

On-line and in-situ measurement of turbidity and COD in wastewater using UV/VIS spectrometry

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Abstract

Advanced treatment plant and sewer network control is a promising application of modelling in the field of urban wastewater management. At the same time there are only vague ideas about the measurement techniques that would be necessary for model based real time prognosis and control. One of the major tasks on the way towards online modelling is the search for and the validation of measurement techniques. An UV/VIS spectrometer (“spectro::lyser”) was successfully used for measuring organic matter at the highly dynamic inflow of a wastewater treatment plant. This poster describes the UV/VIS spectrometer, the calibration procedure and the results obtained.

Keywords

in-situ analysis, on-line monitoring, UV/VIS sensor, wastewater.

INTRODUCTION

Advanced treatment plant and sewer network control is a promising application of modelling in the field of urban wastewater management. At the same time there are only vague ideas about the measurement techniques that would be necessary for model based real time prognosis and control. One of the major tasks on the way towards online modelling is the search for and the validation of measurement techniques.

One task of the presented demonstration project is the development and validation of methods to quantify pollutant loads in real time. The project aims at the integrated management and control of a municipal sewer network and the treatment plant itself, based on information from dedicated measurements.

The devices to be selected for the purpose have to comply with several criteria that reflect especially the demanding situation in sewers. These criteria concern simple technical requirements like power supply but also more sophisticated features like long term stability, fouling prevention and self diagnosis.

One major step beyond the state of the art is expected to be done with the help of a submersible UV/VIS spectrometer (“spectro::lyser” by s::can Messtechnik GmbH, Vienna). This spectrometer was successfully used for measuring turbidity and organic matter parameters at the inflow of a wastewater treatment plant.

It is state of the art to measure light attenuation at one or two fixed wavelengths. The conventional measurement at 254 nm in order to quantify the content of dissolved organic carbons (in some cases compensated with the measurement at 350 nm) showed to be insufficient for the desired measurement. The selected new method is able to solve open questions concerning cross sensitivities, compensation or background elimination.

Feasibility studies indicate strongly that spectrometric measurements can give not only a surrogate for total organic carbon but also for different fractions of the organic load. Different degradation processes affect the spectra in a different manner. Significantly different spectral features correlate to significantly different properties of the organic load. However, this paper deals with results concerning surrogates for conventional parameters, especially BOD, COD, and filtrated COD (COD_f).

An other advantage of sensor measurements as described here is that the costs do not depend on measurement frequency. Therefore they are especially suitable for the monitoring of highly dynamic systems like rainfall runoff in municipal combined sewers and wastewater treatment plants.

MATERIALS AND METHODS

The “spectro::lyser” (Figure 1) is a spectrometric probe of about 0.6 m length and 4.5 cm diameter, records light attenuation in the wavelength region between 200 nm and 750 nm and displays and/or communicates the result in real time. It is a 2-beam 256 pixel UV/VIS spectrometer, with a Xenon lamp as a light source. A path length of 10 mm is used for raw wastewater. All of the controller electronics including a data logger and a water level meter are included in a 44 mm tubular anodised aluminium housing. The communication is via RS232 or RS485 interface. The measurement takes place directly in-situ without sampling or sample treatment. A single measurement typically takes about 15 seconds.



Figure 1. “spectro::lyser” by s::can Messtechnik GmbH, Vienna.

For the compensation of turbidity a mathematical equation was developed which describes the relationship between scattering intensity and wavelength as a function of the particle diameter based on the basic relationships given in Huber and Frost (1998). The turbidity compensation feature uses the original spectrum and estimates two parameters of the turbidity function. The results of the turbidity compensation showed to be very sensitive to the initial values of these parameters.

The company provides a global calibration for a number of parameters valid for typical municipal raw wastewater composition. Usually high correlation coefficients can be achieved using this standard parameter set. For many purposes such as plant control the global calibration often delivers sufficient results.

Due to the different composition of wastewaters, e.g. with significant industrial contributions, a second step for calibration can be required to enhance the accuracy. The local calibration uses laboratory analysis from samples taken from the actual wastewater under consideration. The calibration procedure comprises the following steps: validation of the spectral plausibility to exclude wrong spectra at the very beginning, and a recursive procedure including a multivariate calibration using a PLS-regression (e.g. Legendre and Legendre, 1998), a multiple cross validation (e.g. Otto, 1997), and the detection and elimination of outliers. The recursive procedure is repeated until a good calibration result is obtained. It is also possible to run the local calibration procedure during operation.

RESULTS AND DISCUSSION

The “spectro::lyser” was tested at the influent of a wastewater treatment plant for three weeks. The measurement interval was 2 minutes. The estimated COD values using the standard parameter set of the global calibration for the whole period and for a single day are shown in Figure 2 and Figure 3 respectively. The correlation coefficient between the on-line COD values and grab samples analysed at the plants laboratory was about 90 %. During three weeks of operation the “spectro::lyser” was working without cleaning and maintenance work. No trends, which are a indicator for pollution of the measuring window, could be observed. The criteria of long term stability and prevention of fouling could be achieved.

In Figure 2 and Figure 3 it becomes evident that the high measurement frequency gives a different type of information, compared to grab samples. Figure 3 shows the addition of internal process water in the morning and the cleaning intervals of the screen (10 minutes) at about 4:00 p.m. It is obvious that this type of "pollutogram" contains information which is totally different from an "average COD".

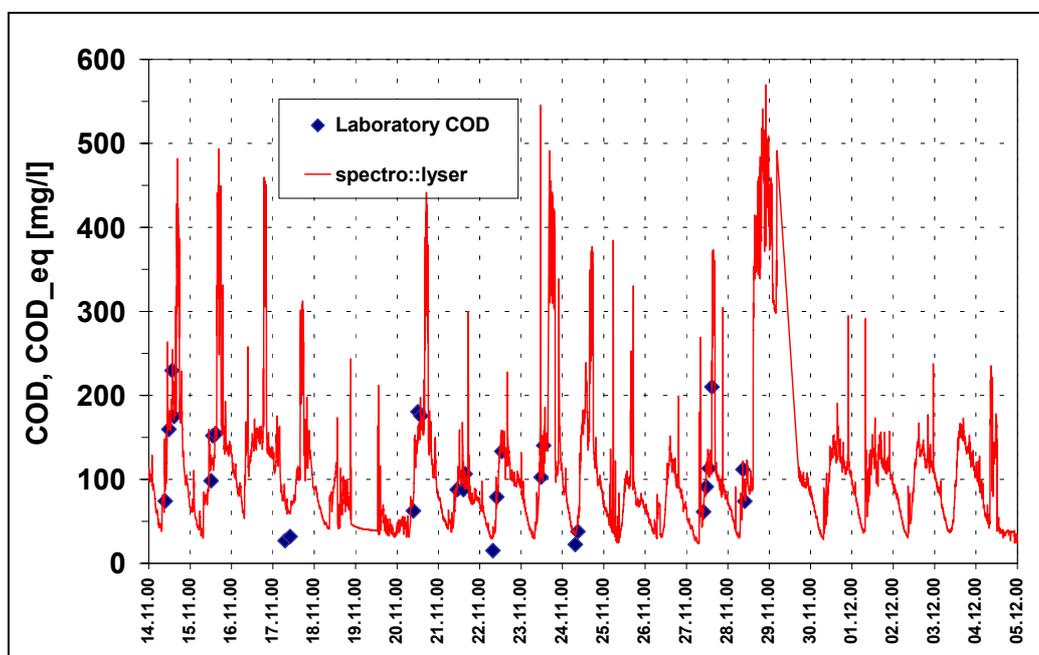


Figure 2. On-line and laboratory COD during the testing period of 3 weeks.

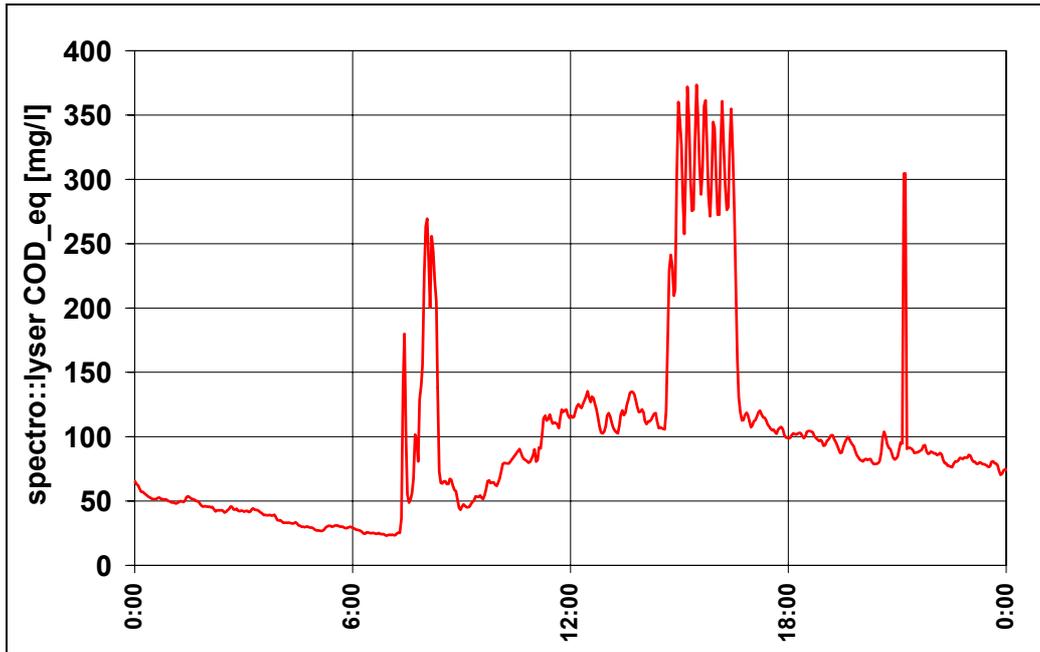


Figure 3. On-line COD for a single day.

For the local calibration 39 data points were used. For these data points analysis of COD, filtrated COD, and BOD were available. None of these data points was excluded due to its non-plausibility, 4 data points were detected as outliers and eliminated. The results shown for the local calibration therefore use 35 data points.

The local calibration increases the correlation coefficient for COD only to a little amount (92 %). Figure 4 shows 1 out of 100 cross validations performed. The data used for validation (circles) scatter no more around the regression line than the data from which the regression line is calculated from (rhombuses). Figure 4 also shows the stability of the obtained calibration: a number of coincidental chosen data points fits the calibration that results from the remaining data points.

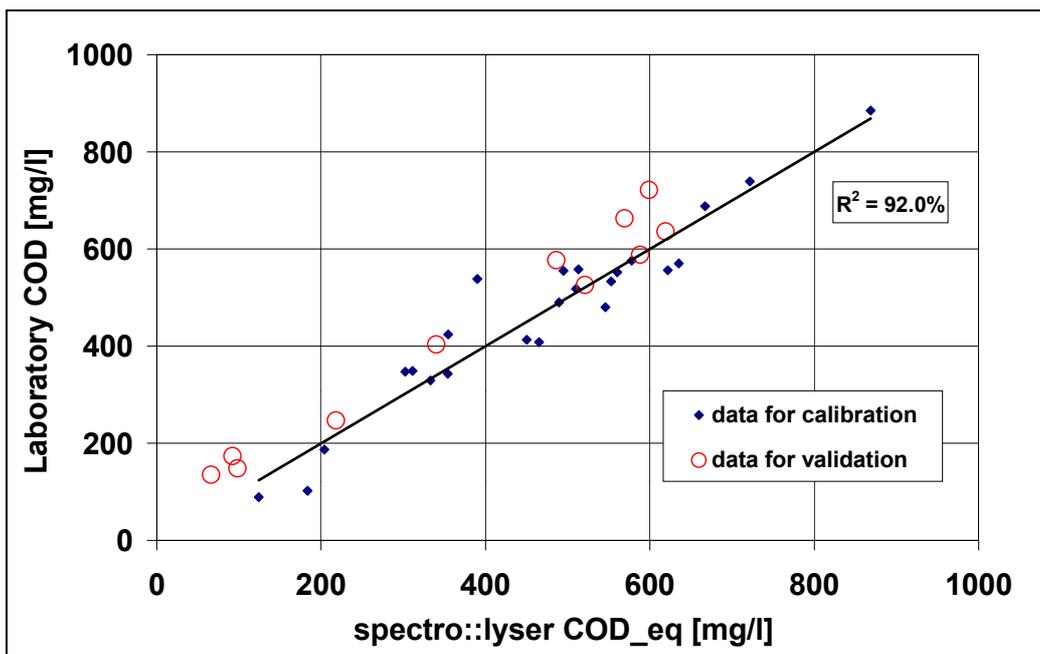


Figure 4. Calibration and validation data of COD.

Figure 5 gives results of cross validations performed for filtrated COD (CODf) and BOD, the correlation coefficient achieved was 96.7 % and 88.2 % respectively. The results show a similar behaviour as obtained for COD.

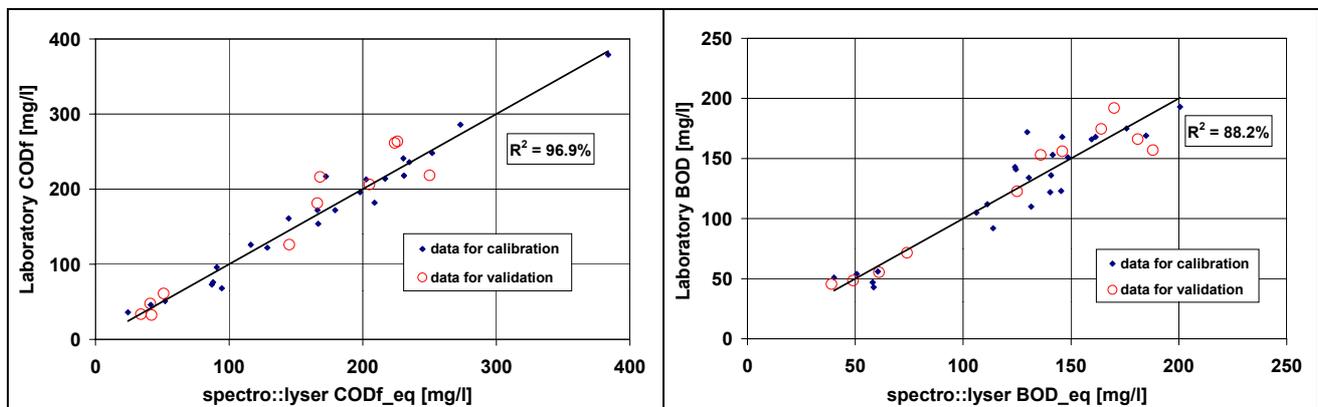


Figure 5. Calibration and validation data of CODf (left) and BOD (right).

As expected the correlation coefficient was highest for filtrated COD. This is due to elimination of the particulate matter for the analysis of filtrated COD. The particulate matter is known as the main contribution to the sampling error (Haider and Haider, 1998) and therefore also contributes to the “total error of measurement” of COD and BOD.

Interpretation of the results has to consider the “total error of measurement” (TOM) which consists of sampling, sample transport and storage error and a usually very small analytical error. Often comparison of field and lab methods only take the analytical error into account and neglect other elements of the sample to lab chain. Unfortunately the major error contributions are unknown in most cases, nevertheless this fact has to be kept in mind. The errors of the sample to lab chain can be avoided by in-situ measurement devices like the “spectro::lyser” and therefore the TOM is reduced significantly.

Another consideration concerns to which extent a sample is representative. Going beyond comparison of sampling and lab error it has to be taken into account that frequent measurement eliminates all statistical problems concerning representativity.

SUMMARY

This poster deals with results concerning surrogates for conventional parameters for organic matter (BOD, COD, and filtrated COD) in the influent of wastewater treatment plants. The measurements using the “spectro::lyser” have shown a sufficient correlation with reference methods especially when taking the “total error of measurement” into account.

At the same time the “spectro::lyser” meets other criteria like affordability at a desired measurement frequency. The high measurement frequency also avoids problems concerning the statistical representativity of a sample. The cost of sensor measurements does not depend on measurement frequency. Therefore in-situ measurement devices like the “spectro::lyser” are especially suitable for the monitoring of highly dynamic systems like rainfall runoff in municipal combined sewers and influents of wastewater treatment plants.

The “spectro::lyser” has proved to be a valuable device for on-line and in-situ measurements of organic matter in highly dynamic systems with high accuracy and only little maintenance work

needed. Defined criteria such as long term stability and fouling prevention are fulfilled completely. Using the “spectro::lyser” enables the quantification of organic loads of wastewater treatment plants in real-time and is therefore a basic requirement for on-line prognosis and control applications.

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