

Spectral in-situ analysis of NO₂, NO₃, COD, DOC and TSS in the effluent of a WWTP

L. Rieger¹, G. Langergraber², M. Thomann³, N. Fleischmann⁴, and H. Siegrist¹

¹) EAWAG, Swiss Federal Institute for Environmental Science and Technology

Ueberlandstr. 133, PO Box 611, 8600 Duebendorf, Switzerland. *leiv.rieger@eawag.ch*

²) Institute of Sanitary Engineering and Water Pollution Control, BOKU – Univ. of Natural Resources and Applied Life Sciences, Vienna, Austria. *guenter.langergraber@boku.ac.at*

³) BMG Engineering AG, Grammetstrasse 14, 4410 Liestal, Switzerland. *michael.thomann@bmgeng.ch*

⁴) hydrophil, Lerchenfeldergürtel 43, Top 6/3, 1160 Vienna, Austria. *niki.fleischmann@hydrophil.at*

Abstract

An in-situ UV spectrometer was applied in the effluent of a WWTP in Switzerland and calibrated using a multivariate calibration algorithm that is based on PLS regression. Except for nitrite the calibration was based on comparative measurements of the effluent in the plant laboratory. For nitrite calibration samples made of stock solution added to three different matrices made in the EAWAG laboratory were used for the calibration because the effluent concentrations were always in the range of 0.06 – 0.26 mg/l. The results show very good precision for nitrite and nitrate. For COD and DOC the measuring range was not completely covered with measurements, so the meaningfulness of the results is limited. Nevertheless the obtained precision for soluble COD is high enough for most applications at WWTP's. The accuracy of the TSS measurement is unsatisfying regarding effluent limits since the used spectrometer does not cover the wavelength region up to 700 nm, which give better signals for TSS calibration due to its strong relation to turbidity.

Keywords

Spectroscopy, in-situ sensor, nitrite, nitrate, COD, DOC, TSS

INTRODUCTION

Nitrite is an intermediate product of the two-step process of nitrification. Since the second step of nitrification is very fast, the nitrite concentration in the effluent of a WWTP is normally very low (around 0.1 mg/l). Enrichment of nitrite in the system usually is a hint that the microbiological processes are disturbed. This means inhibition due to toxic substances or due to unfavourable conditions for the nitrite oxidiser. Nitrite is a strong poison for fishes, which reduce the oxygen transfer capability of the blood (Gujer, 1999). High concentrations of nitrite in the effluent of WWTP's can lead to damages of organisms if the dilution of the receiving water body is too low.

Since lab measurements of grab samples only can give a snapshot and the analysis of 24h-composite samples is critical due to the instable nitrite concentration the meaningfulness is limited. Using on-line analysers, which need a high sample preparation time can lead to similar problems. Therefore in-situ sensors will be advantageously.

The dissolved organic carbon (DOC) and the soluble COD are parameters for the inert or persistent compounds in the effluent, which can not be eliminated in the biological stage of the plant. For industrial plants or future process steps in municipal plants it can be used for an optimization of the carbon degradation processes, e.g. as an input signal for a control concept to treat persistent compounds with ozone.

The concentration of total suspended solids (TSS) in the effluent of the secondary clarifier is one of the most important measurements on a WWTP using normal clarifiers, because it identifies the amount of sludge lost in the effluent. The sludge of municipal WWTP's contains ca. 7% nitrogen, 2.5% phosphorus and consists mainly of biomass (TSS/COD ratio between 0.9 and 1.1). Additionally heavy metals can adsorb on sludge flocs. Therefore the lost sludge could play an important role regarding effluent quality levels (in Switzerland mainly for P due to the strict effluent levels of normally 0.8 mg P/l) or if the clarifier fails completely the loss of the biomass cause lower purification performance.

Measuring all parameters on-line will increase the monitoring capability and therefore enable appropriate control of the plant in order to prevent ecologically harmful discharges. Measuring them with one single probe will reduce the effort and therefore the costs.

MATERIAL AND METHODS

In-situ spectrometer

The tested in-situ spectrometer (spectro::lyser, s::can Messtechnik GmbH, Vienna, Austria) is capable of measuring absorbance of ultraviolet (UV from 200 nm - 400 nm) light, or ultraviolet and visible (UV/VIS from 200 nm - 750 nm) light. A single evaluation of the entire spectrum typically takes 15 seconds. Measuring UV/VIS absorbance is an indirect method for determining wastewater compounds. The sensor can be calibrated to all absorbing substances, typical applications in the water sector are organic matter (e.g. total COD, COD fractions, BOD₅, TOC, or DOC), TSS, turbidity and nitrate (Figure 1). For typical waters (e.g. municipal wastewater – raw and treated, river water, drinking water, ...) a global calibration is provided as default configuration of the UV/VIS spectrometer. Due to the specific wastewater characteristics the sensor has to be calibrated to the wastewater at the measurement location (local calibration). The local calibration improves trueness, precision and long term stability of the results.

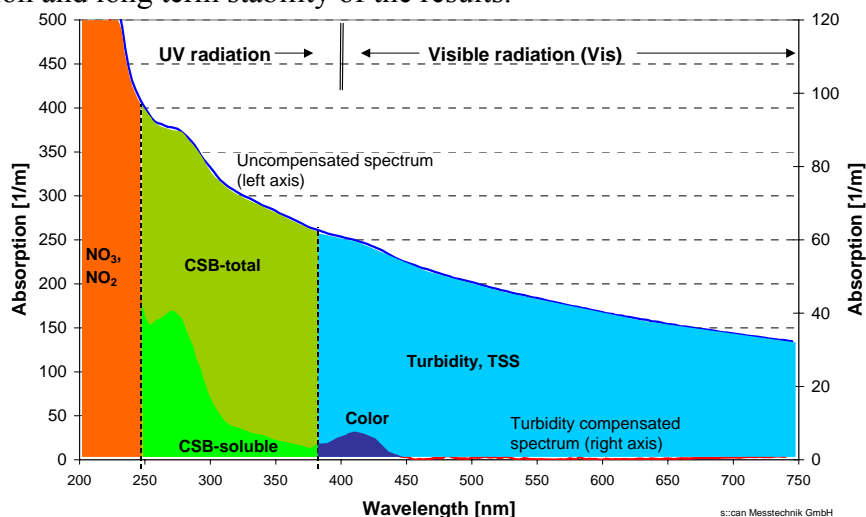


Figure 1: Absorption of different compounds within the spectrum from 200 to 750 nm

The spectrometer is built as a compact submersible sensor enabling measurement of optical spectra with laboratory quality directly in liquid media. Sensitivity can be adapted to the application demands by selecting the optical path length within a range of 1 - 100 mm. This opens a wide range of applications from ultra pure waters (DOC > 10 µg/l) up to concentrated industrial wastewater. The spectrometer is equipped with an auto-cleaning system using pressurized air, which has been proved to work extremely reliable (Winkler *et al.*, 2002). More information about the sensor can be found in Winkler *et al.* (2002) and Langergraber *et al.* (2003).

The sensor located in the secondary clarifier effluent of the WWTP Thunersee is an UV spectrometer equipped with a path length of 10 mm to enable the differentiation between nitrite and nitrate at TSS concentrations up to 15 mg/l (manufacturer specification). Physically 256 wavelengths are measured between 210 and 400 nm (resolution ca. 0.8 nm), which will be converted into a resolution of 1 nm for the calculation of the concentrations.

Sensor calibration

The calibration of the spectrometer is based on a Partial-Least-Square (PLS) regression for the parameters of concern. The PLS regression is an indirect chemometric model correlating the concentrations of the required determinants to spectra and especially accounts for concentration-spectra relationships. The number of significant principal components for the PLS regression is obtained from the minimum residual error (minimum $PRESS_{CV}$ value; $PRESS_{CV}$ value = predictive residual sum of squares based on cross validation; Otto, 1999). For every parameter under consideration a $PRESS_{CV}$ value is calculated. For multivariate calibrations of multiple parameters the mean value of the single $PRESS_{CV}$ values was used to determine the optimal number of principal components in the algorithm described by Langergraber *et al.* (2003). An improved algorithm uses different optimal numbers of principal components for each parameter. Additionally different optimal wavelengths (WL) can be chosen. The applied improved algorithm leads to better calibration results for the single parameters.

Figure 2 shows the spectrum from tap water spiked with nitrite and its de-convolution into the single substance spectra of nitrate and nitrite (4.3 mg/l NO_3 -N and 0.3 mg/l NO_2 -N). The remaining spectrum represents organic matter (1.1 mg/l TOC) which shows the highest absorbance for all wavelengths at about 250 nm. Both nitrate and nitrite have their highest absorbance in the lower wavelength region (210 – 240 nm) and the peaks for nitrate and nitrite at around 300 nm and 360 nm respectively are relatively small compared to the absorbance of organic matter. Therefore no distinction between nitrate and nitrite was possible using only one or two wavelengths (see results and discussion). With PLS regression based on 5 to 7 wavelength an accurate calibration can be achieved (Figure 4).

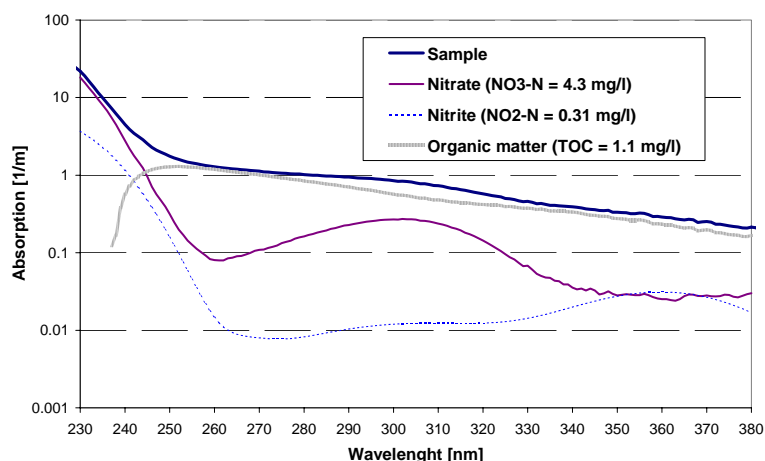


Figure 2: Spectrum for tap water (spiked with nitrite) and the de-convolution into spectra of NO_3 , NO_2 and org. matter

Figure 3 shows spectra for three different matrices with varying NO_2 -N concentrations. A slight increase in absorbance (logarithmic y-axis) over the whole wavelength region can be observed for the spectra from reverse osmosis (RO) water spiked with 1 and 2 mg/l NO_2 -N respectively. The content of organic matter and nitrate in the RO water was below 0.05 mg/l TOC and 0.05 mg/l NO_3 -N respectively. Due to the higher organic matter content in the tap water samples (0.7 mg/l TOC and 1.1 mg/l NO_3 -N) the differences for the same two NO_2 -N concentrations can be observed below

255 nm and around 360 nm. Using samples from the WWTP effluent (12.3 mg/l DOC and 6.2 mg/l $\text{NO}_3\text{-N}$) only below 245 nm differences in the spectra can be observed for the two $\text{NO}_2\text{-N}$ concentrations. Therefore only wavelengths in this region were determined as the optimal wavelengths for $\text{NO}_2\text{-N}$ by the calibration algorithm. It is obvious that the calibration algorithm will result in different optimal wavelengths for $\text{NO}_2\text{-N}$ for different matrices.

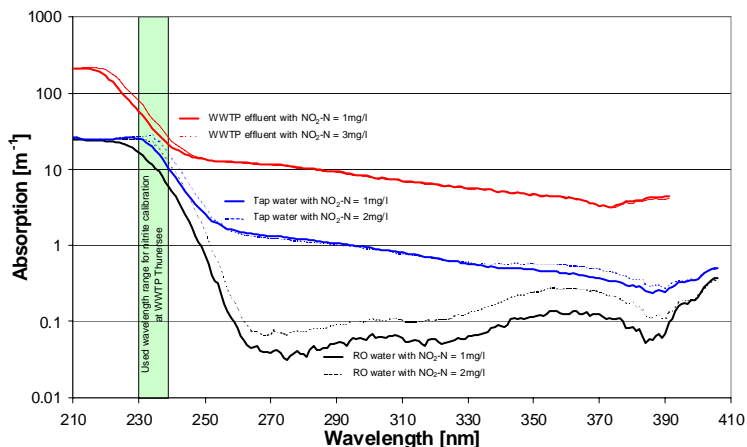


Figure 3: Spectra for three different matrices with different $\text{NO}_2\text{-N}$ concentrations

Application on effluent of WWTP Thunersee

The WWTP Thunersee (CH) treats the wastewater of 130'000 PE and receives mainly municipal wastewater. It is designed for full nitrification, pre-denitrification and EBPR according to the AAO scheme. The goal of monitoring nitrite was to evaluate the influence of low dissolved oxygen concentrations in the biological stage and especially the possible accumulation of nitrite in the effluent.

The spectrometer was installed in the effluent of the secondary clarifier. For the reference analysis the spectrometer was removed from the measurement location and put into a bucket with a grab sample of secondary effluent. Then several spectra were recorded within the bucket maintaining complete mixing. In order to secure the independence of the subsequent spectra – the auto cleaning was triggered after each measurement. For laboratory measurements a grab sample from the bucket was taken and analysed twice with Dr.Lange test kits ($\text{NO}_2\text{-N}$: LCK341, $\text{NO}_3\text{-N}$: LCK339/340, DOC: LCK383, COD: LCK414) using a CADAS 200 and gravimetrical TSS analysis.

Laboratory

Since the concentrations of the comparative nitrite measurements are all in the range between 0.06 and 0.26 mg N/l (Figure 5), a calibration on the measuring range of 0 to 3 mg N/l would imply a significant extrapolation on a weak basis. To overcome this lack of calibration data a nine step addition of stock solution (Merck, 1000 mg $\text{NO}_2\text{/l}$) on three different effluent matrices. The resulting 30 calibration samples were measured with the flow injection analysis method (FIA. ASIA, Ismatec AG, Glattbrugg, Switzerland) and with the spectrometer probe. To get information about the precision of the sensor, each measurement was performed three times.

RESULTS AND DISCUSSION

Except for nitrite all data measured at WWTP Thunersee were needed for calibration. Therefore no validation with independent measurements was possible. For nitrite the calibration was made with the calibration samples described above and the data from the WWTP Thunersee were used for validation.

Nitrite

The precision of the spectrometer for nitrite was analysed with three repeated measurements of each of the 30 calibration samples. The mean standard deviation for nitrite was 0.03 mg N/l. For nitrate and TSS the standard deviation for each of the three matrices was calculated to 0.07 mg N/l for nitrate and 1.12 mg/l for TSS respectively. The data show no dependency between standard deviation and concentration (ISO 8466-1, 1990).

Figure 4 shows a very good correspondence between lab and sensor values. Of course the values over 3 mg/l have a strong influence on the correlation, but without the three data points the correlation coefficient is still good with $R^2 = 0.977$ instead of 0.993. The width of the 95% confidence interval for the calibration curve is very narrow with 0.026 mg/l at the mean value of 0.94 mg N/l. The interval contains all possible calibration curves with a probability of 95%. This means that the precision is very accurate and the linear regression fits well with the data. The 95% prediction interval (also known as 95% confidence interval of a predicted value, Draper and Smith, 1981) is 0.14 mg N/l at the mean lab value. A future value should be in this interval with a probability of 95%.

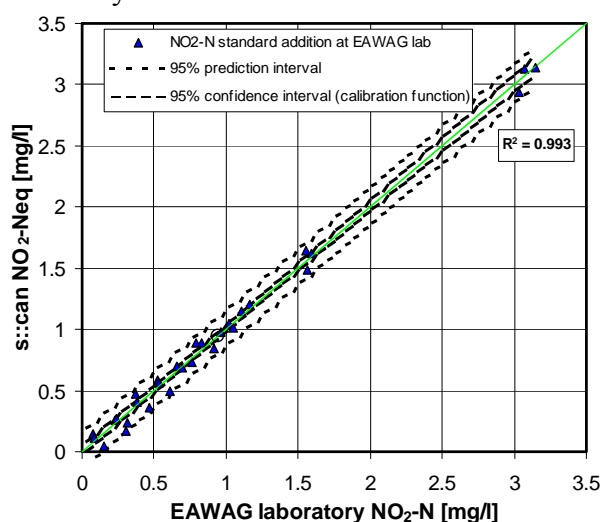


Figure 4: Calibration data for nitrite based on standard addition samples with 95%-confidence interval of the calibration function and 95% prediction interval (width = 0.14 mg/l at mean lab value of 0.94 mg NO₂-N/l).

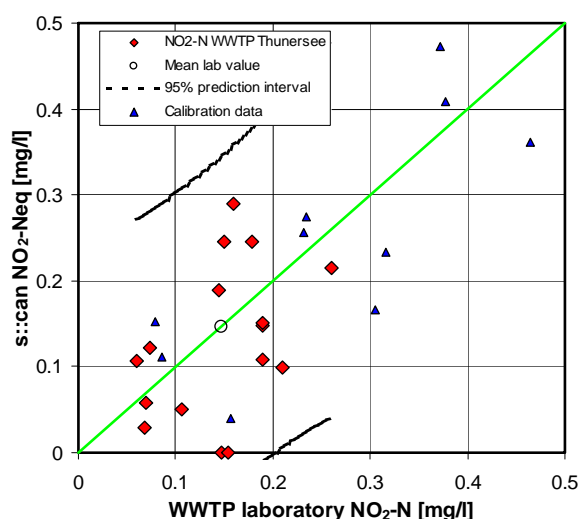


Figure 5: Validation data for nitrite based on WWTP effluent samples with 95% prediction interval (width = 0.2 mg/l at mean lab value of 0.15 mg NO₂-N/l)

In Figure 5 a validation is presented based on measurements in the effluent of the WWTP Thunersee. The working range is very small hence no accurate regression could be calculated. Therefore only the 95% prediction interval is shown based on an ideal calibration (normally the prediction interval is based on a previous regression analysis). For the calibration of nitrite five wavelengths (from 230 to 240 nm) were chosen by means of PLS regression described above. The criteria which calibration fits best is a compromise between longterm stability, trueness and precision. Great emphasis was placed on a robust calibration, therefore a low number of wavelength was chosen in order to desensitise the model.

Nitrate

Nitrate was calibrated using 49 comparative measurements (Figure 6). Since all data were used for calibration only the precision is stated as a 95% prediction interval. The width of the interval is 0.54 mg N/l at the mean laboratory value of 6.7 mg N/l. The correlation coefficient is strongly depending on the value at 17 mg N/l, but without this value the coefficient is still at 0.942 (instead

of 0.978). Also for nitrate five wavelengths (from 230 to 240 nm) gave good longterm stability and accuracy.

Soluble COD

For the calibration of soluble COD only 12 measurements are available in the range between 17.4 and 21.4 mg COD/l (Figure 7). Therefore a statement about the precision for future measurements in a wider range means an extrapolation and is therefore not very accurate. Nevertheless for the covered working range the precision is very good with a 95% prediction interval of 0.93 mg COD/l at the mean laboratory value of 19.3 mg COD/l. Five wavelengths (from 250 to 340 nm) were selected by the calibration algorithm as the optimal number of wavelengths for the correlation to the reference measurements.

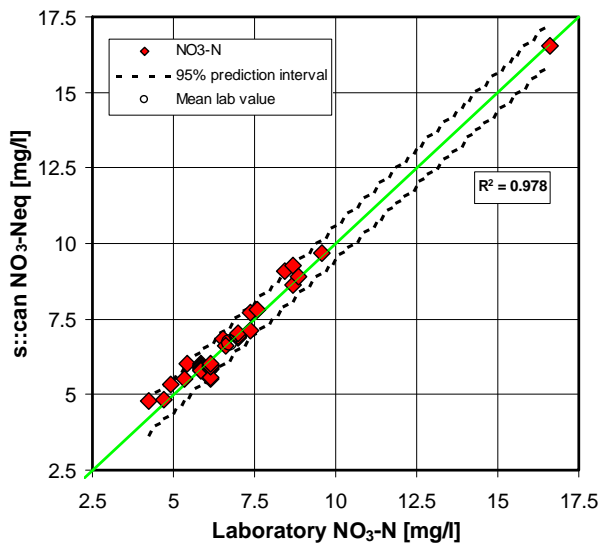


Figure 6: Calibration data for nitrate based on WWTP effluent samples with 95% prediction interval (width = 0.54 mg/l at mean lab value of 6.7 mg NO₃-N/l)

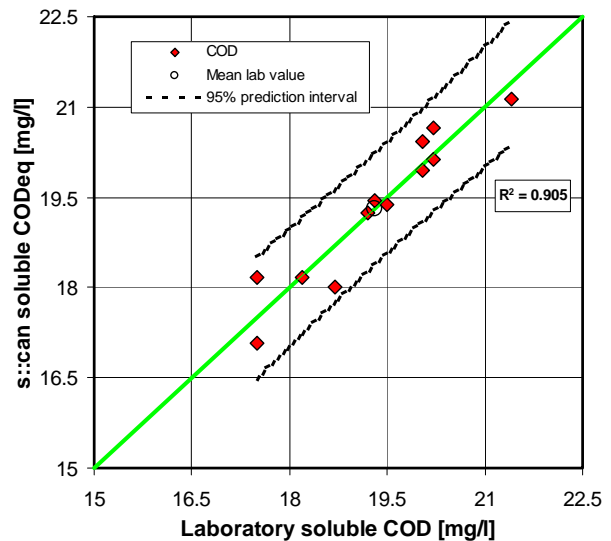


Figure 7: Calibration data for soluble COD based on WWTP effluent samples with 95% prediction interval (width = 0.93 mg/l at mean lab value of 19.3 mg COD/l)

DOC

The DOC calibration resulted in the use of six wavelengths (from 290 to 330 nm). The calibration seems to be less accurate than for soluble COD, but the working range covered with measurements is still very small and the amount of comparative measurements is also limited to 12. The used Dr.Lange test kits (DOC: LCK383; COD: LCK414) should be more accurate for the COD since for the DOC test the analytical steps are more sophisticated. The test kits are specified from Dr.Lange (under standard conditions according to DIN 38402-A51) for a guaranteed precision stated as coefficient of variation of 5% for DOC and 3% for COD respectively. Of course this does not explain the measured differences. Perhaps the method is not sensitive enough to the changing matrix. Future evaluations should be performed using standard methods with a thermal digestion.

Using the lab measurements and the calibration described above the 95% prediction interval amounts to 9.1 mg DOC/l at the mean laboratory value of 9.7 mg/l. Regarding Swiss effluent limits of 10 mg DOC/l (>2000 PE) the accuracy is not suitable to monitor the effluent quality.

TSS

For the TSS calibration 44 comparative measurements were used (including the measurements in the EAWAG lab). The number of chosen wavelengths for calibration amounts to 7 (from 230 to 330 nm). The precision of 5.5 mg TSS/l (95% prediction interval at mean laboratory value of 13.5 mg/l) is not very accurate regarding Swiss effluent limits of 15 mg TSS/l (>10'000 PE). The

reason for the unsatisfying result is that the used spectrometer probe only measure in the wavelength region between 210 and 400 nm. Good results for TSS can only be obtained by using an UV/VIS spectrometer due to the fact that the wavelength range of the visible light has the highest correlation for TSS as for turbidity.

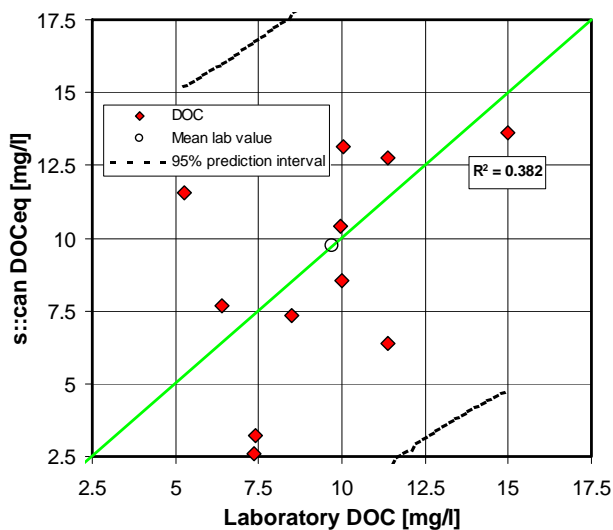


Figure 8: Calibration data for DOC based on WWTP effluent samples with 95% prediction interval (width = 9.1 mg/l at mean lab value of 9.7 mg DOC/l)

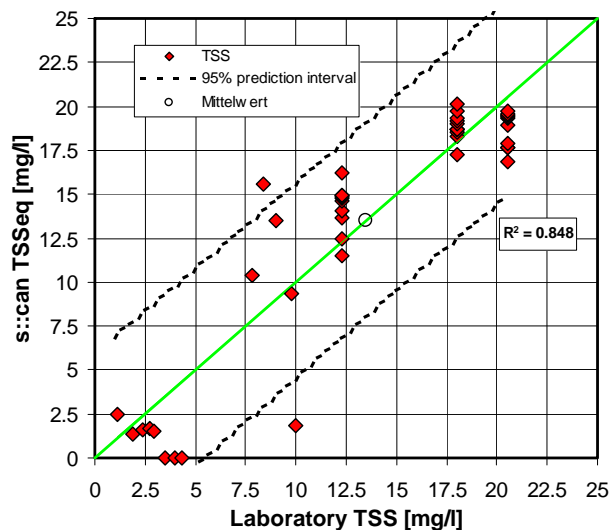


Figure 9: Calibration data for TSS based on WWTP effluent samples with 95% prediction interval (width = 5.5 mg/l at mean lab value of 13.5 mg TSS/l)

Comparison with single-wavelength calibrations

Table 1 compares the correlation coefficients R^2 for single-wavelength calibrations and the calibrations with the multivariate calibration algorithm. For single-wavelength calibrations the wavelength with the maximum correlation coefficient is shown. The same wavelength regions as for the multivariate calibration (230 to 390 nm) and the same number of reference data as described above were used. It can be clearly shown that no distinction between the substances was possible using only one wavelength. Using the multivariate calibration algorithm based on PLS regression accurate calibration can be achieved for nitrite, nitrate, and soluble COD.

Table 1. Comparison of the correlation coefficients R^2 for single-wavelength calibrations (the number in the brackets give the optimal wavelength in nm) and the calibrations with the multivariate calibration algorithm.

	Nitrite	Nitrate	Soluble COD	DOC	TSS
Single-wavelength calibration	0.139 (230)	0.320 (230)	0.316 (230)	0.183 (234)	0.326 (378)
Multivariate calibration algorithm	0.993	0.978	0.905	0.382	0.848

CONCLUSION

The tested spectrometer probe was applied in the effluent of the WWTP Thunersee (CH). Except for nitrite all data were used for calibration, a validation is not available and should be carried out in the future. For nitrite the working range covered with measurements was so small, that an addition of nitrite stock solution to three different matrices was carried out in the EAWAG laboratory. These data were used for the sensor calibration. Good results were achieved for the precision of nitrite and nitrate. A differentiation between nitrite and nitrate in the WWTP effluent is only possible, if the TSS concentration does not interfere the measurement of nitrate and nitrite. The measurements at WWTP Thunersee do not show limitations up to a TSS concentration of 20.5 mg TSS/l, which is higher than the manufacturer specification of 15 mg TSS/l. Future evaluations should be made, up to which TSS concentration the interferences are neglectable.

The results for soluble COD only cover a working range between 17.4 and 21.4 mg COD/l, but the precision is with less than 1 mg/l (95% prediction interval at 19 mg/l) very promising. Future tests have to confirm these results for a broader measuring range.

The achieved precision for DOC is worse than for soluble COD and does not fulfil the requirements regarding Swiss effluent limits. It should be tested, if a calibration with data using a standard method instead of the test kits and more and better spreaded data will lead to a higher precision.

The TSS calibration fails, since the used spectrometric probe is only capable of measuring the UV wavelength range between 210 and 400 nm. To obtain good calibration results also for TSS the evaluation of the wavelength range of the visible light (up to 750 nm) and therefore the use of a UV/VIS spectrometer would be required.

To sum up the used UV spectrometer gave promising results, which have to be confirmed with validation data. A better calibration without extrapolation is needed to guarantee accurate measurements in the complete measuring range. For limited working ranges a calibration procedure with calibration samples made from different matrices was introduced and amounts in very good results for the precision. This method is only suitable for single substances like nitrite or nitrate. For lump parameters like COD or DOC a dilution experiment is needed since no representative stock solution is available. This implies high concentrations in order to cover a wide working range.

It was shown that the calibration results can not simply be applied on other locations and matrices without specific calibration. Since the measuring method is always only a correlation between absorbance and concentration and not a direct measurement a regular monitoring of the measurements has to be considered. The effort for the specific calibration was rather high. In order to get a 'global calibration', which can be adapted e.g. with a simple two-point calibration the results have to be validated at different plants.

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REFERENCES

- DIN 38 402-51 (1986). Deutsche Einheitsverfahren zur Wasser-, Abwasser und Schlammuntersuchung. Allgemeine Angaben (Gruppe A). Kalibrierung von Analyseverfahren, Auswertung von Analyseergebnissen und lineare Kalibrierfunktionen für die Bestimmung von Verfahrenskenngrößen (A51). Normenausschuss Wasserwesen (NAW) im DIN Deutsches Institut für Normung e.V., Beuth Verlag GmbH, Berlin [*in German*].
- Draper N.R. and Smith H. (1981). *Applied regression analysis*. 2nd edn., Wiley, New York.
- Gujer W. (1999). *Siedlungswasserwirtschaft*. Springer-Verlag Berlin, Heidelberg, New York [*in German*].
- ISO 8466-1 (1990). Water quality – Calibration and evaluation of analytical methods and estimation of performance characteristics. Part 1: Statistical evaluation of the linear calibration function. ISO, Geneva, Switzerland.
- Langergraber, G., Fleischmann, N., Hofstaedter, F. (2003). A multivariate calibration procedure for UV/VIS spectrometric quantification of organic matter and nitrate in wastewater. *Wat.Sci.Tech.* **47**(2), 63-71.
- Otto M. (1999): *Chemometrics: Statistics and Computer Application in Analytical Chemistry*; Wiley-VCH Verlag GmbH, Weinheim, Germany.
- Winkler S., Rieger L., Thomann M., Siegrist H., Bornemann C. and Fleischmann N. (2002). In-line monitoring of COD and COD-fractionation: Improving dynamic simulation data quality. In: IWA (ed.): *Proceedings of the 3rd IWA International World Water Congress*, April 7-12, 2002, Melbourne, Australia (paper No. e21604a).