

Detection of (unusual) changes in wastewater composition using UV/VIS spectroscopy

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Abstract

Using measurements of the whole UV/VIS spectrum enables to monitor changes in wastewater concentration as well as in wastewater composition. Operators of wastewater treatment plants benefit when changes of concentration and/or composition of industrial inlets can be detected and therefore a possible failure of the treatment plant performance can be avoided. The instrument used is a submersible UV/VIS spectrometer (spectro::lyser by s::can Messtechnik, Vienna) that utilises the whole UV/VIS range between 200 and 750 nm. With just one single instrument nitrate, organic matter and suspended solids can be measured simultaneously. The spectrometer is installed directly in the process and measures in real-time. It is equipped with a very effective auto-cleaning system using pressured air that enables measurements at the influent of a wastewater treatment plant or directly in the sewer for several weeks (> 4) without maintenance. The paper shows influent measurements at a wastewater treatment plant where significant changes in the wastewater composition occurred. Time series and fingerprints are shown that enabled a identification of wastewater composition changes and polluters.

Keywords

Industrial wastewater, in-situ, monitoring, on-line, polluter identification, UV/VIS spectroscopy, wastewater composition.

INTRODUCTION

For monitoring of the pollutant load of a wastewater treatment plant a submersible UV/VIS spectrometer (spectro::lyser by s::can Messtechnik, Vienna) for in-situ and on-line measurements was used. The submersible spectrometer utilises the UV/VIS range (200-750 nm) for simultaneous measurement of nitrate, organic matter, and suspended solids with just a single instrument. The miniaturised UV/VIS spectrometer is a probe installed directly in the process. Therefore it requires no sampling, no sample preparation, and no reagents. The spectrometer is equipped with an auto-cleaning system that prevents biofouling on the optical devices. The operation of the instrument at wastewater treatment plant influents or directly in sewers for several weeks (> 4) without maintenance is possible.

For the operation of wastewater treatment plants the early detection of changes in wastewater influent quality is a necessity to prevent a possible failure of the treatment plant performance. Quality changes includes both changes of concentration and composition of the wastewater. Changes of the wastewater composition – especially changes of industrial inlets – can lead to operational problems and/or a possible inhibition of the biochemical degradation processes.

The spectral information of the whole UV/VIS range clearly shows the changes in the composition of the organic matter. This information can not be obtained from conventionally used sum parameters like TOC, DOC or TSS. The paper describes the used instrument and shows time series and fingerprints of measurements at a wastewater treatment plant influent where changes in the composition of the wastewater could be detected.

MATERIALS 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.

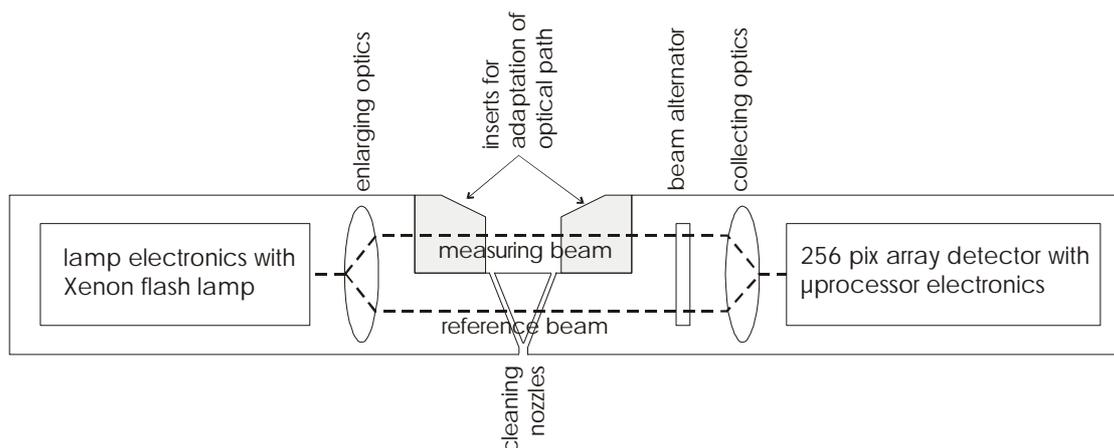


Figure 1. UV-VIS submersible spectrometer.

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.*, 2002). An ex-proof version is available for sewer and industrial applications in explosive atmosphere.

The entire measurement procedure is controlled by on-board electronics which are included in the 44 mm tubular anodised aluminium housing. The communication is 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 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. 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 solid 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 global calibration is provided as default configuration of the UV/VIS spectrometer. Usually high precision can be achieved using this standard parameter set. 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 regression 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

Calibration results

A local calibration for TOC and DOC was carried out by the plant's operator using a simple slope-intercept change of the regression function provided by the global calibration. The correlation coefficients R^2 for TOC and DOC were 0.82 and 0.68 respectively. Although the correlation coefficients are not very high the laboratory results matched the on-line data well. The match was sufficient for the application and a time-consuming local PLS calibration therefore was not performed. For TSS the global calibration was used.

Time series

Figure 2 shows the time series of TOC_{eq} in influent of the wastewater treatment plant for a period of 3 weeks and the laboratory results of the grab samples analysed during this period. In general there is a good correlation between the TOC_{eq} concentrations derived from the UV/VIS spectra and

the grab samples. Typical daily fluctuations can be observed except on July 31 where the concentrations were low and do not show this typical pattern. This low concentration was caused by a rainfall event. At the end of the investigation period a high fluctuation of the concentration could be observed.

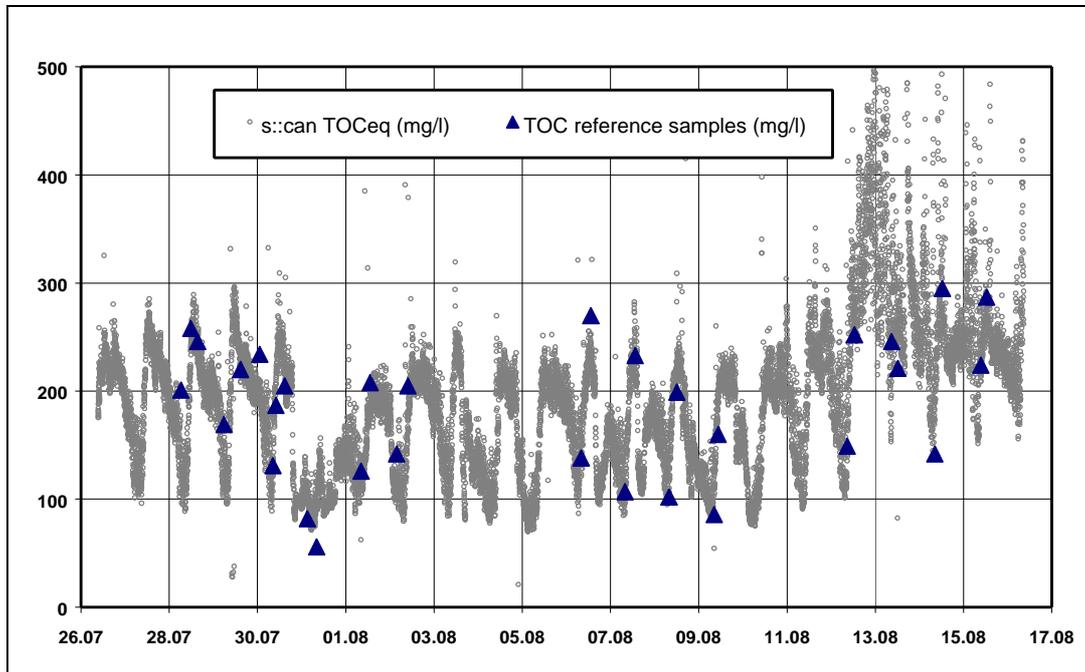


Figure 2. Time series TOCeq and laboratory results for the whole investigation period.

Figure 3 shows a detailed picture of the measurement for a period where high fluctuations can be observed (August 13, between 2:00 and 8:00 hours). The high fluctuations could have been interpreted as failure of the instrument. However, the measurements (measurement interval: 2 minutes) show that these fluctuations were not caused by an error of the instrument but by actual high variations of the wastewater quality.

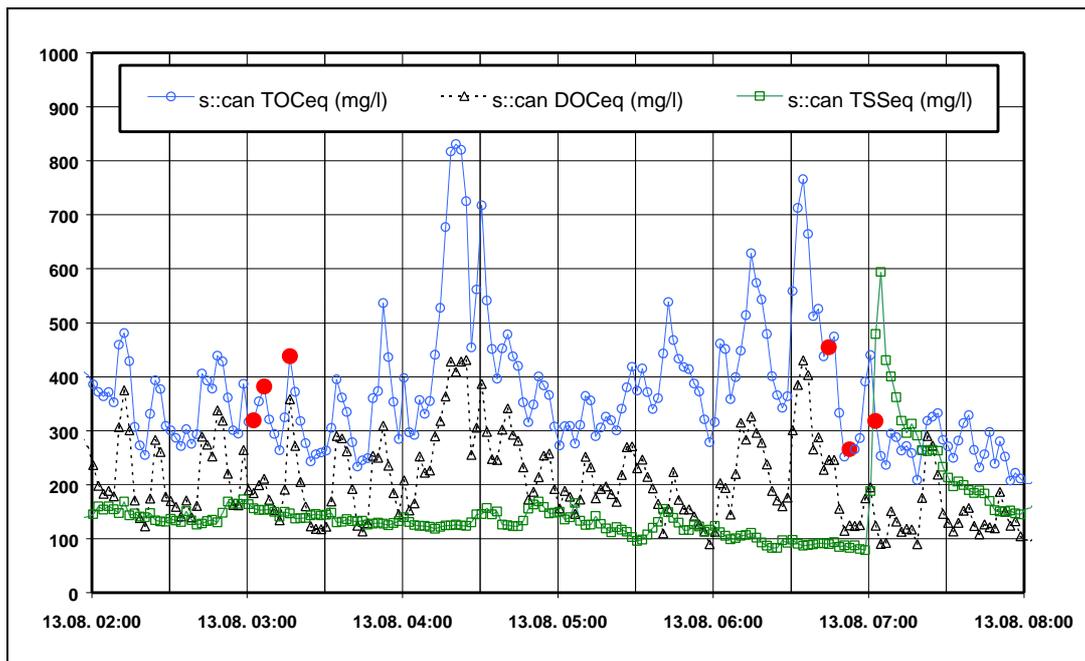


Figure 3. Time series for TOCeq, DOCEq, and TSSeq (detail from Figure 2).

Additionally to the TOCeq (circles) the DOCeq (triangles) and TSSeq (squares) are shown in Figure 3. It is quite clear that the variations in TOCeq are caused by the variations of the dissolved compounds (DOCe_q), the concentration of the particulate matter (TSSeq) is rather constant until about 7:00 hours. The full circles in Figure 3 depict times where a closer look at the fingerprints is taken (see Figure 5 and Figure 6).

At 7:00 hours an increase of TSSeq could be observed whereas TOCeq and DOCeq remained rather constant. This indicates a change of the particulate to dissolved organic matter ratio and this indicates a significant change of wastewater composition during this period. This behavior can only be observed when several parameters are monitored simultaneously and with a high measurement frequency (in this case the interval between the measurements was 2 minutes) which can be easily done with the presented UV/VIS spectrometer.

Fingerprints

Figure 4 shows typical fingerprints of raw municipal wastewater. The spectra increase steadily with decreasing wavelength in the visible range, which is characteristic for the influence of particles. The relative maximum at 280 nm is distinct from the influence of the turbid substances, due to the absorbance by dissolved organic substances.

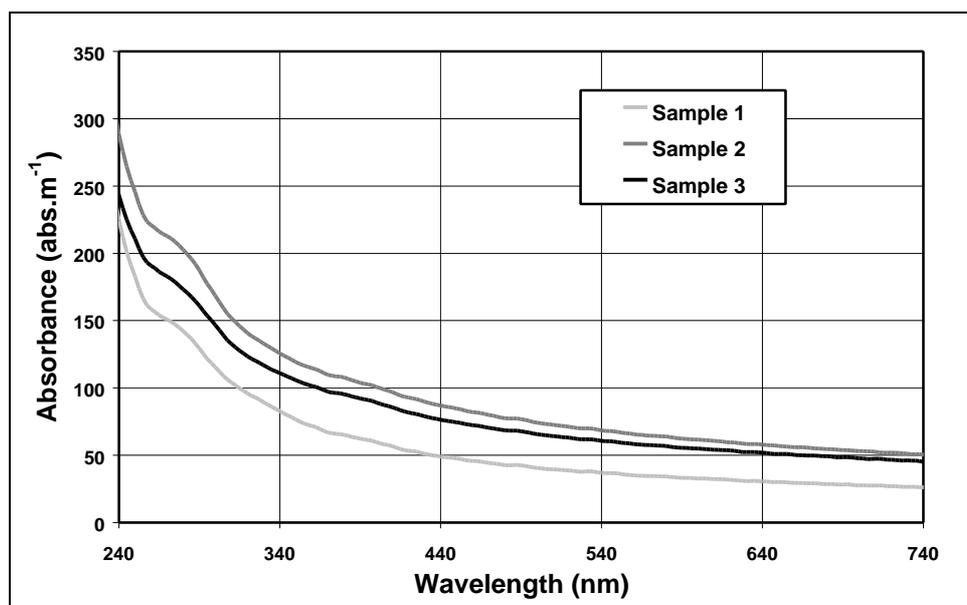


Figure 4. UV/VIS fingerprints of municipal wastewater.

In Figure 5 and Figure 6 the fingerprints marked in Figure 3 are shown. Figure 5 shows the first 3 fingerprints and Figure 6 the second 3 fingerprints respectively. The difference of the fingerprints compared to the one shown in Figure 4 is obvious. The fingerprints show a peak at around 280 nm indicating the presence of special organic substances (most likely phenols and PAKs).

The 3 fingerprints shown in Figure 5 are measured within 14 minutes and show quite a different shape indicating a strong change of the composition within this short period. Besides the peak at around 280 nm the fingerprints at 03:02 and 03:06 hours have a shoulder around 330 nm which is not present at 03:16 hours.

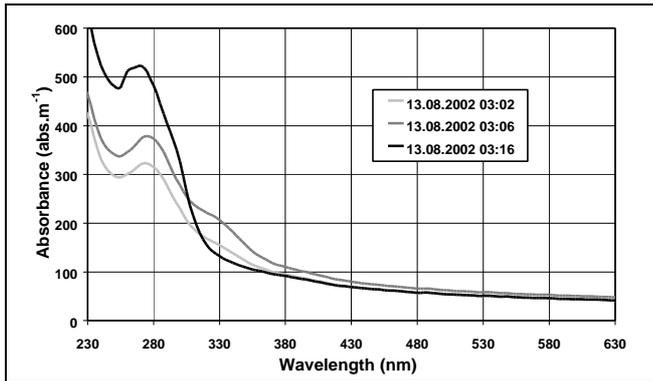


Figure 5. UV/VIS fingerprints (1).

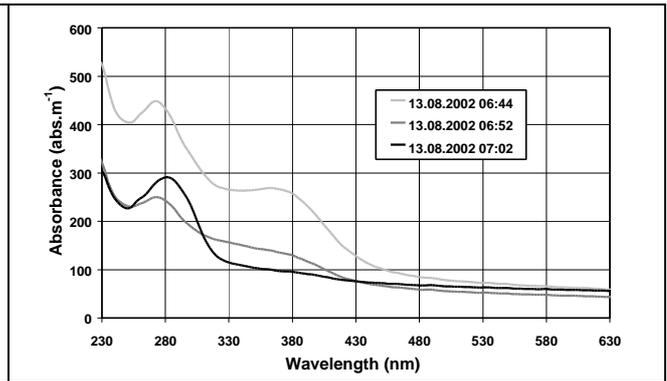


Figure 6. UV/VIS fingerprints (2).

Figure 6 shows the other 3 fingerprints which were measured within 18 minutes around 07:00 hours. Again a different shape compared to the fingerprints shown in Figure 5 can be observed. Additionally to the substances that cause a peak around 280 nm an other peak at around 380 nm can be observed at 06:44 and 06:52 hours. At 07:02 hours – only 10 minutes later – this peak can not be observed any more.

Within only 6 hours at least 3 very different compositions of the wastewater could be detected. The detection of the different wastewater compositions was only possible by using an on-line spectrometer measuring the whole UV/VIS range that has short measurement intervals. However not only the detection of the different compositions is of high interest but also the identification of the reasons for this changes.

Differential spectroscopy

When comparing the first derivation and therefore the slope of the spectrum instead of the original spectrum differences in the shape get much more clearer. Using the derivatives of the spectrum do not increase the information that can be obtained. Figure 7 compares the measured fingerprint at the wastewater treatment plant influent at 06:44 hours with 2 fingerprints measured directly at industrial inlets. In Figure 8 the 1st derivative of the fingerprints is shown.

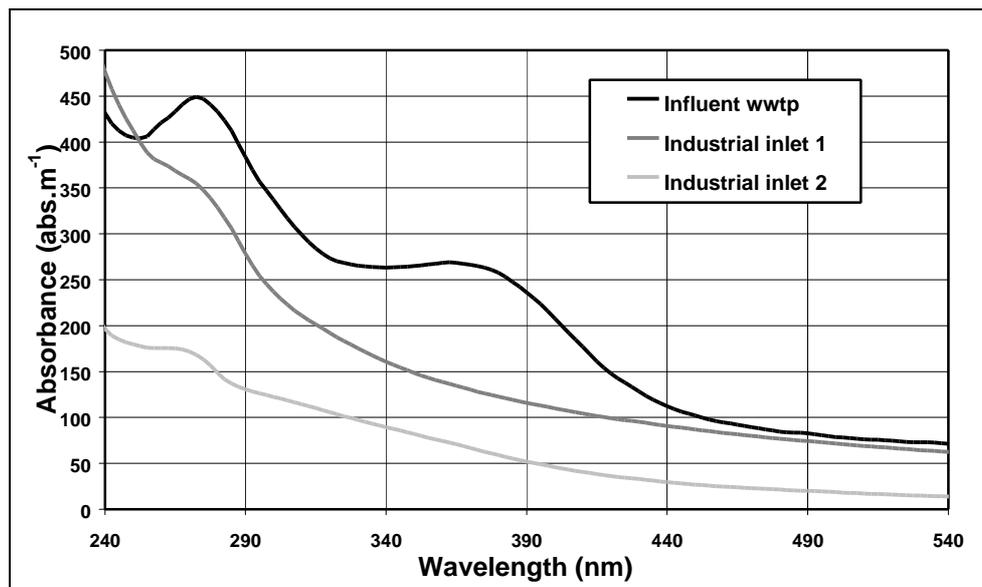


Figure 8. Fingerprints of measured wastewater and 2 industrial inlets.

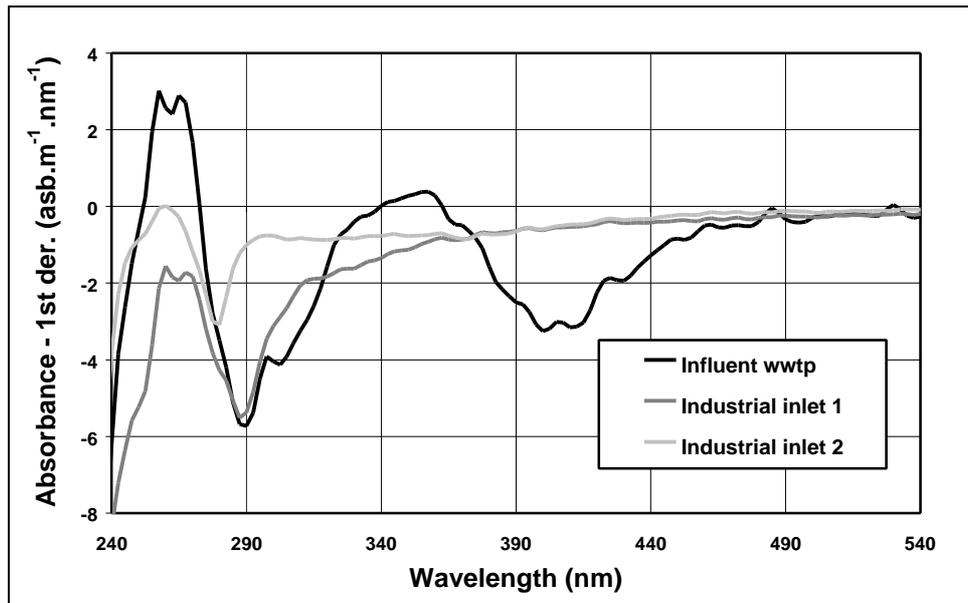


Figure 9. Differentiated spectrum of the fingerprints shown in Figure 7.

The differentiated spectrum of the wastewater treatment plant influent and the industrial inlet 1 are similar – especially the wavelengths region between 255 nm and 295 nm. It can therefore be concluded that the influent of the wastewater treatment plant is mainly influenced by the industrial inlet 1. However, no similarity could be found for the wavelengths region between 330 nm and 450 nm.

It can be summarized that the changes in the spectral behaviour and therefore the wastewater composition was not only caused by industrial inlet 1. Besides the industrial inlets one has to consider that also internal flows of the wastewater treatment plant can be the reason for this changes. So there is still a need for further investigations especially to explain the behaviour between 330 nm and 450 nm.

CONCLUSIONS

It could be shown that by using on-line measurements with the submersible UV/VIS spectrometer changes in the wastewater composition can be detected when applying a high measurement frequency. Further it is possible to identify single industrial inlets and even changes in the operational settings of the industries. Using the differentiated spectrum for comparison enables a better detection of similarities. Several applications already proofed that is possible to identify pollutions by industrial inlets using this method.

In comparison with conventional parameters like COD, TOC or TSS it is possible to get much more information using a fingerprint of the whole UV/VIS range. The instrument measures in-situ, directly in the process. Therefore no sampling, no sample preparation, and no reagents are required. This enables a very high time resolution and therefore also quick changes in wastewater quality (concentration and/or composition) can be detected. Due to the measurement in real-time a quick response to changes by the control system and/or operator of the plant is possible.

The auto-cleaning system of the UV/VIS spectrometer which is operated with pressured air prevents trends in the time series due to film growth on the optical devices. The experience showed that the operation of the instrument at wastewater treatment plant influents or directly in sewers is possible for several weeks (> 4) without maintenance.

The UV/VIS spectrometer proved to be a promising instrument to quantify wastewater pollutant loads for integrated management and control of municipal sewer networks and monitoring of the treatment plant itself e.g. to prevent a possible failure of the plant.

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