5.)

At a pH of 7.5 the following species will be in solution at the following percentages:

$citrate^{3-}$ 92.63%
$H\text{-}citrate^{2-}$ 7.36%
$H_2\text{-}citrate^{-}$ 0.01%
and $H_3\text{-}citrate^{0}$ (free citric acid) practically 0%.
(This, again, from the MCP.)

Using 2% citric acid and titrating to 7.5 with one of the hydroxides will yield the exact same results.

The reasons for my being bugged about the use of an ammonium citrate salt rather than rolling your own are four fold: cost, variation of molecular weight, control, and change in properties with age.

First - cost

Here are the prices for the different forms of citrate. All are from Fisher Scientific, their Arcos Organics line and 98% pure (or better if there is no 98%). I've listed the cost per 250 grams and the cost per mole.

Triiammonium Citrate	\$65.30 / 250g	\$63.52/mole
Diammonium Citrate	\$20.85 / 250g	\$18.86/mole
Ammonium Citrate	\$38.05 / 250g	\$31.83/mole
Citric Acid (anhydrous)	\$14.30 / 250g	\$10.99/mole

Even better, let's do some online shopping. On Amazon.com (for example) we can purchase food grade citric acid for \$6.50/lb. That is:

Citric Acid (anhydrous, food grade)	\$3.57 / 250g	\$2.74/mole.

Second: - variation of molecular weight

Because the ammonium ion has a molecular weight of 17 there is a difference in the molecular weight between citric acid and tri-, di-, and ammonium citrate. If we use each of these expensive salts at 2%, the effective (i.e. citrate) concentrations will be (I've also listed the number of grams per 100 mL of each salt to make a 2% citrate solution):

Triiammonium Citrate	0.082M (2.5g/100mL)
Diammonium Citrate	0.088M (2.36 g/100mL)
Ammonium Citrate	0.096M (2.17g/100mL)
Citric Acid	0.104M (2g/100mL)

Third - control

Whenever possible, I like to know what I'm doing. So I like to know and control the pH of my cleaning solutions. If I dissolve triammonium citrate into water at the kind of concentrations we typically use, the pH will be around 7.4 or 7.5. But unless you are actually measuring the pH, you can't be sure, especially considering the evaporation issue discussed below.

(As a side note, citrate solutions are always chelating agents. They also function as buffers from pH 2.2 – 7.3. Above a pH of 7.3 you will want to add a separate pH buffer to keep the solution pH constant as the cleaning progresses.)

Fourth - change in properties with age

The powder form of the ammonium salts have a weak ammonia smell. This tells us that ammonium ions are evaporating away and being replaced with hydrogen ions on the citrate salt. One published recommendation is to replace the ammonium salts of citric acid after two years when kept dry and tightly sealed.

Once your formerly tightly sealed and dry powder is dissolved in water, the ammonia evaporates more readily. And as it evaporates, the pH will go down. To what degree does this change the pH of the solution? I don't know, but it will decrease. The longer the solution is left sitting out uncapped, the more the composition will change; the more the pH will decrease.

However, if you make your citrate solution with sodium as the counter ion by setting the pH with sodium hydroxide, the pH will not change at all as sodium ions are not volatile. (Hence the use of sodium salts in the MCP solutions. They last forever.)

I hope I have made the case for making your own citrate solutions rather than squandering your money (or your institution's money) on materials that will change pH with age and not give you the kind of control of your cleaning solution's composition you probably thought you had.

[Should you want to use a pH meter to make your own solutions and are not familiar with using one, you might want to view the GCI video prepared for the CAPS workshops, "Calibrating Conventional pH Meters" at youtube.com/watch?v=9Ktlz0uw6kw]

I feel so much better now.