

ON-LINE NITRATE MONITORING IN SEWERS USING UV/VIS SPECTROSCOPY

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ABSTRACT

The paper describes on-line and in-situ measurements of the nitrate nitrogen concentration in a sewer. The measurements were carried out to enable automated control of iron nitrate dosing to prevent odour problems. A submersible UV/VIS spectrometer (spectro::lyser by s::can Messtechnik, Vienna) was used for the measurements. It utilises the whole UV/VIS range (200-750 nm) for simultaneous measurement of nitrate, COD, and TSS with just one single instrument. The so-called global calibration for nitrate (based on UV/VIS spectra of municipal waste water of different origin) performed well, no local calibration was necessary. The ex-proof version of the spectrometer was installed directly in the sewer and measured in real-time. An optical path length of 2 mm showed the best results for monitoring NO₃-N in sewage water. The instrument is equipped with a very effective auto-cleaning system using pressured air. A maintenance interval of > 4 weeks seems to be sufficient, and only a manual cleaning of the instrument should be carried out.

KEYWORDS

On-line monitoring, odour control, sewer lines, UV/VIS spectroscopy.

INTRODUCTION

The paper describes on-line and in-situ measurements of the nitrate nitrogen concentration in a sewer. The measurements were carried out to enable automated control of iron nitrate dosing to prevent odour problems. The odour problems at this location were caused by too low flow velocities in the sewer that led to low ORP and anaerobic processes in the sewer solids, biological generation of hydrogen sulphide (Nowak and Schattovits, 2003). Iron nitrates are added to prevent odour: iron precipitates sulphur compounds and nitrate increases ORP (Matsché, 2003).

MATERIAL AND METHODS

The UV/VIS spectrometer

The instrument used is a submersible UV/VIS spectrometer (Figure 1), a spectrometric probe of about 0.6 m length and 44 mm diameter. It records light attenuation in the wavelength region between 200 nm and 750 nm and displays and/or communicates the results in real time. The instrument is a 2-beam 256 pixel UV/VIS spectrometer, with a Xenon lamp as a light source. A single measurement typically takes about 30 seconds.

The measurement takes place directly in-situ without sampling or sample treatment. Thus, measurement errors due to sampling, transport, storage, dilution etc. are not relevant. The instrument is equipped with an auto-cleaning system using pressurised air. Due to the compact size the sensor can be easily applied in 2" bore holes, e.g. for groundwater

monitoring (Langergraber *et al.*, 2002a). An ex-proof version is available for sewer and industrial applications in explosive atmosphere.

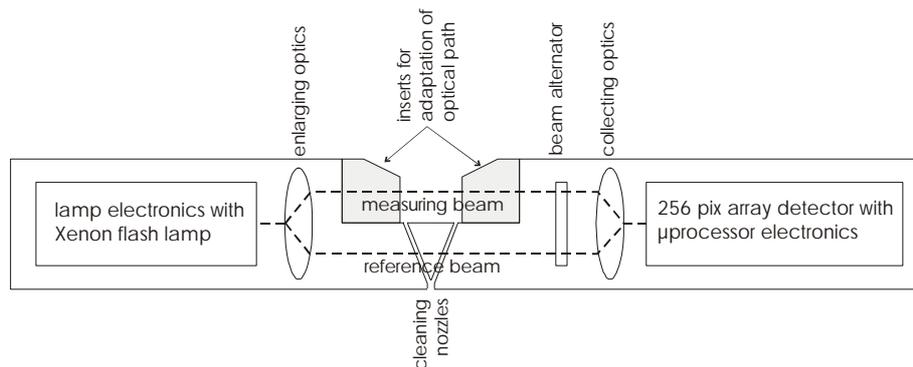


Figure 1. UV-VIS submersible spectrometer.

The entire measurement procedure is controlled by on-board electronics which are included in the 44 mm tubular anodised aluminium housing. The communication is possible via RS232 or RS485 interface. The power supply can be by means of AC 220 V/50 Hz, 110°V/60°Hz or DC 12-24 V, respectively. The low power consumption eases field application by means of battery or solar power supply. The probe can be equipped with a temperature sensor, a pressure sensor for measuring the water level meter and a data logger on board. The data logger is capable to store complete absorption spectra of 1 month at a measuring interval of 30 minutes.

The path length can be adjusted from 1-100mm opening a wide range of applications from ultra pure waters (DOC > 10 µg/l) up to concentrated wastewaters with a COD of several 1000 mg/l (e.g. Langergraber *et al.*, 2002b). A path length of 5 mm is usually used for wastewater applications. Spectrometric measurement methods are defined for single substances (e.g. Nitrate, Nitrite, Benzene, Phenol) as well as for surrogate parameters (e.g. SAC254, Turbidity, TSSeq, CODEq, TOCeq, DOCEq).

Turbidity compensation

A major influence on in-situ absorption measurements is turbidity due to suspended substances that cause light scattering, shading and thus influences absorption over the entire spectrum. Turbidity compensation has two tasks: the measurement of turbidity / suspended solids and baseline compensation for the measurement of dissolved substances. A mathematical equation describing the relationship between scattering intensity and wavelength as a function of the particle diameter based on the basic relationships given by Huber and Frost (1998) and the well known spectral shape caused by suspended solids, which depends upon the wavelength with a factor λ^x , where x depends on the particle diameter, is used. The turbidity compensation feature uses the original spectrum and estimates two parameters of the turbidity function.

Sensor calibration

For typical municipal wastewater a so-called global calibration is provided as default configuration of the UV/VIS spectrometer. Usually high precision can be achieved using this standard parameter settings. For many purposes such as plant control precision is more important than trueness and the global calibration often delivers sufficient results. By a second calibration step (local calibration) improvements concerning trueness, precision and long term stability of the results can be achieved.

Global calibration. The UV/VIS spectrometer provides a global calibration that 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 (Danzer *et al.*, 2001) and the applied PLS regression especially accounts for concentration-spectra relationships (Otto,1999). The broad range of available wavelengths allows high flexibility for the choice of the best correlating wavelengths for the calibration function and the avoidance of cross sensitivities. This is an advantage compared to systems, which provide absorption measurements of a single or two wavelengths only. A detailed description of the calibration procedure implemented is given in Langergraber *et al.* (2003).

Local calibration. Due to the different composition of wastewaters, e.g. with significant industrial contributions, a local calibration can be required. The local calibration is based on grab samples analysed for the parameters of interest and can be performed without demounting of the probe. The experience showed that most of the times the laboratory data are the critical part of the calibration procedure. Therefore it is essential to guarantee the quality of the laboratory measurements (regarding laboratory analysis method, measurement range, sampling errors, identity of samples and randomisation of sampling) to obtain good calibration results. The local calibration can be performed either by running a complete calibration procedure based on PLS regression as described by Langergraber *et al.* (2003). However, the experience showed that a simple change of the slope-intercept of the regression function that can be easily done by the user is enough to improve the calibration significantly.

RESULTS AND DISCUSSION

The expected measurement range was 0 to 50 mg/l NO₃. Figure 2 shows the global calibration (correlation coefficient $R^2 = 95\%$) and the 95 % confidence interval. The global calibration for nitrate performed well, no local calibration was necessary. Figure 3 shows a typical daily pattern measured by using 2 mm path length. Additionally analysis results from reference samples are shown. Additionally, the reference samples were also analysed for COD. Also the spectral COD measurement correlated well with the reference data ($R^2 = 77\%$). This measurements can be used e.g. to predict the organic load of wastewater treatment plants.

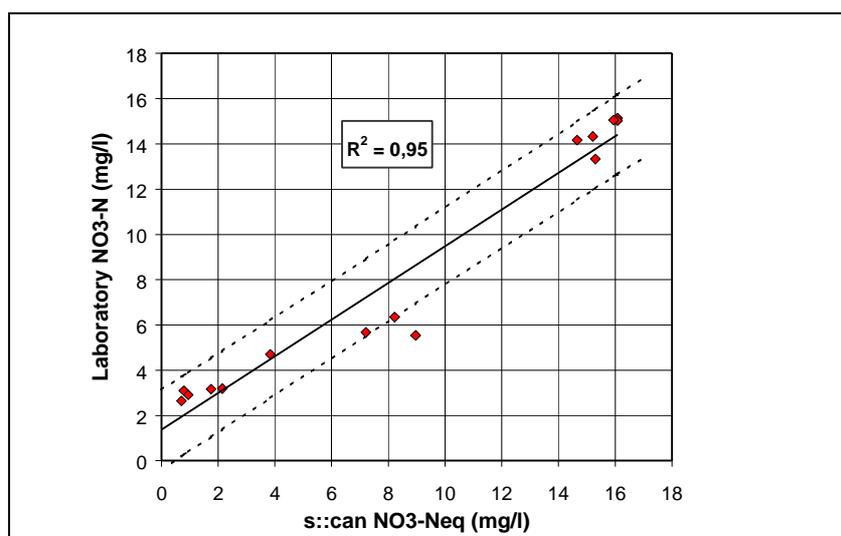


Figure 2. Global calibration and 95 % confidence interval for NO₃-N.

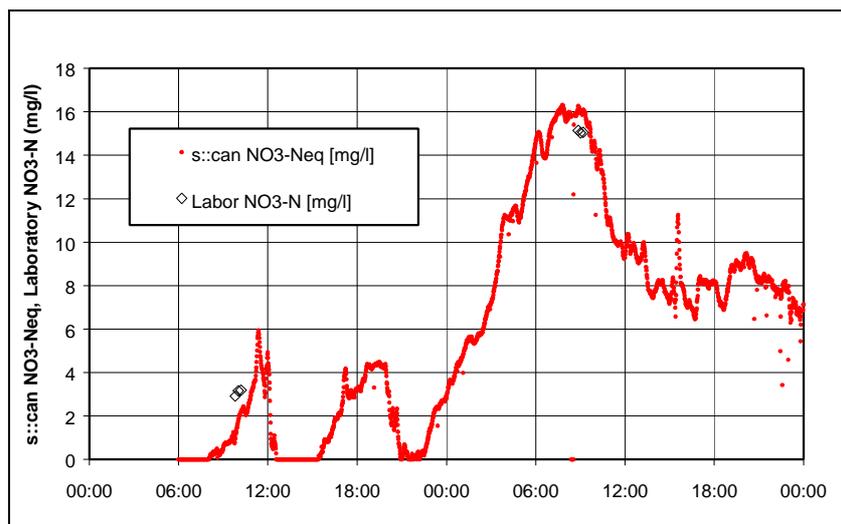


Figure 3. Measured daily pattern for NO₃-N.

The instrument was installed for periods of 2°weeks using 5 mm path length and 4 weeks using 2 mm path length respectively. For monitoring NO₃-N in sewage water containing high loads of suspended solids a path length of 2 mm should be used, for monitoring CODEq and TSSeq also 5 mm can be used. Turbidity compensation is essential for monitoring dissolved substances like NO₃-N in municipal sewage water.

CONCLUSIONS

Using the submersible UV/VIS spectrometer it was possible to measure nitrate in sewers on-line and in-situ. For odour control the automated control of iron nitrate dosing is possible. The automatic cleaning device using pressurised air achieved that also during the 4 week period no maintenance of the instrument was required. A maintenance interval of > 4 weeks seems to be sufficient, and only a manual cleaning of the instrument should be carried out.

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