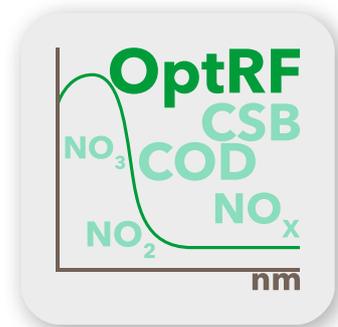


Online measurement brought into the lab

OptRF - optical, reagent-free measurement of COD, Nitrate and Nitrite

The chemical oxygen demand (COD), nitrate, nitrite and ammonium are among the central wastewater parameters, in order to ensure safe, optimized and smooth wastewater treatment processes. COD is a sum parameter, whose composition is very plant-specific due to the different contents of the respective wastewaters (the so-called wastewater matrix).

The COD determination in the lab cannot be done in a rush: The DIN standard-compliant COD measurement requires a time period of approx. 2.5 hours. Besides, health-related and environmentally hazardous substances such as potassium dichromate are used, which are also light-sensitive and therefore prone to drifts. As a consequence, in addition to the DIN procedure, the cuvette test with smaller volumes and simple operation has made its mark for self-control purposes at wastewater treatment plants. Yet, even such shortened procedures - not DIN compliant - still require about 30 minutes to obtain the COD value.



The nitrate and nitrite determination by means of cuvette tests is not as time-consuming, but quickly causes significant costs too, when fulfilling "good laboratory practice" (GLP) requirements with double and triple determinations.

Revolutionary: WTW brings the online world into the lab

Continuous measurement of the parameters COD, nitrate and nitrite to provide control and regulation for process optimization, as well as monitoring of the inlet and effluent of wastewater treatment plants have been used successfully for more than ten years in the spectral sensors in WTW's IQ SENSOR NET online system.

The measuring principle is based on an absorbance measurement in the UV wavelength range between 200 and 390 nm. In the background, the measured absorption spectrum is evaluated across the entire wavelength range with parameter-specific models. Thus, the concentration is calculated and the reading displayed instantly. This spectral measuring procedure for direct measurement of COD, nitrate and nitrite of the WTW online world has now been transferred to the photometer:

Reagent-free reading of COD, nitrate and nitrite

By a spectral scan from 200-390 nm, the new WTW photoLab® 7600 UV-VIS spectrophotometer can now also evaluate, calculate and directly display these parameters **optically** and **reagent-free (OptRF)**! Just like with the online sensors, the evaluation models are based on a multitude of spectrally measured real wastewater samples with their respective lab reference values.

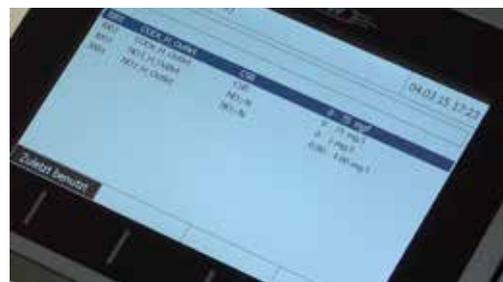
The photometric OptRF methods can presently be used in the effluent of municipal wastewater treatment plants, where relatively few particles are expected. A high number of particles can interfere spectral measurement due to their settling behavior. Hence, the incorporated OptRF models are based on "average" particle quantities.

The composition of substances in the wastewater - so called wastewater matrix - differs between sewage plants at least slightly. Therefore, a user calibration should generally be performed for all used OptRF methods in order to achieve the best possible and most accurate measuring results.

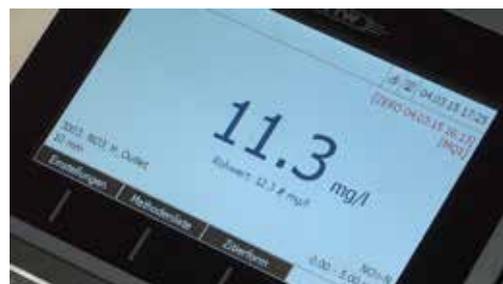
Measurements in relatively particle-free surface waters are usually also possible, however, the suitability of the OptRF methods for the respective water must be tested first. With filtered samples, very good results can often be achieved using the "COD_{dissolved}" method.

OptRF measurement in routine lab operations

The demand for quick daily routine checks and for the testing of retention samples in the sewage plant effluent without additional costs is fulfilled by OptRF, although test sets will continue to be necessary for self control and user calibrations. But the number



Selection of the OptRF measurement on the start screen of the photometer and list of OptRF methods



Results displayed for the parameters COD and nitrate after user calibration with result and raw value

Simply measure!

- Pipette an untreated sample into a 10 mm quartz cuvette
- Read the measured value directly

Mühlbachl, Tyrol

Sample 1	OptRF #	OptRF (calibrated)	Ref. median value
COD	22,70	25,9	26
Nitrate	0,88	0,8	0,77
Nitrite	0,28	0,01	0,078

Sample 2	OptRF #	OptRF (calibrated)	Ref. median value
COD	22	25,1	25,6
Nitrate	0,78	0,8	0,77
Nitrit	0,34	0,080	0,079

Sample 3	OptRF #	OptRF (calibrated)	Ref. median value
COD	22,7	25,9	25,6
Nitrat	0,78	0,8	0,80
Nitrite	0,34	0,080	0,080

Adelsdorf, Bavaria

Sample 1	OptRF #	OptRF (calibrated)	Ref. median value
COD	30,80	28	28,1
Nitrate	0,91	0,71	0,70
Nitrite	0,17	0,100	0,111

and thus the cost for the required test sets can now for the first time be significantly reduced.

OptRF measurements in practical applications

Measurements of effluent samples in the municipal wastewater treatment plants Mühlbachl (Tyrol, Austria) and Adelsdorf (Bavaria, Germany) show the good match of the photoLab® 7600 UV-VIS's OptRF methods with cell tests. You can see that the results of the OptRF measurements can be optimized even more by performing a user calibration and using cuvette tests with optimal measuring range. This is true especially for nitrite, whose concentration usually lies in the region of detection limit.

The user calibration can be performed easily and conveniently and results in an adaptation of the calibration curve for the respective wastewater treatment plant. A user calibration causes the displayed value differs from the "raw value" (marked with #).

Conclusion

The examples show the good match of the spectral OptRF measurements with the reference measurements with standard cuvette tests. Despite the low concentrations, the nitrite measurement also yields acceptable measuring accuracies especially following a user calibration.

The table shows the measured results of COD, nitrate and nitrite, determined via OptRF and via cell tests in the sewage plants Mühlbachl and Adelsdorf. The listed reference values are median values from triple determinations.

Used cuvette test sets

COD	14560 4-40 mg/L CSB
Nitrate	Nitrate N2/25 0,5-25 mg/L NO ₃ -N
Nitrite	Nitrite N5/25 0,010-0,700 mg/L NO ₂ -N

Advantages of the OptRF methods at one glance:

- Faster than any digestion method
- Cost-free measurement
- No health hazards
- Eco-friendly without chemical disposal costs



The OptRF measurement can be performed with the WTW spectrophotometer photoLab® 7600 UV-VIS .
For further information, please visit www.wtw.de/de/spektralphotometer



Any further questions?
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