Challenge

Quick and easy determination of the water quality of surface water by sum parameters such as turbidity, color and SAC_{254} according to regulatory specifications for water analysis laboratories.

Solution

Highly precise yet simple analysis of drinking water to heavily contaminated wastewater samples using the double beam spectrophotometer SPECORD 200 PLUS.

Determination of turbidity, color and SAC_{254} in surface water using UV/Vis spectroscopy according to DIN EN ISO 7027-1, DIN EN ISO 7887 and DIN 38404-3

Introduction

The German standard methods for the examination of water, wastewater and sludge include among others the determination of physical and physico-chemical parameters (Group C) for various water samples.[1]
UV/Vis spectrophotometry is a quick and easy method for analysis encompassing numerous parameters for most water samples. In addition to the common individual parameters such as phosphate, ammonium, nitrate and nitrite, the sum parameters of turbidity (DIN EN ISO 7027-1)[2], color (DIN EN ISO 7887)[3] and the spectral absorption coefficient at 254 nm (SAC_{254}, DIN 38404-3)[4] are also recorded to monitor the quality of drinking water, surface water, groundwater and wastewater.
Turbidity is defined as the reduction in transparency of a liquid caused by the presence of undissolved substances. In the case of color, a distinction is made between the apparent color of the water caused by dissolved substances and suspended particles (in the original water sample), and the true color of the water, caused only by dissolved substances.

The spectral absorption coefficient SAC_{254} is a measure of the summary determination of dissolved organic water components in water samples.

As the quality of our water also determines the quality of our life, we should be giving our utmost attention into achieving the highest level of water quality control.
The double beam spectrophotometer SPECORD 200 PLUS with the basic software ASpect UV is the device of choice for all of the above-specified measurements. Due to the high energy yield, the SPECORD PLUS spectrophotometer is perfectly suited for highly contaminated samples. Furthermore, even lowest concentrations can be detected with the high-precision optics. As well as individual samples using rectangular or round cuvettes, a large number of up to 116 samples can be automatically analyzed using the autosampler, depending on the requirements and the number of samples.

Materials and methods

Instrumentation and software settings

All measurements were performed with a SPECORD 200 PLUS spectrophotometer with a standard cuvette holder. For the measurements according to DIN EN ISO 7027-1[2] and DIN EN ISO 7887[3], 10 mm glass cuvettes were used, while 10 mm quartz cuvettes were used for measurements according to DIN 38404-3[4]. The absorbance for each parameter was measured using the software ASpect UV 1.5 (other ASpect UV versions give identical results). Table 1 lists the software settings.

Table 1: Software settings for measurement according to DIN EN ISO 7027-1, 7887 and DIN 38404-3

	DIN EN ISO 7027-1	DIN EN ISO 7887	DIN 38404-3
Measurement module	Spectrum	Spectrum	Photometry
Measurement mode	Absorption	Absorption	Absorption
Wavelength [nm]	830 – 890	350 – 780	254 and 550
Measuring points [nm]	1	1	-
Speed [nm/s]	10	10	-
Integration time [s]	0.1	0.1	0.1

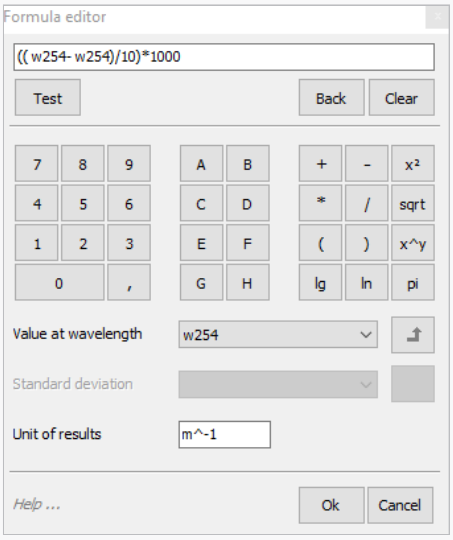
The spectral absorption coefficient SAC(λ), or α(λ) (1) and the turbidity correction factor $\mu(\lambda)_{corr}$ (2) were evaluated according to DIN 38404-3 using the following formulas:

$$SAC(\lambda) = \alpha(\lambda) = \frac{A(\lambda)}{d} * f \tag{1}$$

$$SAC_{254-550} = SAC_{254} - SAC_{550} = \mu(\lambda)_{korr} = \frac{(A_{254} - A_{550})}{d} * f \tag{2}$$

SAC(λ) = α(λ) = spectral absorption coefficient [m^{-1}]
A(λ) = absorbance of the water sample at wavelength λ [nm]
d = optical path length of the cuvette [mm]

f = factor to obtain the spectral absorption coefficient in m^{-1},
here f = 1000
μ(λ) = spectral decadic attenuation coefficient [m^{-1}]



((w254- w254)/10)*1000

Value at wavelength: w254

Standard deviation

Unit of results: m^-1

Figure 1: Formula editor

The equations were entered in the method setup directly into the formula editor (Fig. 1), so as to instantly display the calculated result after the sample measurement.

Samples and reagents

The sampling and sample preparation were carried out as described in the standards[2-4]. All samples were brought to room temperature before measurement.
For DIN EN ISO 7887 and DIN 38404-3, the pH value of the samples was determined using a pH electrode after 3-point calibration at pH 4, 7 and 9. There was no need to filter the distilled water because a comparison between the used freshly deionized water and the freshly filtered water (0.2 µm pore size) gave no evidence of any extinction differences.

DIN EN ISO 7027-1[2]

The thoroughly mixed samples were measured directly against the calibration curve. No further sample preparation was necessary.

Preparation of the standards

A 500 FNU formazin reference solution and distilled water were used to prepare the calibration standards. First, a 400 FNU stock solution was created using 40 mL formazin reference solution and 10 mL distilled water. The stock solution was used to prepare calibration standards of different concentrations (see Table 2). For this purpose, defined volumes of the stock solution were each placed in 50 mL volumetric flasks and filled with distilled water. Such diluted standards are only viable for 24 hours.

Table 2: Calibration standards

Calibration standard [FNU]	Volume of the stock solution [mL]
0	-
10	1.25
20	2.50
30	3.75
40	5.00

DIN EN ISO 7887[3]

The samples were agitated to dissolve all the soluble substances and then passed through a 0.45 µm membrane filter.

DIN 38404-3[4]

The samples were shaken in the sample bottle to ensure the particles causing turbidity were evenly distributed. In order to determine the spectral absorption coefficients, a particle-containing sample was measured immediately after the shaking process. The turbidity correction requires a filtered sample, for this purpose the samples were filtered through a membrane filter with a pore size of 0.45 µm.

Measurements

In preparation for all measurements, quartz and glass cuvettes with the same specifications were compared by measuring the absorption spectrum. All cuvettes were rinsed with distilled water and ethanol before use. Only cuvettes with the lowest deviations (ΔA) from each other were used for the sample measurement.

DIN EN ISO 7027-1[2]

Two 10 mm glass cuvettes each were used for the reference, standard and sample measurements. For the reference measurement, the cuvettes were first filled with distilled water. One was positioned in the measurement beam and the other in the reference beam of the SPECORD 200 PLUS. For the measurement of the sample, the cuvette was taken out of the measurement beam, emptied and rinsed three times with the unfiltered sample. After rinsing, the cuvette was filled with the sample and measured against the cuvette that remained in the reference beam. To measure the standard, the cuvette was rinsed three times with the corresponding calibration standard. After rinsing, it was filled with the calibration standard and measured. For the sample measurement, the cuvettes were also rinsed three times with the unfiltered sample, then filled and measured with the fourth filling.

DIN EN ISO 7887[3]

The reference and sample measurements of the filtered samples were performed in 10 mm glass cuvettes. The reference and sample measurements were performed according to the measurement section in DIN EN ISO 7027-1. The cuvette was rinsed three times with the filtered sample. After rinsing, it was filled and measured.

DIN 38404-3[4]

Two suitable 10 mm quartz cuvettes were used for the reference and sample measurement. The reference, standard and sample measurements were performed as described in the measurement section of DIN EN ISO 7027-1. The same procedure was applied to measure the filtered sample.

Results and Discussion

Water samples of various origins were provided for the determination of turbidity, color and SAC_{254}. Besides surface water taken from flowing and standing water bodies in Gera, Weimar, Jena and the surrounding area (federal state Thuringia, Germany), landfill eluats from Leipzig (federal state Saxony, Germany) were analyzed. Table 3 provides an overview of the standards, parameters and measurement methods used.

Table 3: Comparison of parameters listed in the standards DIN EN ISO 7027-1, DIN EN ISO 7887 and DIN 38404-3[2-4]

	DIN EN ISO 7027-1	DIN EN ISO 7887	DIN 38404-3
Parameter	Turbidity	Color	Spectral absorption coefficient SAC_{254}
Measurement	Undissolved substances and dissolved colloidal substances	Dissolved substances (and suspended matter for apparent color)	Dissolved organic compounds
Wavelength	Above 800 nm (here 860 nm)	436 nm, also at 525 nm and 620 nm for industrial wastewater	254 nm (also at 550 nm for turbid samples)
Effect	Reduction in transparency	Change in the spectral composition of the transmitted visible light	Attenuation of the light at 254 nm
Example of impurities	Plankton, hydrated metal oxides, sediment particles	Organic and inorganic (mineral) particles, iron, humic substances	Humic substances, aromatic compounds, lignins, tannins
Interferences	Dissolved, light-absorbing and colored substances	Undissolved substances, suspended particles	Nitrate, particulate matter, gas-emitting substances
Type of water	For all types of water samples	Natural water, raw and drinking water, slightly colored industrial water	For all types of water samples
Method used	Method A for water with low turbidity	Method B for slightly colored industrial water	One method available for all types of water
Limit values for drinking water[5]	1.0 NTU (in waterworks discharge)	0.5 m^{-1}	No limit value available

DIN EN ISO 7027-1 – Turbidity[2]

Turbidity is a reduction in transparency of a water sample caused by the scattering of undissolved substances, which is why the unfiltered original samples are analyzed. The sum of all the small, undissolved particles is a basic indicator for water quality. Turbidity can be determined with two different methods: nephelometry uses the 90° method and is suited for slightly turbid water from 0.05 NTU (Nephelometric Turbidity Unit). Turbidimetry is performed using the transmitted light method and is suited for more turbid water from a value of 40 FAU (Formazin Attenuation Unit). A 1:1 conversion between NTU and FNU units is possible for diluted formazin standards. In natural water bodies, turbidity has an important influence on the light conditions, and therefore photosynthesis and growth of aquatic plants and plankton as these directly depend on the available solar radiation.

In general, the spectral decadic attenuation coefficient $\mu(\lambda)$ is calculated as the sum of the spectral scattering coefficient $s(\lambda)$ and the spectral absorption coefficient $\alpha(\lambda)$, see Formula 3 and Figure 2. The influence of dissolved substances is taken into account in the spectral absorption coefficient $\alpha(\lambda)$, and undissolved substances in the spectral scattering coefficient $s(\lambda)$. Although strictly speaking, only the undissolved particles, i.e., the spectral scattering coefficient $s(\lambda)$, are relevant for turbidity, the proportion of the spectral absorption coefficient $\alpha(\lambda)$, i.e., the dissolved particles, are also determined in the measurement.

To reduce the influence of the spectral absorption coefficient $\alpha(\lambda)$, the measurement is performed at wavelengths above 800 nm, as filtration would have had a significantly greater impact on the measurement results. In most cases, the measurements are carried out at a wavelength of 860 nm.

$$\mu(\lambda) = s(\lambda) + \alpha(\lambda) \tag{3}$$

$\mu(\lambda)$ = spectral decadic attenuation coefficient $[m^{-1}]$
$s(\lambda)$ = spectral scattering coefficient $[m^{-1}]$
$a(\lambda)$ = spectral absorption coefficient $[m^{-1}]$

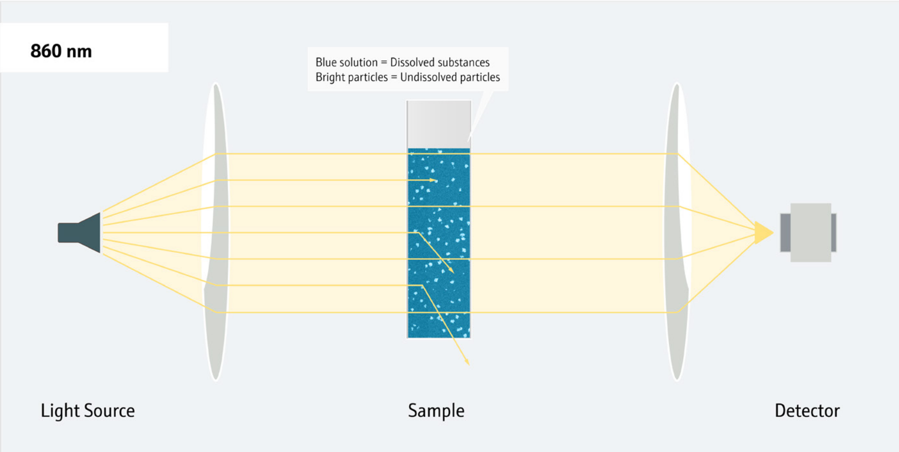
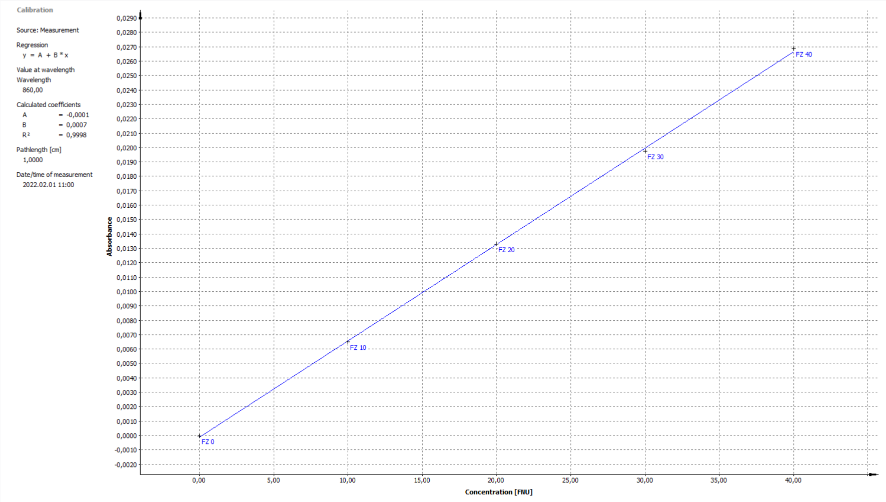


Figure 2: Schematic representation of the turbidity measurement according to DIN EN ISO 7027-1

In the present case, the turbidimetry method was performed with diluted formazin stock solutions of between 0 FNU and 40 FNU, as the SPECORD 200 PLUS spectrophotometer has a linear arrangement of radiation source and detector. All samples were analyzed in the range from 830 nm to 890 nm and the maxima were determined. As all samples had a maximum around 860 nm, this value was used for further analyses.
To create the calibration curve, five formazin stock solutions were prepared with distinct yet known concentrations between 0 and 40 FNU. These were analyzed at 860 nm and the absorbance obtained was plotted on the y-axis against the known concentration on the x-axis. The calibration curve is shown in Figure 3. The R^2 value is 0.9998. A good linearity of the calibration curve is especially important for samples with low concentration in order to avoid errors in the measurement data.



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Calibration

Source: Measurement

Regression
  y  =  A  + B * x

Value at wavelength
Wavelength
  860,00

Calculated coefficients
  A            =  -0,0001
  B            =  0,0007
  R²           =  0,9998

Pathlength [cm]
  1,0000

Date/time of measurement
  2022.02.01 11:00
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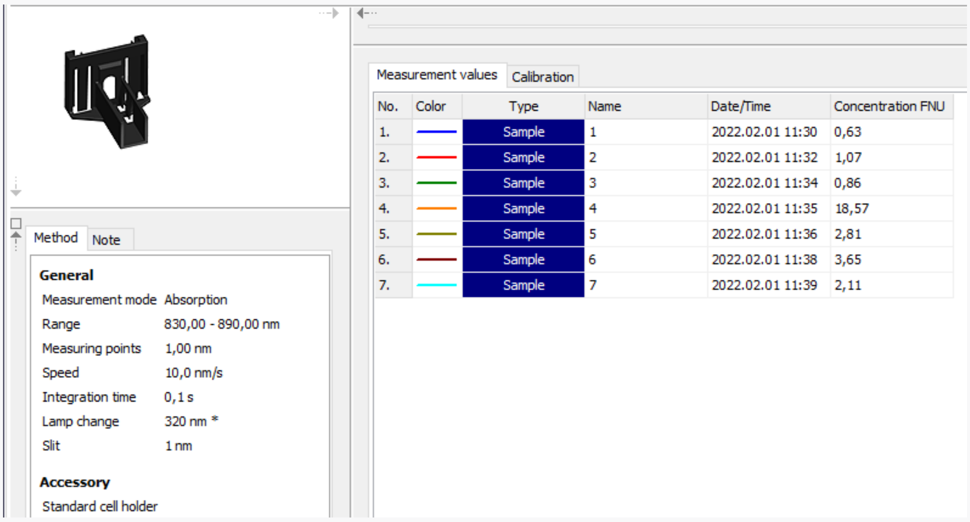
Figure 3: Calibration curve of the formazin solution in the range 0–40 FNU at 860 nm, the R^2 value is 0.9998

By comparing the measured absorbance of samples with unknown concentration, the incumbent sample concentration can be determined. The ASpect UV software automatically correlates the measured absorbance of samples 1–7 at 860 nm with the calibration curve shown in Figure 3 and displays the results in FNU (Figure 4). A tabular listing of the results can be found in Table 4. According to DIN EN ISO 7027-1, results for values below 1 are specified with two decimals, values smaller than 10 with one decimal and values greater than 20 are displayed without any decimals. Sample 4 has the highest turbidity. Sample 1 and 3 are below 1.0 FNU, values which are permitted for drinking water output by water treatment works.[5]
Sudden or sharp increases for the parameter turbidity in the drinking water distribution network must be monitored and reported.



General

Measurement mode	Absorption
Range	830,00 - 890,00 nm
Measuring points	1,00 nm
Speed	10,0 nm/s
Integration time	0,1 s
Lamp change	320 nm *
Slit	1 nm

Accessory

Standard cell holder

No.	Color	Type	Name	Date/Time	Concentration FNU
1.	—	Sample	1	2022.02.01 11:30	0,63
2.	—	Sample	2	2022.02.01 11:32	1,07
3.	—	Sample	3	2022.02.01 11:34	0,86
4.	—	Sample	4	2022.02.01 11:35	18,57
5.	—	Sample	5	2022.02.01 11:36	2,81
6.	—	Sample	6	2022.02.01 11:38	3,65
7.	—	Sample	7	2022.02.01 11:39	2,11

Figure 4: Measurement results of samples 1-7 with automatic calculation of FNU values in ASpect UV software

Table 4: Measurements for DIN EN ISO 7027-1

	FNU
Sample 1	0.63
Sample 2	1.1
Sample 3	0.86
Sample 4	19
Sample 5	2.8
Sample 6	3.7
Sample 7	2.1

DIN EN ISO 7887 – Color[3]

Color is related to both dissolved substances and suspended solids. In addition to the absorption of organic particles, the absorption of inorganic (mineral) particles is also recorded at 436 nm. This method is suited for all water bodies. The distinction between true color and apparent color is relevant in this case – for true color only physically dissolved substances are recorded whereas for apparent color, suspended matter is also taken into account (see Figure 5 and Table 5). Therefore, filtration is required to remove suspended particles for the determination of true color. The determination of the pH value is necessary during sampling due to its direct impact in color.

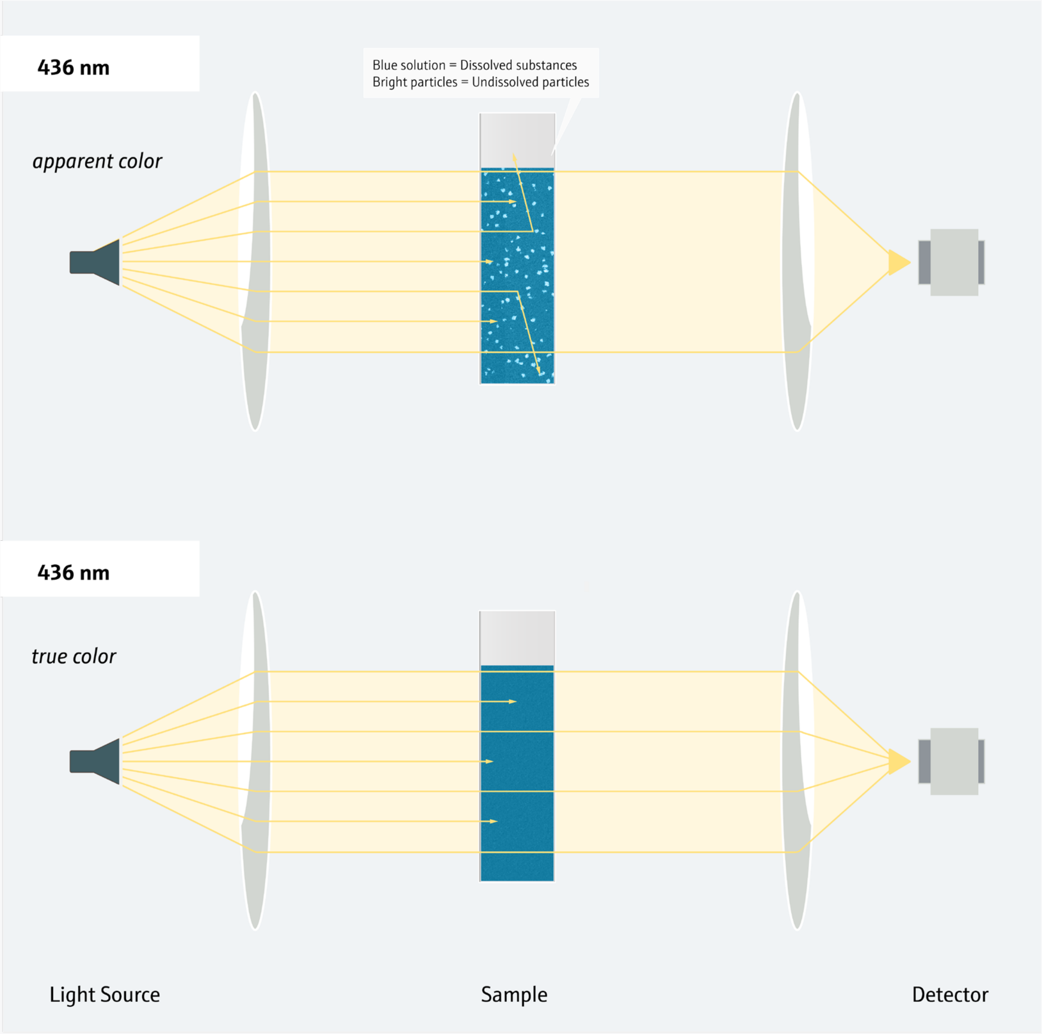


Figure 5: Schematic representation of color measurement according to DIN EN ISO 7887

Table 5: Comparison of parameters of the standard DIN EN ISO 7887

	Apparent color	True color
Physical parameter	Dissolved substances and suspended matter	Dissolved substances
Sample treatment	Original water sample without filtration	Filtration through membrane filter 0.45 µm

Four different methods are described when measuring color according to DIN EN ISO 7887 (Table 6). Method A is used to investigate the apparent color through visual observation of a water sample. This method is only suitable for a preliminary analysis and rough classification. Method B was used in the present case as it deals with the spectrophotometric determination of the true color of slightly colored industrial waters, as well as raw and drinking water. Depending on the water sample, the determination is performed at up to three different wavelengths (436 nm, 525 nm and 620 nm). Method C is also a spectrophotometric determination, which determines the color of a sample through comparison of a defined calibration solution of potassium hexachloroplatinate and cobalt chloride at 410 nm. In method D, the intensity of the color is analyzed by visual comparison with platinum stock solutions.

Method B is clearly the preferred method as photometric determination provides higher accuracy and is independent of the user in contrast to the visual approaches in method A and D. Method C is only suitable for optically clear samples, whereas method B is also suitable for slightly colored samples and can therefore be used more universally. Consequently, method B is a simple, accurate and universal method for the determination of the true color of a water sample.

Table 6: Comparison of the four different methods of the standard DIN EN ISO 7887

	Method A	**Method B**	**Method C**	**Method D**
Parameter	Apparent color	True color	True color	Color
Method	Visual comparison	Photometer	Photometer, comparison with hexachloroplatinate concentration	Visual comparison with hexachloroplatinate standard solutions
Suitability	Deviating sample color from the reference solution	Raw water and drinking water, slightly colored industrial water; deviating color tone of the sample from the reference solution	Optically clear samples	Raw and drinking water
Wavelength	-	Natural water at 436 nm; Additional measurements at 525 nm and 620 nm if required	410 nm	-

Initially, an absorption spectrum in the range between 370 nm and 780 nm was recorded for all samples. As no significant peaks were observed, only the measured values at 436 nm, 525 nm and 620 nm were evaluated for further analysis, as specified in the standard. The measurement of yellow coloration at 436 nm is mandatory in the standard, the two other wavelengths are given as optional parameters and are primarily recommended for industrial wastewater. Table 7 lists the generated measurement data and the pH value of the samples. In accordance with the German drinking water ordinance, the pH value of drinking water must be between 6.5 and 9.5. Only samples 2 and 4 were outside this range.[5] For the parameter color, sample 2 deviates significantly from the other samples with a value of 5.3 m^{-1}. Only sample 3 meets the conditions for classification as drinking water at 436 nm, a coloring of up to 0.5 m^{-1} is permitted.[5] The limit values for wastewater at the discharge point are 7 m^{-1} for the yellow coloration at 436 nm, 5 m^{-1} for the red coloration at 525 nm and 3 m^{-1} for the blue coloration at 620 nm.[6]

Table 6: Measurement results and calculated values for DIN EN ISO 7887

	pH value	**α(436 nm) [m^{-1}]**	**α(525 nm) [m^{-1}]**	**α(620 nm) [m^{-1}]**
Sample 1	7.74	1.1	0.5	0.2
Sample 2	9.95	5.3	0.7	0.1
Sample 3	7.96	0.2	0.7	0.1
Sample 4	12.03	1.5	1.1	0.9
Sample 5	7.82	0.9	0.5	0.3
Sample 6	8.01	1.7	0.8	0.5
Sample 7	7.81	0.7	0.3	0.1

DIN 38404-3 – SAC_{254}[4]

The SAC_{254} is an important parameter for water analysis as it is a sum parameter for water contamination by dissolved organic substances such as aromatic compounds, as well as being a potential indicator of bacterial contamination. With few exceptions (sugar, alcohols, short-chain aliphatic compounds), most organic compounds are detected at 254 nm.
The determination of the SAC_{254} according to DIN 38404-3 is possible for all water samples, even highly colored and turbid samples can be analyzed. A correction is necessary if particulate substances are present. This requires either the filtration of the sample or the measurement of the SAC_{550} in addition to the SAC_{254}. The SAC_{550} is subtracted from the SAC_{254} ($SAC_{254-550}$) for compensation of the turbidity, see Figure 6.

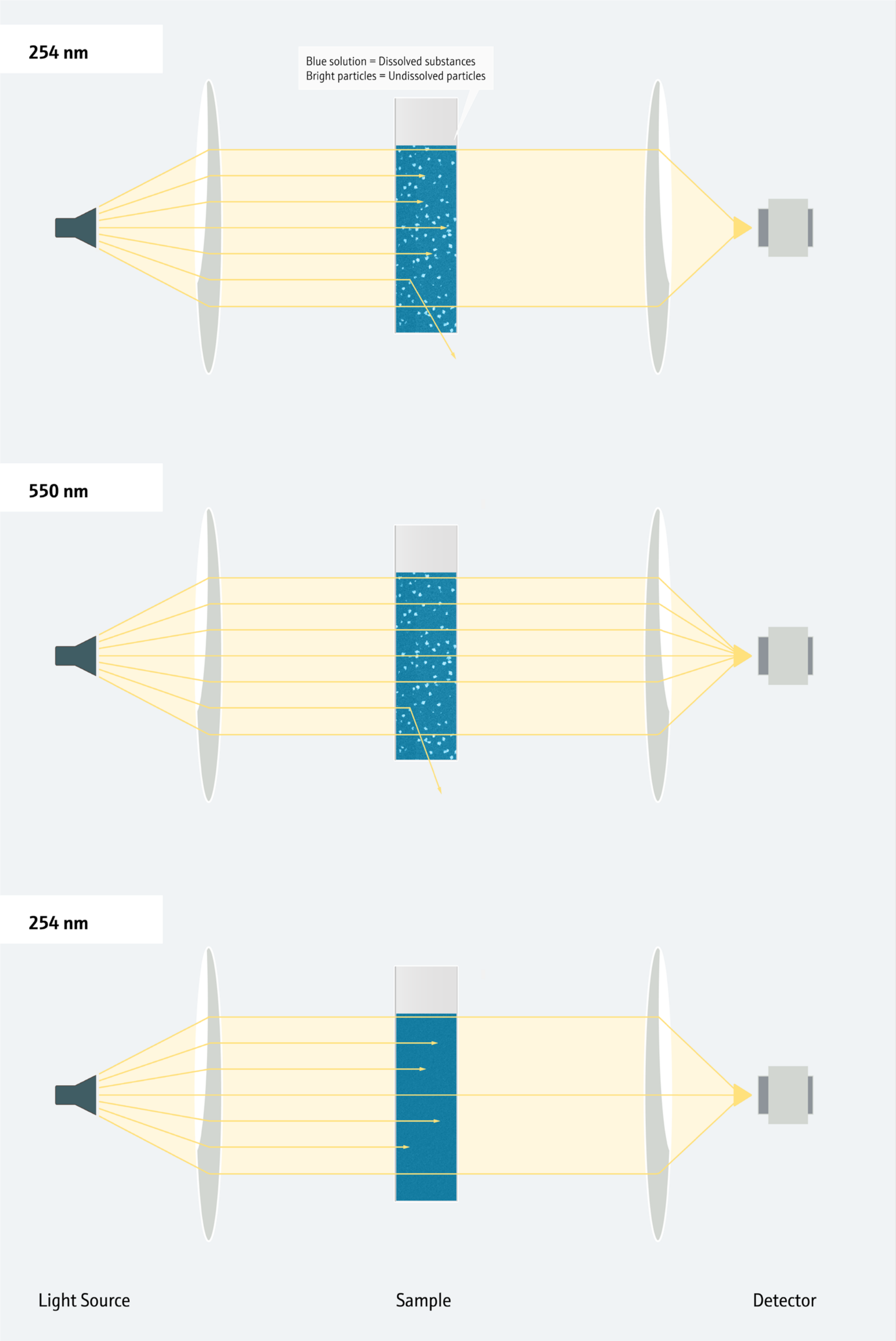


Figure 6: Schematic representation of the determination of the SAC_{254} according to DIN EN ISO 38404-3

Table 8 shows the measurement results and the calculated SAC_{254} values for the different samples according to DIN 38404-3. Except for sample 2 (SAC_{254} at 511 m^{-1}), all values are below 100 m^{-1}. Four out of seven surface water samples (samples 3 and 5-7) are in the range below 25 m^{-1}. As the SAC_{254} does not differentiate between the various organic materials (e.g., bacteria, germs, decomposition products, humic substances), it is not recommended to evaluate or compare the measured data from different water sources.

Table 8: Measurement results and calculated values for DIN 38404-3

	A (254 nm)	A (254 nm), filtered	A (550 nm)	SAC_{254}	SAC_{254} filtered	$SAC_{254-550}$
Sample 1	0.2936	0.2846	0.0038	29.4	28.5	29.0
Sample 2	5.1102	4.0430	0.0077	511.0	404.3	510.3
Sample 3	0.0950	0.0907	0.0007	9.5	9.1	9.4
Sample 4	0.6606	0.6336	0.0382	66.1	63.4	62.2
Sample 5	0.0698	0.0470	0.0026	7.0	4.7	6.7
Sample 6	0.2195	0.1705	0.0099	22.0	17.1	21.0
Sample 7	0.0994	0.0518	0.0032	9.9	5.2	9.6

The low absorption values in 10 mm cuvettes clearly reveal that only slightly organically contaminated samples of surface water were available in the present case. As for the analysis of drinking water, the usage of a cuvette with 50 mm path length is therefore recommended for these measurements. Due to low SAC_{254} values, additional filtration or measurement at 550 nm is not necessary, as the SAC_{254} and the corrected $SAC_{254-550}$ only differ slightly. With a relevant amount of suspended solids, sample 4 can be considered an exception. For all other samples, the corrected $SAC_{254-550}$ is in the range of the uncorrected SAC_{254}.

As specified in the standard as a possible source of error, absorption or oxidation processes can occur at the surface of the filter during filtration. This can lead to alteration of the measured values. The significantly lower values after the filtration (SAC_{254} filtered) indicate the considerable influence of the filter surface, especially at low concentrations. As the filtration of the samples is also cost-intensive and time consuming, an additional measurement at 550 nm is principally an easier, quicker and more accurate alternative. The calculations of the measurement data can directly be performed in the ASpect UV software (see Figure 1 in Materials and Methods).

Summary

The German standard method for the examination of water, wastewater and sludge were first published in 1981. Since then, the standards as well as the analytical instruments have been continuously adapted.

The double beam spectrophotometer SPECORD 200 PLUS and the software ASpect UV offer diverse possibilities especially for the analysis of individual and sum parameters in water analysis. The hardware of the SPECORD PLUS (Figure 7) provides optimal measurement results for drinking water as well as for turbid samples. A range of sophisticated accessories enables the usage of cuvettes of different shapes and path lengths, as well as automation for up to 116 samples. The ASpect UV software can run automatic calculations and determine concentrations.

Figure 7: SPECORD 200 PLUS

References

[1] German standard methods for the examination of water, wastewater and sludge (DEV), October 2021.

[2] DIN 38404-3:2005-07 (C 3)

[3] DIN EN ISO 7027-1:2016-11

[4] DIN EN ISO 7887:2012-04

[5] German drinking water ordinance

[6] German waste water ordinance

Headquarters
Analytik Jena GmbH
Konrad-Zuse-Strasse 1
07745 Jena · Germany

Phone +49 3641 77 70
Fax +49 3641 77 9279

info@analytik-jena.com
www.analytik-jena.com

Version 1.0 · Author: JuTy/SaWu
de · 05/2022