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Reagent-free Measurement of COD, Nitrate and Nitrite via Optical Methods in the Lab and Online Directly in the Process

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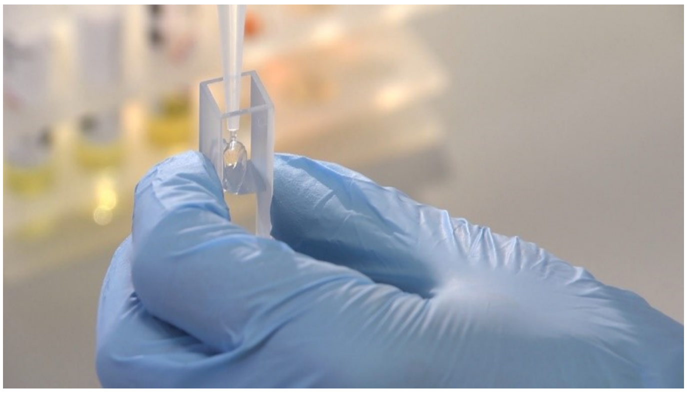

The Method

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.

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 with WTW's IQ Sensor Net online measuring systems.

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:

Spectrophotometer WTW photoLab® 7600 UV-VIS

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 measurements 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 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 #).

The tables 1 and 2 show the measured results of COD, nitrate and nitrite, determined via OptRF and via cell tests in the sewage plants Mühlbachl and Adelsdorf.

The listed values are median values from triple determinations.

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.

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

Tab.1: 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
Nitrite	0,34	0,080	0,079

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

Tab.2: 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

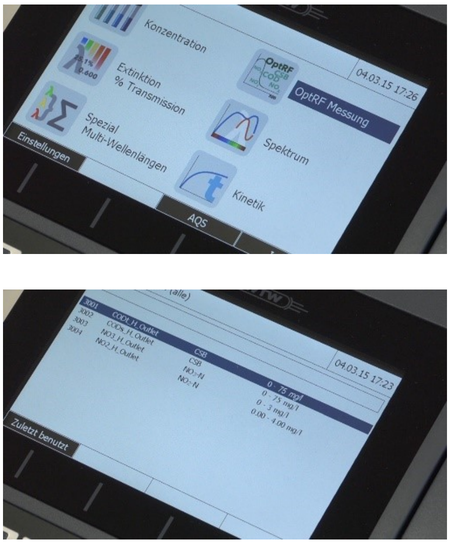

Fig.1: Selection of the OptRF measurement on the start screen of the photometer and list of OptRF methods

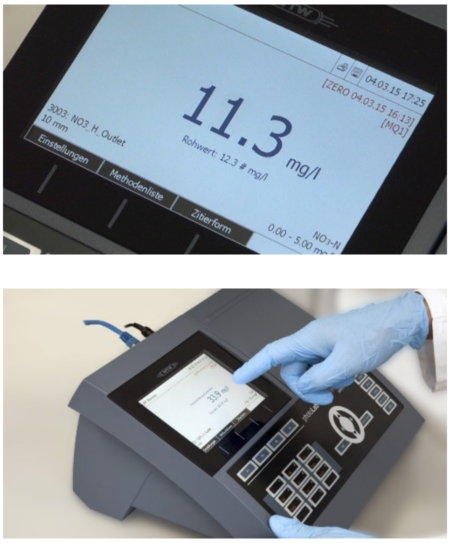

Fig.2: Results displayed for the parameters COD and nitrate after user calibration with the result and raw value

A Long-term test in the Municipal Wastewater Treatment Plant Peißenberg

The wastewater treatment plant (WWTP) Peißenberg permitted WTW to perform long-term testing of the reagent-free measurement of COD and nitrate for a period of approx. 6 weeks. In addition to that, the WWTP plant personnel supported the sampling as well as measurements in the laboratory. Two different WTW reagent-free measuring methods were tested: One was the IQ Sensor Net spectral sensor, the other was the new reagent-free photometry (OptRF) with the photoLab® 7600 UV-VIS. These two methods were compared to laboratory results from photometric cuvette tests. The goal was to evaluate how well the results of the optical reagent-free methods under dynamic conditions match those of the cuvette tests.

The WWTP Peißenberg is a municipal treatment plant with a capacity of 27,000 PE with little industrial influence. It was taken into operation in 1974. In the eighties, there was an expansion by a Tertiary treatment, and in 2007, the site was modernized by means of extensive reconstruction measures.

Test equipment

For the online measurements the UV-VIS spectral sensor NiCaVis® 705 IQ with integrated ultrasound cleaning and an additional air pressure cleaning was used. Due to structural conditions, the sensor could not be installed directly in the final effluent of the WWTP. Instead the sensor was mounted in the final clarifier (Figure 3). This facilitated ease of frequent grab sampling for the laboratory measurements. The two laboratory methods – the optical, reagent-free measurement (OptRF) and cuvette tests – were performed using the spectral photometer photoLab® 7600 UV-VIS. To determine the concentration by means of cuvette tests, the WTW COD test kit 14560 (4.0 – 40.0 mg/l COD) as well as the nitrate test kit N2/25 (0.5 – 25.0 mg/l NO_3-N) were used. Additional measurements were conducted for analytical quality assurance with a CSB standard of 20 mg/l (CombiCheck 50, 14695).

Test procedure and measured results

The test phase began in early November 2015 at a time when, due to seasonal changes, dynamics of the nitrate and COD concentrations at the effluent of the WWTP could be expected. The continuous measuring data of the spectral sensor was stored internally on the IQ Sensor Net Controller 2020 XT. The data were transferred to the computer for further evaluation via a USB stick.

Fig. 3: Installation of the NiCaVis® 705 IQ sensor in the clarifier of the wastewater treatment plant Peißenberg

For the laboratory measurements, grab sample were taken almost every working day with a water sample dipper directly at the sensor in order to ensure that the measured results of the laboratory methods and the online sensor could be compared side by side. The photometric measurement of the COD and nitrate concentrations via the reagent-free OptRF laboratory methods was conducted directly after sampling. The samples for the photometric reference with the cuvette tests were initially stored in the refrigerator to preserve them and tested once to twice a week as per analysis instructions by means of the photoLab® 7600 UV-VIS. A double determination as well as a determination with a control standard was conducted for the cuvette tests to detect possible measuring outliers and to eliminate them where possible.

Table 3 shows an excerpt from an Excel table with measured results from the three different measurement methods: In addition to the date, the time of day of the grab sampling was documented in order to be able to plot the laboratory data together with the online data in one graph. The cuvette test kits represent approved standard lab methods and thus represent the central reference measurement for the reagent-free measuring methods. The match (correlation) of the nitrate and COD measurements with sensor and OptRF methods compared to the cuvette test kits was very good (Figures 4 and 5).

Tab. 3: Excerpt of the results using the photometric OptRF procedure, the determination using cuvette testing and the spectral sensor NiCaVis® 705 IQ

Date, Time	OptRF values (mg/L)		Lab reference values (mg/L)		Sensor values (mg/L)	
	COD	NO_3-N	COD average values	NO_3-N average values	COD	NO_3-N
02.11.2015 14:53	27,0	3,03	24,4	2,50	22,4	3,20
03.11.2015 10:20	27,1	2,55	26,2	2,50	24,4	2,79
03.11.2015 15:07	28,4	2,78	24,1	2,40	22,9	2,90
04.11.2015 08:32	27,0	3,12	23,8	3,30	23,7	3,60
05.11.2015 14:40	28,0	2,83	21,8	2,70	23,0	3,10

Two-point user calibration for the best measuring accuracy

In order to optimize the measurement accuracy for the WWTP Peißenberg, a two-point user calibration of the online sensor as well as of the photometric OptRF methods was performed. For this, one measured value of the optical reagent-free methods as well as the corresponding measured values of the cuvette test kits was selected from the lower as well as from the upper measurement ranges. These values were entered into the sensor and the photometer as so-called value pairs. By this procedure, the optical, reagent-free methods can be adapted in an optimal way to the site specific WWTP conditions and best possible results can be achieved.

Conclusion: Optical methods offer high measurement reliability

The measuring results show a very good compliance of the different measuring methods for online and in the lab: The COD (Figure 4) as well as the nitrate concentrations (Figure 5) were measured reliably and satisfactorily - by means of the sensor as well as the innovative OptRF methods by the photoLab® 7600 UV-VIS. Especially with the COD determination using cuvette test kits and the occurring tolerances, the COD values measured reagent-free show comparatively similar fluctuations and are therefore comparably good. User calibration versus default factory settings achieved an even more optimized measuring accuracy for these two reagent-free methods. Also, the high dynamics, partially caused by strong rains, were well-shown by both reagent-free methods.

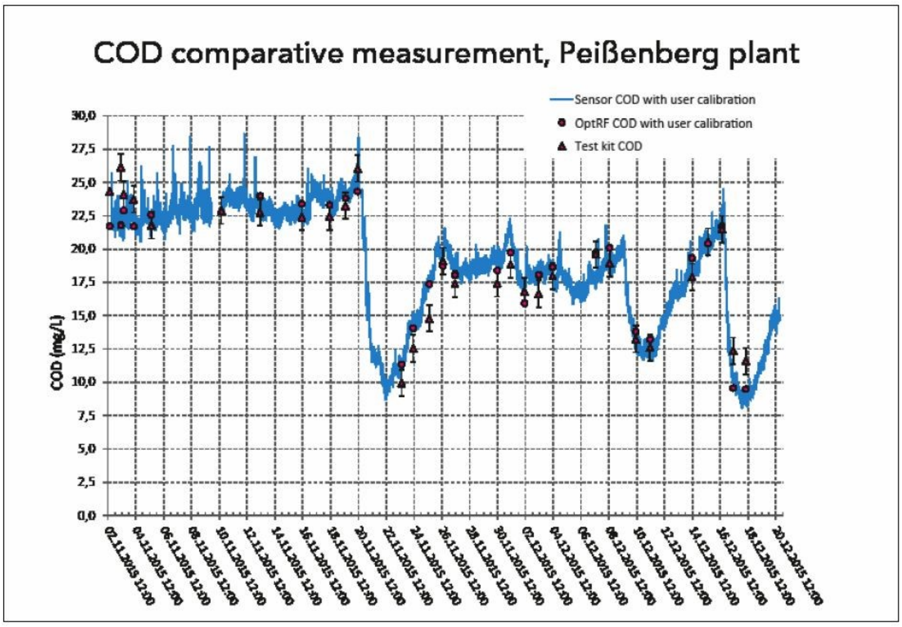

Fig. 4: COD comparison measurement of the three measuring methods after a two-point user calibration of the reagent-free methods

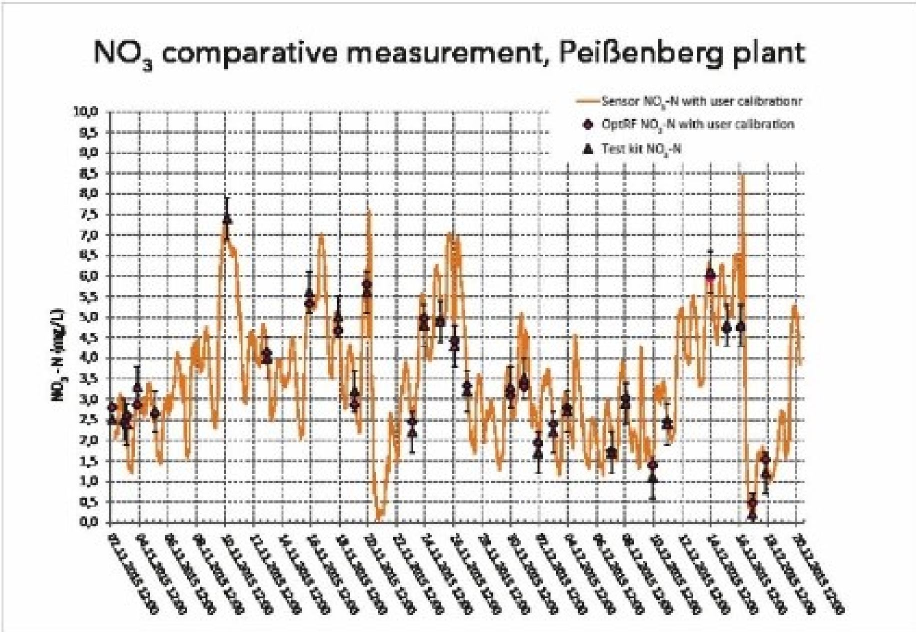

Fig. 5: Nitrate comparison measurement of the three measuring methods after a two-point user calibration of the reagent-free methods.