Applications Note

Insight on Color Vol. 15, No. 5

APHA Q & A

HunterLab Technical Support representatives probably answer more questions concerning the APHA color index than any other color scale or index. This *Applications Note* is designed to answer some of the most frequently asked questions concerning this index. For more basic information concerning the APHA index, refer to the November 16-30, 1996 *Applications Note* entitled "APHA."

• What is the Formula for APHA?

There is no published formula for APHA. The ASTM method on APHA (D1209) describes only visual evaluation of APHA, where samples are visually compared to known standards. While instrumental determination of APHA is allowed by D1209 and D5386, no formula is prescribed by either method.

In order to allow you to determine APHA with your instrument, HunterLab uses a correlation it developed by comparing solutions of known APHA values to instrumental measurements. Since APHA is a yellowness scale, HunterLab based its correlation on yellowness index (YI E313) values. This correlation was optimized for each of its instruments that is capable of measuring APHA. These correlations are proprietary and apply only to HunterLab instruments.

• Why Doesn't My APHA Value Make Sense?

If your APHA value is negative or much lower than you expected, your sample may be off-hue.

The APHA index was originally designed to evaluate the color of near-colorless waste water by visual comparison of the water to dilutions of a platinum-cobalt (PtCo) stock solution. PtCo solutions are yellow, as were the waste water samples of interest. While other types of samples, such as liquid chemicals, petrochemicals, plastics, and pharmaceuticals, are now evaluated using the APHA index as well, the expectation that the liquids measured would be of a yellow hue similar to PtCo solutions has not changed. APHA is a yellowness index, and cannot be used in evaluating liquids of other hues, such as blue or red. Even those liquids that appear colorless, yet when measured by a spectrophotometer that is more sensitive than the human eye are actually determined to be of a hue other than yellow, should not be evaluated using the APHA index. Off-hue samples can yield negative or meaningless APHA values.

ASTM D1209 states that the method is "applicable only to materials in which the color-producing bodies present have light absorption characteristics nearly identical with those of the platinum-cobalt color standards used." It later directs, "If, owing to differences in hue between the specimen and the standards, a definite match cannot be obtained, report the range over which an apparent match is obtained, and report the material as 'off-hue'."

If your APHA value is very high, your sample may be of the correct yellow hue, but more saturated than even the APHA 500 PtCo stock solution that marks the upper limit of the scale. In this case, you might be better off evaluating your sample using the Gardner Index, which is designed for liquids that are darker yellow or browner than PtCo solutions, or you could use a tristimulus color scale like CIEL*a*b* or Hunter L, a, b.

Examine the values in the table below. The PtCo 500 ppm stock solution is still very light (L = 97.35 on a scale of 0 to 100) and not that saturated in b (yellowness; 14.39). It is also slightly green (small negative a). Many, many yellow solutions will be more saturated than the stock solution and will not be well-described by the APHA index.

ppm PtCo	APHA-10mm	L	a	b
0 (distilled water)	0	100.00	0.00	0.00
500	500	97.35	-1.98	14.39

Values from ColorQuest II Sphere, C/2°.

For readings that don't match expectations, it is also possible that your sample is hazy, and the light scattering caused by suspended solids is affecting your measurements. ASTM D1209 section 7.1 states that you should "pass the specimen though a filter if it has any visible turbidity." In other words, steps should be taken to ensure that the sample is clear and non-scattering, or the APHA evaluation will be biased.

Based on HunterLab's years of experience, a measured haze value above 5% is visually hazy. The sample should be labeled as such or filtered before measurement to make it clear.

• Why Do My APHA Values Seem to Vary So Much?

Unless there is a problem with your instrument or measurement method, the variation is probably not as significant as you think.

Table 4 in ASTM D1209 reports precision obtained in a study of APHA values assigned visually. At APHA 25, the repeatability for a single operator was determined to be 3 units. At APHA 475, repeatability was 16 units. Reproducibility among 10 analysts was 10 units at APHA 25 and 49 units at APHA 475. The difference is because it is easier to visually determine differences between similar solutions in the lower APHA ranges than in the higher ranges. A similar phenomenon is observed instrumentally.

According to ASTM D5386, single operator repeatability when determining APHA instrumentally is within 0.9 unit under APHA 30 (corresponding with ASTM D5386's direction to report APHA to the nearest whole unit under APHA 30), and multiple operator reproducibility is within 2 units, to a 95% confidence level. This means that if your instrument is operating properly and your methodology is sound, one operator should be able to make multiple measurements of the same solution that match within 0.9 APHA unit and multiple operators should be able to make measurements of the same solution that match to within 2 APHA units <u>when reading solutions with APHA values (ppm concentrations) below 30</u>. If you are unable to measure to within this repeatability, you should consider that either your instrument or your method may be faulty.

Why is a one to two unit variation in APHA allowable when much smaller variations in tristimulus color values are achievable? It's due to the math.

Small variations in tristimulus values (such XYZ or L, a, b) normally occur in instrumental measurements. Remember, though, that APHA is determined by a correlation to YI E313, which is a calculation using X, Y, and Z. [$YI\,E313 = \frac{100\left(C_x X - C_Z Z\right)}{Y}$; see your User's Manual for more information about this calculation]. Small variations in X, Y, and Z yield larger variations in YI (and therefore APHA) when plugged into this formula, due to the multiplication and division. Therefore, an instrument range (such as 2 units) that seems very large when applied to a tristimulus value (such as X or L), is not as extreme when applied to APHA.

To check the repeatability of your instrument on a known, stable standard, run the repeatability test described in your user's manual.

As far as methodology, ensure that you are always using the same size of sample cell when making APHA measurements, and that the APHA index selected in your software matches the cell size in use. For example, if you measure your solutions in a transmission cell with a path length of 20 mm, be sure that your software lists "APHA-20 mm" as the selected index. You should be consistent with both the cell size used and the cell size indicated in the software or else your measurements will not be comparable. Make sure all samples are prepared the same way and are measured at the same temperature, after the same amount of mixing, etc.

• How Close Should My Instrument Read to the Known Values of the Stock Standards?

Distilled water should yield an APHA value of zero to within a unit or two. A difference less than 2 units is not visually significant at this level, according to ASTM D1209.

The 500 ppm PtCo stock solution as purchased should yield an APHA value of 500 to within twenty units or so.

Why aren't they closer? Additive error.

Dilutions of the stock solution theoretically have APHA values equivalent to their ppm concentrations. However, the dilution itself introduces some error into the equation due to calibration error in the glassware (both the pipette and the volumetric flask), as well as operator imperfections. Add to that the instrumental variations described in the last question, and you'll see why the raw numbers come out a little further from the "known" than you might expect.

When in doubt as to whether your numbers are acceptable, run the diagnostic tests described for your instrument (such as the green tile check and the didymium filter test) in its user's manual to ensure that your instrument is in good working order.

• Where Can I Get APHA Standards?

The APHA zero (0) standard is distilled water, which should also be used as a blank during the standardization process.

The APHA platinum-cobalt 500 ppm stock solution is available from Fisher Scientific at www.fishersci.com. Search on "platinum cobalt." Intermediate standards can then be prepared from the stock as described in ASTM D1209.

Pre-mixed and certified intermediate standards can be purchased from RICCA Chemical, www.riccachemical.com. Search on "APHA."

• What are Some Good References on APHA?

"APHA," HunterLab *Applications Note*, November 16-30, 1996.

Designation D1209-00, "Standard Test Method for Color of Clear Liquids (Platinum-Cobalt Scale)," ASTM International, West Conshohocken, Pennsylvania, 2000.

Designation D5386-04, "Standard Test Method for Color of Liquids Using Tristimulus Colorimetry," ASTM International, West Conshohocken, Pennsylvania, 2004.

Hazen, A., "A New Color Standard For Natural Waters," *American Chemist Journal* (14:300), 1892.

Hazen, A., "The Measurement of the Colors of Natural Waters," *American Chemist Journal* (18:264), 1896.

ISO 2211, "Liquid Chemical Products -- Measurement of Colour in Hazen Units (Platinum-Cobalt Scale)," International Organization for Standardization, Geneva, Switzerland, 1973.

ISO 6271, "Clear Liquids -- Estimation of Colour by the Platinum-Cobalt Scale," International Organization for Standardization, Geneva, Switzerland, 1997.

Method 110.2, "Color - Colorimetric - Platinum-Cobalt," *Methods for the Chemical Analysis of Water and Wastes*, U.S. Environmental Protection Agency, Washington, D.C., 1983.

Method 2120, "Color by Visual Comparison," *Standard Methods for the Examination of Water and Wastewater*, American Public Health Association, Washington, D.C., 1998.

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