

5910 UV-ABSORBING ORGANIC CONSTITUENTS*

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 wastewaters.^{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 has been used to monitor industrial wastewater effluents¹¹ 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 UV 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 high-performance liquid chromatography (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.

2. References

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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 samples to control particle-related variations in UV absorption. The sample's pH should be adjusted before filtration; however, 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 pH before filtration.

UV absorption historically 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 compound(s) 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 treated drinking waters 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 between 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 cm^{-1} 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 tetrafluoroethylene (TFE)-lined caps. If individual TFE 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 Pre-cleaned containers from commercial vendors may also be available. Store samples at <6°C; samples requiring shipping should be transported on ice. Adjust pH (if needed) and analyze within 48 hours.

Samples may be filtered in the field. If samples require pH adjustment, make the adjustment before filtration. Do not adjust pH of samples for SUVA determination.¹

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, or use TFE, 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. Pre-rinse 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 2 hours) 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 $0.45 \mu\text{m}$ 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 $0.45\text{-}\mu\text{m}$ filters.⁵

c. Filter assembly, glass, TFE, 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.

* Whatman grade 934AH; Gelman type A/E; Millipore type AP40; ED Scientific Specialties grade 161; or other products that give demonstrably equivalent results.

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

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

d. *Phosphate buffer* (optional): Dissolve 4.08 g dried anhydrous KH_2PO_4 and 2.84 g dried anhydrous Na_2HPO_4 in 800 mL organic-free water. Verify that pH is 7.0 and dilute to 1 L with organic-free water. Store in a brown glass bottle at 4°C. Prepare fresh weekly (or more frequently if microbial growth is observed).

e. *Organic carbon stock solution*: Dissolve 2.1254 g anhydrous primary-standard grade potassium biphthalate, $\text{C}_8\text{H}_5\text{KO}_4$ [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 sample volume based on cell path length, volume needed for filter rinsing, and/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 filter and filter assembly by passing a sufficient volume of organic-free water through the filter (to waste) to yield a filter blank of $<0.010 \text{ cm}^{-1}$. For specific applications and correlations, 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. Take care to avoid precipitate formation during pH adjustment. UV absorbance of fulvic acid solutions apparently remains constant between pH 4 and 10.² Samples analyzed for SUVA determination should be run without adjusting the pH of the original sample. Report sample pH value used with recorded absorbance. Once sample pH has been adjusted and/or measured, rinse filter with sample and discard 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 spectrophotometer equilibrate according to manufacturer's instructions. Set wavelength to 253.7 nm (or 254 nm) and adjust spectrophotometer to read zero absorbance with organic-free water. Measure UV absorbance of at least two 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 100.

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

where:

UV_{λ}^{pH} = mean UV absorption, cm^{-1} (subscript denotes wavelength used, nm, and superscript denotes pH used if other than 7.0),

b = cell path length, cm,

\bar{A} = mean absorbance measured, 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.

6. Quality Control

The quality control (QC) practices considered to be an integral part of each method are summarized in Table 5020:I. Additionally, follow all QC described in the method itself.

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

b. *Duplicate analyses*: Analyze every tenth 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 $>0.045 \text{ cm}^{-1}$, the RPD limit is $\leq 10\%$. For UV values $<0.045 \text{ cm}^{-1}$, the RPD limit is $\leq 20\%$.

c. *Baseline absorbance*: Check 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 $<0.010 \text{ cm}^{-1}$; if not, larger rinsing volumes may be required. Also, the appropriateness of the filter and/or 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 nephelometric turbidity units (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 (3d) reagent water without acidification and analyzed in

UV-ABSORBING ORGANIC CONSTITUENTS (5910)/Ultraviolet Absorption Method

TABLE 5910:I. PRECISION OF UV ANALYSES AND CORRELATION TO KHP SAMPLES

Analysis	UV ₂₅₄ Result for Given KHP Sample Concentration*							
	cm ⁻¹							
	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	.0136	0.0384	.0708	0.1461
Relative standard deviation, %†	12.8	11.1	11.7	9.56	9.38	10.7	10.0	10.0

* KHP sample concentration mg/L as C, measured as in Section 5310C.

† The percent relative standard deviation is given by:

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

five laboratories. Results suggest acceptable precision (Table 5910:I). These data also are useful for checking spectrophotometer results with KHP standards commonly used for total organic carbon (TOC) and/or COD analysis. A correlation equation for this 40-sample data set is:

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

with correlation coefficient (r^2) = 0.987, UV₂₅₄ 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 UV₂₅₄ analyses is performed and results are in the 0.010 range, prepare a KHP standard of 0.5 mg/L as C. The projected UV₂₅₄ of this KHP standard would be 0.009 cm⁻¹. If measured UV₂₅₄ is outside the 13% relative standard deviation (RSD) of 0.009 cm⁻¹ (using the RSD in Table 5910:I as a

guide), the spectrophotometer may be suspect and require maintenance. The correlation between UV₂₅₄ 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:I 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:II 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 (ICR).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 Information Collection Rule minimum reporting level (MRL= 0.009 cm⁻¹). Results were as follows:⁸

TABLE 5910:II. SINGLE-OPERATOR PRECISION FOR UV ABSORPTION MEASUREMENTS OF FULVIC ACID SOLUTIONS

Replicate No.	Result		
	cm ⁻¹		
	DOC Concentration		
	mg/L		
	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

Data Quality Variable	Percentile					
	N	10	25	50 (median)	75	90
Precision (RPD)	33306*	0.0	0.0	0.0	2.2	4.9

* 2744 excluded - both samples less than MRL.

NOTE: Median sample result was 0.040 cm⁻¹.

8. References

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UV-ABSORBING ORGANIC CONSTITUENTS (5910)/Ultraviolet Absorption Method

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