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Application note

Reagent-free Measurement of COD and Nitrate via optical methods

LONG-TERM TESTING IN THE MUNICIPAL WASTEWATER TREATMENT PLANT PEISSENBERG

The wastewater treatment plant (WWTP) in Peißenberg permitted Xylem 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 Xylem 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 in Peißenberg is a municipal WWTP 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.

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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 (Figures 1, 2). 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 (Figure 3). To determine the concentration by means of cuvette tests, the Xylem 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 NO3-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. The data were transferred to the computer for further evaluation via a USB stick.
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 1 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).

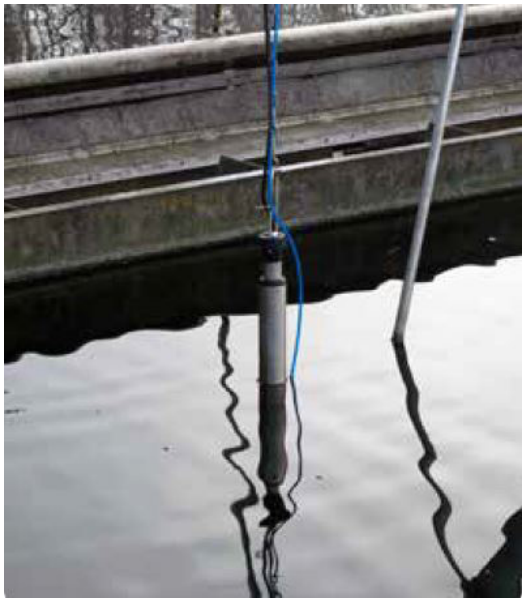
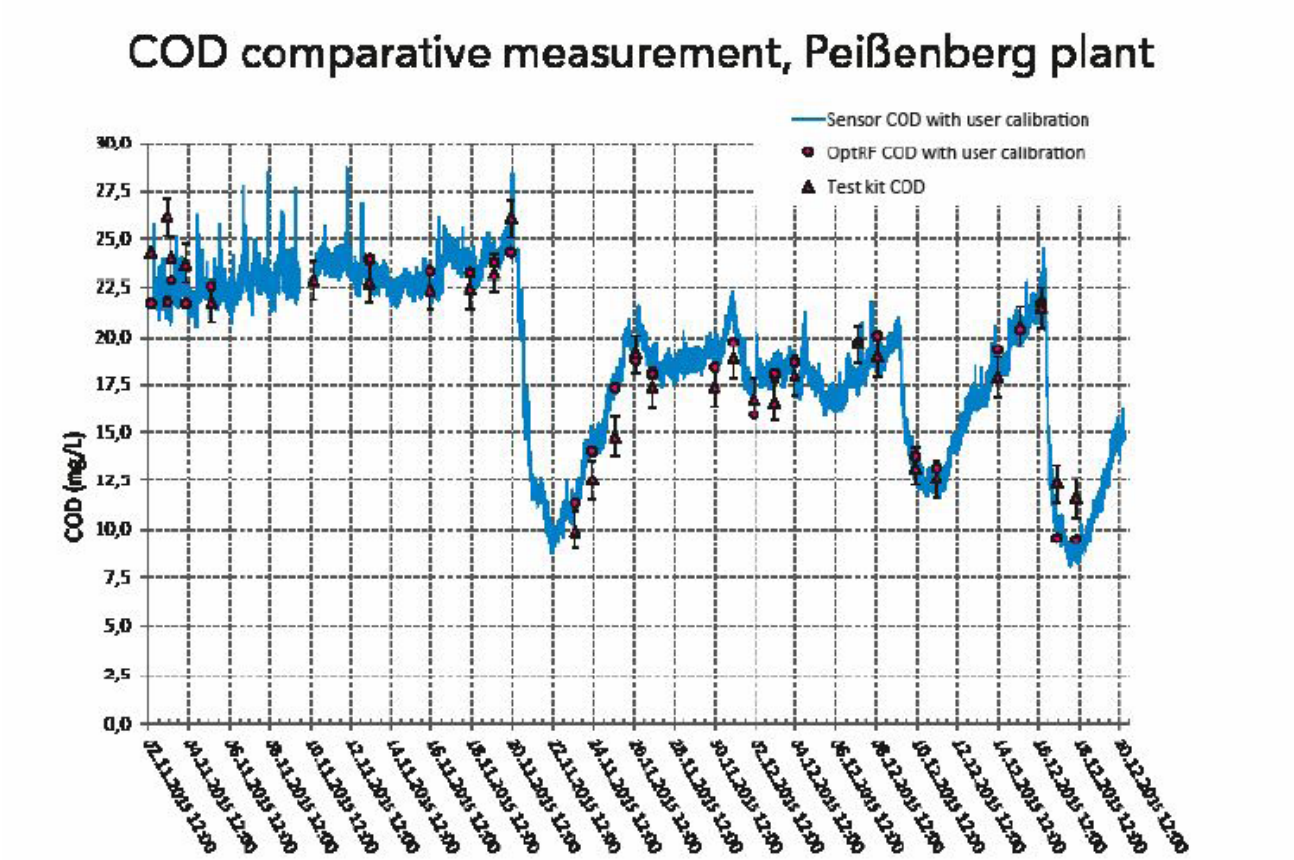


Fig. 1-2: Installation of the NiCaVis® 705 IQ sensor in the clarifier of the wastewater treatment plant Peißenberg

Table 1: 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



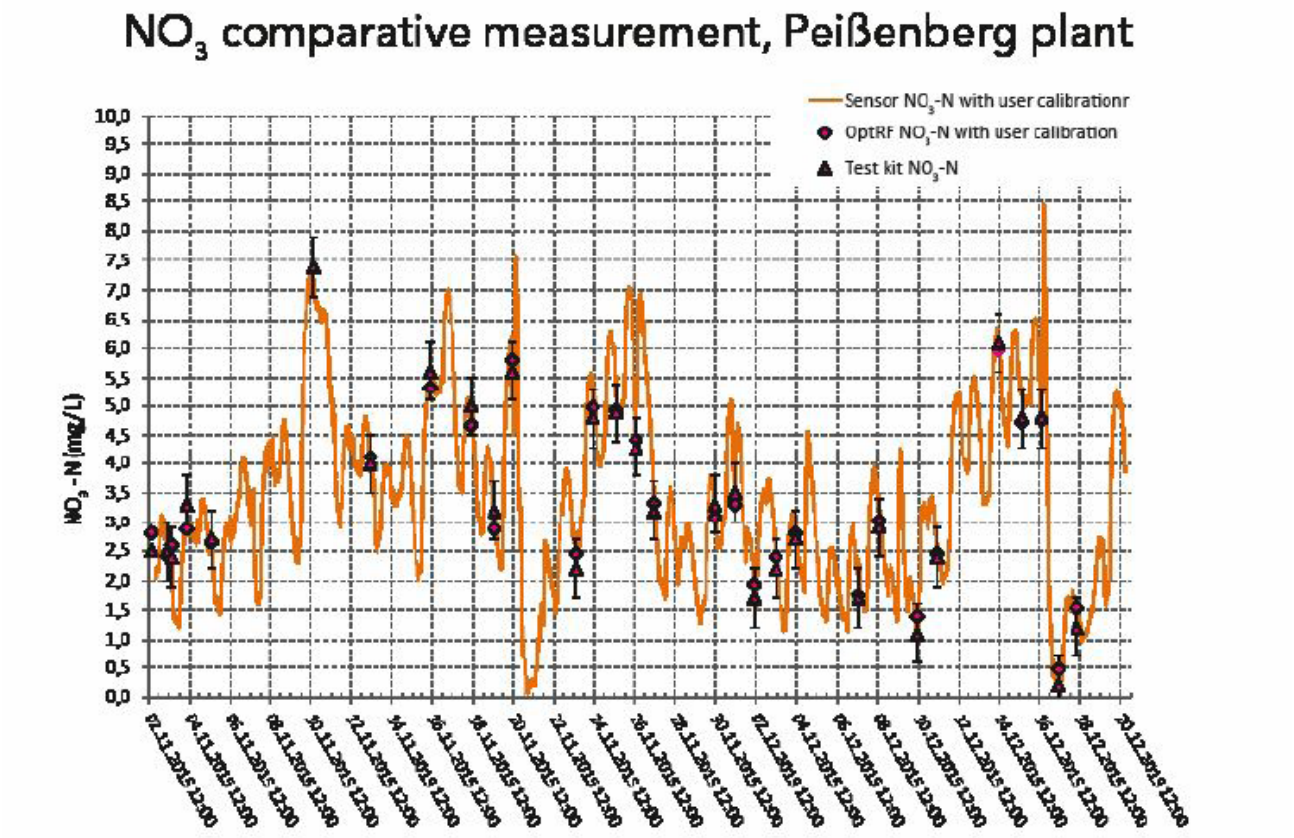


Fig. 4: COD comparison measurement of the three measuring methods after a two-point user calibration of the reagent-free methods
Fig. 5: Nitrate comparison measurement of the three measuring methods after a two-point user calibration of the reagent-free methods

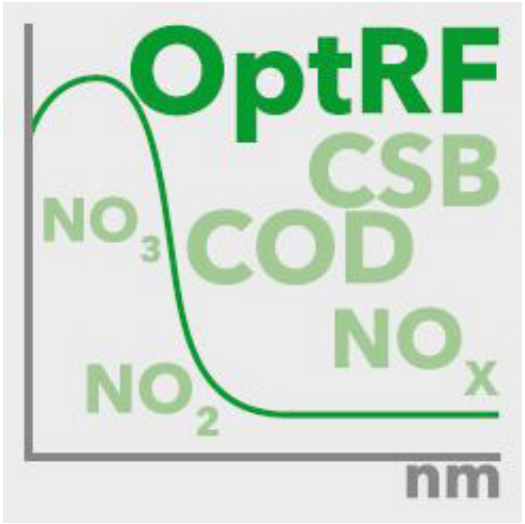
Two-point user calibration for the best measuring accuracy

In order to optimize the measurement accuracy for the WWTP in 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 measure-ment 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. 3: photoLab® 7600 UV-VIS photometer for the meas-urement of optical, reagent-free (OptRF) methods in the laboratory of the WWTP Peißenberg



The optical reagent-free methods symbol on the display screen of the photoLab® 7600 UV-VIS

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Do you have further questions?
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