or, for SDS testing:

$$\text{SDS-DHAA, } \mu\text{g/L as DCAA} = \text{SDS-DHAA, } \mu\text{M} \times 129$$

The definitions given in 5710 A-C also are valid. For example, if the initial concentration of disinfectant byproducts (DHAAs, for instance) is zero or insignificant, then:

$$\text{DHAAFP} = \text{DHAA}_7.$$

Alternatively, if there is a significant concentration of initial byproduct, then:

$$\Delta\text{DHAAFP} = \text{DHAA}_7 - \text{DHAA}_0.$$

### 6. Quality Control

The quality control practices considered to be an integral part of each method are summarized in Table 5020:1.

See 5710 B.6 for check on reagent purity or as a check on analytical precision and control by using a reaction with a pure, organic compound under more stable, standardized conditions.

The test detailed in 5710 B.6 applies only to THM formation using excess free chlorination conditions.

### 7. Precision and Bias

Precision and bias measurements depend, in part, on the analytical procedure used to measure each specific disinfectant byproduct concentration. These measurements also depend on compound properties such as stability toward oxidation and biodegradation. In general, however, formation potential reactions should be reproducible to the extent indicated in 5710 B for chlorination reactions. SDS-type reactions (5710 C) are not, however, be expected to be as accurate or as precise, although such reactions should predict distribution system concentrations reasonably well.

### References

1. Method 551. Methods for the determination of organic compounds in drinking water, Supplement I. Washington DC: Office of Research and Development, U.S. Environmental Protection Agency; 1990.
2. Methods 552 and 552.1. Methods for the determination of organic compounds in drinking water, Supplements I and II. Washington DC: Office of Research and Development, U.S. Environmental Protection Agency; 1990.
3. Flesch J, Fair P. The analysis of cyanogen chloride in drinking water. Proceedings of the 16th Annual AWWA Water Quality Technology Conference;1988 Nov. 13–17; St. Louis (MO); Denver (CO): American Water Works Association; 1988; p. 465.



# 5910

# UV-Absorbing Organic Constituents

Approved by Standard Methods Committee, 2013. Editorial revisions, 2021. Joint Task Group: Suzanne M. Teague (chair), Ali Haghani, Edward W.D Huffman, Jr., Louis A. Kaplan, Ilke E. McAliley, Mark A. Schlautman

## 5910 A. Introduction

### 1. Applications

Because some organic compounds commonly found in water and wastewater (e.g., lignin, tannin, humic substances, and various aromatic compounds) strongly absorb ultraviolet (UV) radiation, UV absorption is a useful surrogate measure of such constituents in fresh waters,[1–3] salt waters,[4–6] and wastewater.[7,8] Strong correlations may exist between UV absorption and organic carbon content, color, and precursors of trihalomethanes (THMs) and other disinfection byproducts.[9,10] UV absorption also has been used to monitor industrial wastewater effluents[11] and to evaluate the effectiveness of coagulation,[10] carbon adsorption,[12–14] and other water treatment processes that remove organics.[10,15] Specific absorption (the ratio of UV absorption to organic carbon concentration) has been used to characterize natural organic matter.[10,16–18] Some regulatory programs include specific ultraviolet absorbance (SUVA)—a ratio of UV absorption to dissolved organic carbon concentration—to help control disinfection byproducts.

Although UV absorption can be used to detect certain individual organic contaminants after separation (e.g., by HPLC), as described in Part 6000, the method described here is not suitable for detecting trace concentrations of individual chemicals. Rather, it provides an *indication* of the aggregate concentration of UV-absorbing organic constituents.

### References

1. Dobbs RA, Wise RH, Dean RB. The use of ultra-violet absorbance for monitoring the total organic carbon of water and wastewater. Water Res. 1972;6(10):1173–1180.
2. Wilson AL. Determination of fulvic acids in water. J Appl Chem. 1959;9(10):501–510.
3. Cooper WJ,Young JC. Chemical non-specific organic analysis. In: Minear RA, Keith L, eds. Water analysis, Vol. 3. New York (NY): Academic Press; 1984.

4. Ogura N, Hanya T. Ultra-violet absorbance of the seawater, in relation to organic and inorganic matters. Int J Oceanol Limnol. 1968;1:91.
5. Ogura N, Hanya T. Ultra-violet absorbance as an index of the pollution of seawater. J Water Pollut Control Fed. 1968;40(3 pt 1):464–467.
6. Foster P, Morris AW. The use of ultra-violet absorption measurements for the estimation of organic pollution in inshore sea waters. Water Res. 1971;5(1):19–27.
7. Bunch RL, Barth EF, Ettinger MB. Organic materials in secondary effluents. J Water Pollut Control Fed. 1961;33(2):122–126.
8. Mrkva M. Use of ultra-violet spectrophotometry in the determination of organic impurities in sewage. Wasserwirtsch Wassertech. 1971;21:280.
9. Singer PC, Barry III JJ, Palen GM, Scrivner AE. Trihalomethane formation in North Carolina drinking waters. J Amer Water Works Assoc. 1981;73(8):392–401.
10. Edzwald JK, Becker WC, Wattier KL. Surrogate parameters for monitoring organic matter and THM precursors. J Amer Water Works Assoc. 1985;77(4):122–132.
11. Bramer HC, Walsh MJ, Caruso SC. Instrument for monitoring trace organic compounds in water. Water Sewage Works 1966;113(88): 275–278.
12. Bishop DF, Marshall LS, O'Farrell TP, Dean RB, O'Connor B, Dobbs RA, Griggs SH, Villiers RV. Studies on activated carbon treatment. J Water Pollut Control Fed. 1967;39(2):188–203.
13. Sontheimer HN, Heilker E, Jekel MR, Nolte H, Vollmer FH. The Mulheim process. J Amer Water Works Assoc. 1978;70(7):393–396.
14. Summers RS, Cummings L, DeMarco J, Hartman DJ, Metz D, Howe EW, MacLeod B, Simpson M. Standardized protocol for the evaluation of GAC; No. 90615. Denver (CO): AWWA Research Foundation, American Water Works Association; 1992.
15. Krasner S, Westerhoff P, Chen B, Rittmann B, Nam S, Amy G. Impact of wastewater treatment processes on organic carbon, organic nitrogen and DBP precursors in effluent organic matter. Environ Sci Technol. 2009;43(8):2911–2918.
16. Thurman EM. Organic geochemistry of natural waters. Dordrecht, Netherlands: Martinus Nijhoff/Dr. W. Junk Publishers; 1985.
17. Owen DM, Amy GL, Chowdhury ZK. Characterization of natural organic matter and its relationship to treatability; No. 90631. Denver (CO): AWWA Research Foundation, American Water Works Association; 1993.
18. Weishaar JL, Aiken GR, Bergamaschi BA, Fram MS, Fujii R, Mopper K. Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. Environ Sci Technol. 2003;37(20):4702–4708.

# 5910 B. Ultraviolet Absorption Method

## 1. General Discussion

*a. Principle:* UV-absorbing organics in a sample absorb UV light in proportion to their concentration. Filter the sample to control particle-related variations in UV absorption. The sample's pH can be adjusted before filtration, but certain organic constituents (e.g., humic substances) may be lost to filters, suspended particles, or vessel walls at lower pH values.[1] When filtering samples for SUVA determination, do not adjust the pH before filtration.

Historically, UV absorption has been measured at 253.7 nm (often rounded to 254 nm), but the choice of wavelength is arbitrary. Experienced analysts may choose a wavelength that minimizes interferences while maximizing absorption by the compounds of interest. If using a wavelength other than 253.7 nm, state that wavelength when reporting results.

*b. Interferences:* The primary interferences in UV-absorption measurements are from colloidal particles and UV-absorbing inorganics—notably iron, nitrate, nitrite, and bromide. Certain oxidants and reducing agents (e.g., ozone, chlorate, chlorite, chloramines, and thiosulfate) also absorb ultraviolet light at 253.7 nm. Many natural waters and waters processed in drinking water treatment plants have been shown to be free of these interferences.

Evaluate and correct for UV absorption contributed by specific interfering substances. If cumulative corrections exceed 10% of the total absorption, select another wavelength and/or method. Also, UV absorption by organic matter may vary when pH is below 4 or above 10, so avoid these ranges.[2]

A UV absorption scan from 200 to 400 nm can be used to determine the presence of interferences. Typical absorption scans of natural organic matter are featureless curves of increasing absorption with decreasing wavelength. Sharp peaks or irregularities in the scan may indicate inorganic interferences. Because many organic compounds in water and wastewater (e.g., carboxylic acids and carbohydrates) do not absorb significantly in UV wavelengths, correlate UV absorption to dissolved organic carbon (DOC) or soluble chemical oxygen demand (COD). However, use such correlations with care because they may vary from water to water, seasonally or during storms on the same water, and between raw and treated waters. In addition, chemical oxidation of the organic material (e.g., ozonation, chlorination) may reduce UV absorption without removing organics and thus may change correlations. Because UV absorption and correlations with UV absorption are site-specific, they may not be comparable from one water source to another.

*c. Minimum detectable concentration:* The minimum detectable concentration cannot be determined rigorously because this is a nonspecific measurement. Also, the minimum detectable concentration of a particular constituent depends on the relationship among UV absorption, the desired characteristic (e.g., trihalomethane formation potential or DOC), and any interfering substances. For precise measurement, select cell path length to provide a minimum absorbance of approximately 0.005 and a maximum absorbance of approximately 0.950 $cm^{-1}$. Dilute high-strength samples to fall within the determined range.

*d. Sampling and storage:* Collect samples in amber glass bottles that have been washed, thoroughly rinsed with organic-free water, and baked at 400 °C for at least 1 hour. Seal with PTFE-lined caps. If individual PTFE septa are used, wash and rinse thoroughly with organic-free water, wrap in foil, and bake at 100 °C for 1 hour or soak the septa in 10% sodium persulfate for 1 hour at 60 °C and rinse thoroughly with organic-free water.[3] Precleaned containers from commercial vendors may also be available. Store samples at <6 °C; samples requiring shipping should be transported on ice. Adjust the pH (if needed) and analyze within 48 h.

Samples may be filtered in the field. If these samples require pH adjustment, make the adjustment before filtration.

## 2. Apparatus

*a. Spectrophotometer*, for use between 200 and 400 nm with matched quartz cells providing a light path of 1 cm. For low-absorbance samples, use a path length of 5 or 10 cm. A scanning spectrophotometer is useful.

*b. Filter:* Use a glass fiber filter without organic binder with a nominal 1 ± 0.5 µm particle retention or use PTFE, polycarbonate, or silver filters. Polyethersulfone (PES) or hydrophilic polypropylene (HPP) filters are also recommended.[4] Other filters that neither sorb UV-absorbing organics of interest nor leach interfering substances (e.g., nitrate or organics) into the water may be used, especially if colloidal matter must be removed. The specific filter used should be reported with the data. Practical filter diameters are 2.2 to 4.7 cm, although this may vary. Prerinse the filter with a sample of organic-free water to remove soluble impurities. As an option, glass fiber filters may be combusted at high temperatures (450 to 500 °C for at least 6 h) before rinsing. If alternate separation techniques, filters, or filter preparations are used, demonstrate that equivalent results are produced.

Filter pore size will influence test results, especially in raw waters. When filtering samples for SUVA determination, check the applicable regulatory constraints to see if a filter with an absolute pore size of 0.45 µm is required, because glass fiber filters generally do not meet this requirement. For highly turbid samples, pre-filters (including glass fiber) may be used to remove interferences and minimize clogging of 0.45-µm filters.[5]

*c. Filter assembly, g*lass, PTFE, stainless steel or other material that neither sorbs UV-absorbing organics nor leaches interfering substances, capable of holding the selected filters. Polypropylene syringes with syringe-type filter holders or peristaltic pumps with in-line filter holders may be used as an alternative to vacuum filtration.[3]

## 3. Reagents

*a. Organic-free water:* Reagent water containing less than 0.010 $cm^{-1}$ of UV-absorbing compounds. For optimum performance, reagent water of less than 0.0045 $cm^{-1}$ is recommended.

*b. Hydrochloric acid* (HCl) (optional), 0.1 M.

*c. Sodium hydroxide* (NaOH) (optional), 0.1 M.

*d. Phosphate buffer* (optional): Dissolve 2.5 g dried anhydrous $KH_2PO_4$ and 4.5 g dried anhydrous $Na_2HPO_4$ in 800 mL organic-free water. The pH should be close to 7; verify that it is between 6 and 8 and then dilute to 1 L with organic-free water. Store in a brown glass bottle at 4 °C and re-prepare when the pH falls out of the 6 to 8 range or if microbial growth is observed. Commercially prepared reagent is also available.

*e. Organic carbon stock solution:* Dissolve 2.1254 g anhydrous primary-standard grade potassium biphthalate, $C_8H_5KO_4$ [also known as potassium hydrogen phthalate (KHP)], in organic-free water and dilute to 1000 mL (1.00 mL = 1.00 mg carbon). Commercially prepared standards are also available.

## 4. Procedure

*a. Sample volume:* Select a sample volume based on cell path length, volume needed for filter rinsing, or dilution required to produce a UV absorbance between 0.005 and 0.950 $cm^{-1}$. For most applications, a 50- to 125-mL sample is adequate.

*b. Sample preparation:* Wash the filter and filter assembly by passing a sufficient volume of organic-free water through the filter (to waste) to yield a filter blank of <0.010 $cm^{-1}$. For specific applications and correlations, the sample pH may be adjusted with HCl or NaOH. In poorly buffered samples, an appropriate non-UV absorbing buffer system (e.g., a phosphate buffer) may be used. Add enough buffer to maintain a constant pH during analysis. Take care to avoid precipitate formation during pH adjustment. Ideally, the volume of buffer added should be <5% of the sample volume. If 5% is exceeded, apply an appropriate dilution correction factor. UV absorbance of fulvic acid solutions apparently remains constant between pH 4 and 10.[2] Do not adjust the pH of the original sample when analyzing samples for SUVA. Record the sample pH value used with recorded absorbance. Once the sample pH has been measured or adjusted (if needed), rinse the filter with the sample and discard the filtrate. If using 4.7-cm PES or HPP filters, they can be adequately rinsed with 25 mL sample to bind sites that may adsorb UV-absorbing constituents.[4] This volume is also adequate for glass fiber filters. Smaller filters may require proportionately less. If other filter materials are used, confirm whether these volumes are adequate or if more is needed. Analyze the subsequent filtrate as a sample. Prepare an organic-free water filter blank and the sample in an identical manner.

*c. Spectrophotometric measurement:* Let the spectrophotometer equilibrate according to the manufacturer's instructions. Set the wavelength to 253.7 nm (or 254 nm) and adjust spectrophotometer to read zero absorbance with organic-free water. Measure the UV absorbance of at least 2 filtered portions of sample at room temperature.

## 5. Calculation

Report mean UV absorption in units of $cm^{-1}$ using the following notation. To report units in $m^{-1}$, multiply the equation by one hundred.

$$UV_{\lambda}^{pH} = \left[\frac{\bar{A}}{b}\right]D$$

where:

$UV_{\lambda}^{pH}$ = mean UV absorption, $cm^{-1}$ (subscript denotes wavelength used, nm, and superscript denotes pH used if other than 7.0),
$\bar{A}$ = mean absorbance measured,
$b$ = cell path length (cm), and
$D$ = dilution factor resulting from pH adjustment and/or dilution with organic-free water.

$$D = \frac{\text{final sample volume}}{\text{initial sample volume}}$$

Correct results for absorption contributed by known interfering substances. If UV absorption contributed by interfering substances exceeds 10% of total UV absorption, do not use UV absorption at 253.7 nm as an indicator of organics. Record the pH if other than 7.

## 6. Quality Control

*a. Replicate measurements:* Use at least 2 portions of filtered sample.

*b. Duplicate analyses:* Analyze every 10th sample in duplicate (i.e., duplicating the entire procedure) to assess method precision. Calculate relative percent difference (RPD) for duplicate analyses ($D_1$ and $D_2$, where each duplicate is the average of replicate readings) using the formula below:

$$RPD = \frac{|D_1 - D_2|}{(D_1 + D_2)/2} \times 100$$

For UV values >0.045 $cm^{-1}$, the RPD limit is ≤10%. For UV values <0.045 $cm^{-1}$, the RPD limit is <20%.

*c. Baseline absorbance:* Check the system baseline UV absorbance after every 10 samples by measuring the absorbance of an organic-free water blank. A non-zero absorbance reading for the blank may indicate the need for cell cleaning, problems with the reference cell if a dual-beam instrument is being used, or a variation in spectrophotometer response caused by heating or power fluctuations over time.

*d. Filter blanks:* With each batch of filtered samples, analyze a portion of organic-free water that has been passed through a rinsed filter. The volume of organic-free water should be equal to the volume of a sample. Filter blanks should read <0.010 $cm^{-1}$; if not, larger rinsing volumes may be required. Also, the appropriateness of the filter and the filtering apparatus may need to be evaluated.

*e. Filtrate turbidity check (optional):* If a UV value or calculated SUVA value seems unusually high for a specific sample source, check filtrate turbidity. Turbidities greater than 0.5 NTU indicate that the sample may require pretreatment steps, such as centrifugation.[5]

*f. Spectrophotometer check:* Difficulties in comparing UV absorption data from different spectrophotometers have been reported. KHP standards were prepared in pH 7, phosphate-buffered (5910 B.3*d*) reagent water without acidification and analyzed in 5 laboratories. Results suggest acceptable precision (Table 5910:1). These data also are useful for checking spectrophotometer results with KHP standards commonly used for TOC and COD analysis. A correlation equation for this 40-sample data set is:

$$UV_{254} = 0.0144KHP + 0.0018$$

with correlation coefficient ($r^2$) = 0.987, $UV_{254}$ expressed in $cm^{-1}$, and KHP expressed as mg/L as C.

This equation can help verify spectrophotometer performance. For example, if a set of $UV_{254}$ analyses is performed and results are in the 0.010 range, prepare a KHP standard of 0.5 mg/L as C. The projected $UV_{254}$ of this KHP standard would be 0.009 $cm^{-1}$. If measured $UV_{254}$ is outside the 13% relative standard deviation (RSD) of 0.009 $cm^{-1}$ (using the RSD in Table 5910:1 as a guide), the spectrophotometer may be suspect and require maintenance. The correlation between $UV_{254}$ and KHP standards is presented solely as a useful means of verifying spectrophotometer performance. Prepare at least one KHP standard in the range of interest and measure it with each analytical run. Commercially prepared standards may also be available for this purpose.

## 7. Precision and Bias

Table 5910:1 shows interlaboratory precision data for 40 KHP samples. The RSD ranged from 9.38 to 12.8%.

Single-operator precision data are presented in Table 5910:2 for fulvic acid solutions.[6] The RSD ranged from 0.9% to 6%. Because UV absorption is an aggregate measure of organic carbon, true standards are unavailable and bias cannot be determined.

The precision of analyses by this method was determined under the Information Collection Rule.[7] Precision was determined as RPD for duplicate analyses and was calculated only when both analyses in the duplicate pair showed concentrations at, or greater than, the ICR minimum reporting level (MRL = 0.009 $cm^{-1}$). Results were as follows:[8]

| Data Quality Variable | Percentile | | | | | |
|---|---|---|---|---|---|---|
| | N | 10 | 25 | 50 (median) | 75 | 90 |
| Precision (RPD) | 33306[a] | 0.0 | 0.0 | 0.0 | 2.2 | 4.9 |

[a] 2744 excluded—both samples less than MRL.
Note: Median sample result was 0.040 $cm^{-1}$.

Table 5910:1. Precision of UV Analyses and Correlation to KHP Samples

| Analysis | $UV_{254}$ Result for Given KHP Sample Concentration ($cm^{-1}$)[a] | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 0.54 | 0.93 | 1.79 | 4.87 | 9.61 | 25.0 | 50.0 | 100.0 |
| Laboratory 1 | 0.008 | 0.015 | 0.034 | 0.079 | 0.158 | 0.323 | 0.638 | 1.282 |
| Laboratory 2 | 0.009 | 0.016 | 0.026 | 0.070 | 0.134 | 0.401 | 0.803 | 1.612 |
| Laboratory 3 | 0.010 | 0.017 | 0.027 | 0.081 | 0.161 | 0.353 | 0.695 | 1.343 |
| Laboratory 4 | 0.007 | 0.020 | 0.033 | 0.070 | 0.132 | 0.319 | 0.750 | 1.590 |
| Laboratory 5 | 0.009 | 0.018 | 0.030 | 0.087 | 0.140 | 0.394 | 0.643 | 1.447 |
| Mean | 0.0086 | 0.0172 | 0.0300 | 0.0774 | 0.1450 | 0.3580 | 0.7058 | 1.4548 |
| Standard deviation | 0.0011 | 0.0019 | 0.0035 | 0.0074 | 0.0136 | 0.0384 | 0.0708 | 0.1461 |
| Relative standard deviation (%)[b] | 12.8 | 11.1 | 11.7 | 9.56 | 9.38 | 10.7 | 10.0 | 10.0 |

[a] KHP sample concentration mg/L as C, measured as in Section 5310C.
[b] The percent relative standard deviation is given by:

$$\%RSD = \left[\frac{\text{standard deviation } (s)}{\text{mean } (\bar{X})}\right] \times 100$$

Table 5910:2. Single-Operator Precision for UV Absorption Measurements of Fulvic Acid Solutions

| | Result ($cm^{-1}$) | | |
|---|---|---|---|
| | DOC Concentration (mg/L) | | |
| Replicate No. | 2.5 | 4.9 | 10.0 |
| 1 | 0.110 | 0.240 | 0.480 |
| 2 | 0.120 | 0.230 | 0.480 |
| 3 | 0.110 | 0.240 | 0.470 |
| 4 | 0.100 | 0.230 | 0.480 |
| 5 | 0.110 | 0.240 | 0.480 |
| 6 | 0.100 | 0.240 | 0.470 |
| 7 | 0.110 | 0.240 | 0.480 |
| 8 | 0.110 | 0.230 | 0.480 |
| 9 | 0.120 | 0.240 | 0.480 |
| 10 | 0.110 | 0.240 | 0.480 |
| Mean | 0.110 | 0.237 | 0.478 |
| Standard deviation | 0.0067 | 0.00483 | 0.00422 |
| Relative standard deviation, % | 6.06 | 2.05 | 0.882 |

## References


1. Kaplan LA. Comparison of high-temperature and persulfate oxidation methods for the determination of dissolved organic carbon in freshwaters. Limnol Oceanogr. 1992;37(5):1119–1125.
2. Edzwald JK, Becker WC, Wattier KL. Surrogate parameters for monitoring organic matter and THM precursors. J Amer Water Works Assoc. 1985;77(4):122–132.
3. Kaplan LA. A field and laboratory procedure to collect, process, and preserve freshwater samples for dissolved organic carbon analysis. Limnol Oceanogr. 1994;39(6):1470–1476.
4. Karanfil T, Erdogan I, Schlautman M. Selecting filter membranes for measuring DOC and $UV_{254}$. J Amer Water Works Assoc. 2003;95(3):86–100.
5. Karanfil T, Erdogan I, Schlautman M. The impact of filtrate turbidity on $UV_{254}$ and $SUVA_{254}$ determination. J Amer Water Works Assoc. 2005;97(5):125–136.
6. Malley Jr JP. A Fundamental study of dissolved air flotation for treatment of low turbidity waters containing natural organic matter. Ph.D. thesis (unpublished), University of Massachusetts, Amherst; 1988
7. U.S. Environmental Protection Agency. 1996. Monitoring requirements for public drinking water supplies: *Cryptosporidium*, *Giardia*, viruses, disinfection byproducts, water treatment plant data and other information requirements. Final Rule. Fed Reg. 61(94):24354.
8. Fair PS, Sorrell RK, Karapondo M, Bohl BJ, Frebis CP, Feige MA. Quality of ICR monitoring data. In: McGuire MJ, JMcLain J, Oblensky A, eds. Information collection rule data analysis. Denver (CO): American Water Works Association Research Foundation; 2002.