

## Applications Note

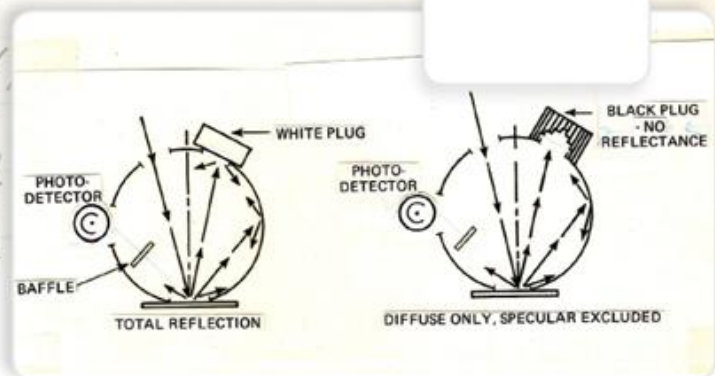
$$\Delta = 2t + \frac{\lambda}{2} \quad (\text{must equal a whole number of } \lambda \text{ for a bright fringe or})$$

$$n\lambda = 2t + \frac{\lambda}{2}$$

$$t = \frac{n\lambda - \frac{\lambda}{2}}{2} = \frac{\lambda}{2} \left( n - \frac{1}{2} \right)$$

$$\frac{D^2}{4} = 2s \left[ \frac{\lambda}{2} \left( n - \frac{1}{2} \right) \right]$$

AN 1001



# Measuring APHA/Pt-co/Hazen Value of Liquids

## Abstract

As the chemical, petroleum, plastic, and pharmaceutical industries have grown, they developed criteria to judge the color of their products. Descriptions of slightly colored clear liquids were based on visual comparisons to dilutions of platinum-cobalt (Pt-Co) stock solutions. The whiter the solution, the more desirable the purity of the product and the more dilute the stock solution. Related to this, A Hazen documented in 1892, the American Public Health Association (APHA) color index. APHA ranges from near zero for clean water and up to 500 for waste water discolored by undesirable impurities and organic materials.

This application note considers the use of the APHA index to measure the color of liquids.

***“The purer the solution, the more visually clear and the closer to zero the APHA index.”***



## What is APHA?

Prior to the 1890s, descriptions of slightly colored clear liquids were based on the concept of "water white." There were many interpretations of purity and it became necessary to have a more specific method for describing the color of waste water. In 1892, chemist A. Hazen described the American Public Health Association (APHA) color index. The index was initially used to evaluate the color of waste water by comparison with dilutions of a platinum-cobalt (PtCo) stock solution. The index was used as an indication of purity, as the color of waste water is produced by undesirable impurities and organic materials.

As the chemical, petroleum, plastic, and pharmaceutical industries grew, they also developed the need to measure the color of their products, some of which were similar in hue to the PtCo solutions in A. Hazen's method. In many cases, the color of their products was an indication of purity, the level of refinement, or the cleanliness of the product container. In 1952, ASTM Test Method D1209 was adopted using a PtCo scale similar to that described by A. Hazen.

APHA is a single number yellowness index where each APHA unit is based on a dilution of the 500 ppm stock solution of PtCo. A detailed description of solution preparation and measurement procedures may be found in ASTM D1209 and ASTM D5386.

ASTM Designation D5386, "Standard Test Method for Color of Liquids Using Tristimulus Colorimetry," describes how color measurement instruments correlate to the physical APHA/PtCo color standards described in ASTM D1209.

While instrumental determination of APHA is allowed by D1209 and D5386, no formula is prescribed by either method. For APHA, HunterLab uses a custom correlation based on known APHA values compared to instrumental measurements. Please note that these correlations apply only to HunterLab instruments able to read in Transmittance (2° Standard Observer/ Illuminant C).

## 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.

## Preparation of APHA standards

The APHA zero (0) standard is physically represented by distilled water (for water-based products, toluene or benzene for resins, and mineral oil for oils), can be used as a blank during the standardization process. Pre-mixed and certified intermediate standards can be purchased from RICCA Chemical ([www.riccachemical.com](http://www.riccachemical.com)). The APHA platinum-cobalt 500 ppm stock solution is available from Fisher Scientific. Intermediate standards can also be prepared from the stock as described in ASTM D1209.

## Sample Preparation

This index is often used by the water processing, chemical, petroleum, plastic, and pharmaceutical industries for measurement of color in products that are nearly clear.

All APHA samples are to be prepared the same way and measured at the same temperature, after the same amount of mixing, etc.

In order for the APHA index to be meaningful, samples must be clear or slightly colored liquids that are similar in hue to the PtCo standards. In addition, steps should be taken to ensure that samples are 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.

APHA Method Parameters	
Mode	TTRAN - Total Transmittance
Illuminant/Standard Observer	C/2°
Color Scale	APHA Index
Pathlength	Any
Standards	Zero Standard, intermediate dilutions prepared to ASTM D1209
Sample Preparation Parameters	Temperature, Mixing Time, Filtering

If an APHA value is negative or much lower than expected, the sample may be off hue. If an APHA value is very high, the sample may be of the correct yellow hue, but more saturated than the upper limit of the stock solution. In this case, the Gardner Index, which is designed for liquids that are darker yellow or brown may be used. Alternately a tristimulus color scale like CIE L\*a\*b\* or Hunter L, a, b could be used.

## APHA Sample Measurement

The instrument must be standardized in Total Transmittance (TTRAN) mode using a transmittance cell of the same path length as will be used in the measurement. Samples may be measured using any size cell, and the calculations performed are specific to the cell size. Consistency with both the cell size used and the cell size indicated in the software is important or the measurements will not be comparable. For example, if a transmittance cell with a path length of 20 mm is used this should also be selected in the software as APHA-20 mm.

## Method Precision

Precision of the visual method is non-linear to the increase in APHA value. For example, repeatability for a single operator at an APHA value of 25, is determined to be 3 units. At an APHA 475, repeatability was 16 units. Experimental reproducibility among 10 analysts is 10 units at APHA 25 and 49 units at APHA 475. A similar phenomenon is observed instrumentally. Single operator repeatability when determining APHA instrumentally is within 0.9 unit under APHA 30 and multiple operator reproducibility is within 2 units, to a 95 % confidence level.

## 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 yellow solutions will be more saturated than the stock solution and will not be well-described by the APHA index.

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

For readings that do not 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 through 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 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 three units. At APHA 475, repeatability was sixteen units. Reproducibility among ten 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 two 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 when reading solutions with APHA values (ppm concentrations) below 30. If you are unable to measure 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 is 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. 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 two 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, the same size sample cell must be used 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 transmittance cell with a path length of 20 mm, be sure that your software lists "APHA-20 mm" as the selected index. 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.

Cell size must be consistent 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 of 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.

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 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 will 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.

### **Conclusion**

The APHA/Pt-Co/Hazen Color Index is useful for measuring the trace yellowness associated with the degree of contamination or processing quality of transparent liquid samples that are near-colorless.

## References

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

APHA 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.

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

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

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

## About HunterLab

HunterLab, the first name in color measurement, provides ruggedly dependable, consistently accurate, and cost effective color measurement solutions. With over 6 decades of experience in more than 65 countries, HunterLab applies leading edge technology to measure and communicate color simply and effectively. The company offers both diffuse/8° and a complete line of true 45°/0° optical geometry instruments in portable, bench-top and production in-line configurations.

HunterLab, the world's true measure of color.

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12/2023

