

Real-time detection of possible harmful events using UV/vis spectrometry

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Introduction

Operators of water or wastewater treatment plants benefit when changes of concentration and/or composition of inlet water can be detected and, therefore, a possible failure of the treatment plant performance can be avoided. When monitoring drinking water, either at the source or in the distribution system, identification of low probability/high impact events that might compromise water quality and, as a consequence, public health is an important goal. Early identification is the prerequisite for an effective response that reduces or entirely prevents the adverse impacts of such a contamination. For wastewater treatment plants, the early detection of, for example, inhibiting substances in the influent is of great importance and can prevent negative impact on the biological degradation processes.

Systems that facilitate such early detection and identification are referred to as early warning monitoring systems or alarm systems. Typical causes of high impact contaminations are natural events (for example, flooding, anoxia, algal blooms), accidental anthropogenic events (for example, inadvertent discharges, spills) or intentional discharges (for example, vandalism, terrorism). As the number of potentially harmful compounds is enormous, only a fraction of these can be monitored, as the development of specific sampling strategies for all contaminants would be an impossible task.

The development of new variables, such as alarm parameters, that allow for an integrated assessment of changes in water quality using surrogate or aggregate variables, instead of searching for all specific contaminants individually, can be a useful strategy to cover a much broader range of potential threats than possible with conventional monitoring solutions.¹ As spectral data, and their evolution over time, are very rich in information, the loss in compound-specific information is compensated for by a much better overall picture of change in water quality and the possibility to detect changes that will not be picked up by conventional, single contaminant directed, monitoring programmes. Furthermore, it can be expected that alarm parameters developed from spectral data are accurate, selective and transferable amongst applications to an extent that is beyond the state-of-the-art. This contribution describes how alarm parameters can be derived from spectral data.

Methodology

The instrument

For the development of alarm parameters an s::can Messtechnik GmbH submersible ultraviolet/visible (UV/vis) spectrophotometer, spectro::lyser, was used. This measures absorbance of ultraviolet and visible light from 200 to 750 nm.² The instrument is built as a compact submersible sensor, enabling measurement of UV/vis spectra with laboratory quality directly in liquid media. For high robustness and long-term stabil-

ity, even under harsh conditions, the spectrometer is equipped with an auto-cleaning system using pressurised air. Furthermore, the long-term stability of the measurements is guaranteed by a two-beam-design, which allows zero-compensation for changes in the instrument as well as for the detection of instrumental failures, see preceding article in this issue of *Spectroscopy Europe*.

Alarm parameters derived from spectral measurements

Alarm parameters are in many ways different from measurements of well-defined chemical substances.³ Most importantly, they must show a quick response to suspect quality changes, which implies the need for real-time measurements. Furthermore, a high sensitivity and, at the same time, low probability for false alarms, as well as a broad-band response to diverse contamination sources are prerequisites. In many cases this will mean that application- and location-specific, tailor-made, parameters will need to be developed. Less important for alarm parameters are their parameter selectivity and their compliance to analytical laboratory norms; when monitoring surrogate parameters, the results of the measurements will be difficult to compare with the results of regular analytical methods.

Broadband optical instruments, like spectrometers, allow the development of such alarm parameters. Spectroscopy fulfils most of the requirements, because it allows:

1. Direct and selective spectrometric measurements

Single substances or substance groups that are detectable in the UV/vis spectrum can be identified using spectral algorithms evaluating the spectra. Parameters derived from spectral information include surrogates and single substances.⁴ Changes in the low ppb range can be monitored using on-line spectrometry. However, the selectivity is rather low and single-substance identification below 100 ppb is difficult, if not impossible, for many substances.

2. Monitoring of indicator parameters instead of contaminants

Indicator parameters can be used instead of monitoring contaminants directly. An example would be to use nitrate measurements as an indicator for pesticides in groundwater.

3. Monitoring of matrix parameters instead of contaminants

The whole UV/vis spectrum can be used as a fingerprint of the water composition ("matrix"). For the monitoring of matrix changes, evaluation of these fingerprints allows the detection of very small changes. When using derivatives of the fingerprints, most of the natural deviations of the baseline spectrum are eliminated and, therefore, a better identification of abnormal spectral features is possible. An example of such an application is the tracing of differences between spectra over time or space. Often, the detected changes are not directly related to known substances but, nevertheless, provide a sensitive alarm parameter.

Time-resolved delta spectrometry

There are several ways to evaluate the information provided by the fingerprints, including the qualitative interpretation of spectral deviations from a site-specific reference spectrum (for example, peaks, shoulders, gradients, analysis of the derivative spectra etc.), the comparison of spectral differences between measuring points in a measurement network, i.e.

spatially-resolved delta spectrometry and the evaluation of changes of the spectral features over time, i.e. time-resolved delta spectrometry. The latter will be discussed in more depth in the following paragraphs.

Time-resolved delta spectrometry⁵ tracks changes in the shape of the fingerprint over time, as well as the speed with which changes occur. As changes due to extreme natural events and anthropogenic changes are typically faster than gradually occurring natural changes, such as seasonal changes in water composition, it is possible to identify unusual water compositions solely on the basis of changes in time. This means that contaminants that do not provide very distinct signals can still be detected, because they still cause a (non-distinct) change in the absorption spectrum. It also means that in cases where no water body can serve as a reference for unimpaired water quality, for example due to continuous fluctuations, the use of UV/vis spectrometry nevertheless provides the possibility to detect irregularities on the basis of the size and speed of changes in the fingerprint. The multi-dimensional information provided in UV/vis spectra offers a much greater information potential on top of the "normal" baseline compared to single parameters such as turbidity or dissolved organic carbon (DOC), for which time-resolved data analysis will not allow such an identification of abnormal changes.

For definition of spectral alarm parameters, the following procedure has to be followed.

- Learning period: during the learning period (usually some months) spectra are collected. After this period the baseline spectrum (shape and features) is established.
- Abnormality definition: absorption spectra or their 1st- and 2nd-order derivatives can be used to identify deviations from "normal" spectral features. Detection of deviations is possible even with a continuously changing baseline, as in this case the trigger values for abnormal changes will be set outside the limits of the normal deviations or at wavelengths little affected by the normal fluctuations.

- Alarm definition: alarm definition is based on the concept of virtual contaminants. Since one never knows in advance which contaminant may be the next to enter the system, several groups of "virtual" contaminants are defined. These virtual contaminants are designed in such a way that by monitoring this limited set of parameters, the whole range of contaminants visible in the UV/vis spectrum is covered.
- Sensitivity definition: sensitivity of the virtual contaminants to changes in the water matrix has to be adjusted individually with respect to risks involved and acceptable false alarm levels. This is based on empirical and statistical evaluation.
- Definition of actions to be taken in case of alarm. Examples for possible actions in the case of an alarm would be: *alarm level 1*—slight deviation from normal situation: automatic sampling triggered, waiting for laboratory analysis, no additional action needed; *alarm level 2*—strong abnormalities: automatic sampling plus urgent action at site needed.

Applications

Detection of (unusual) changes in wastewater composition⁶

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 include both changes in 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. In one example, the spectrometer was operated in the influent of a wastewater treatment plant for several weeks. During most of the monitored period the concentrations showed only typical daily variations. During some periods, however, strong fluctuations occurred (Figure 1). From these data it is quite clear that the variations in the total organic carbon equivalent (TOCeq) concentration were caused by variations of the dissolved

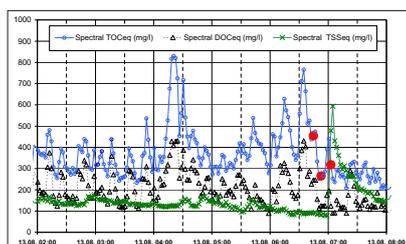


Figure 1. Detailed picture of strong fluctuations (13 August, between 02:00 and 08:00 hours).⁶

organic carbon equivalent (DOCeQ). The concentration of the particulate matter (TSSeq—total suspended solids equivalent) was rather constant until about 07:00 hours when a peak occurred. This specific behaviour could only be observed because several parameters are monitored simultaneously with a high measurement frequency (in this case the interval between the measurements was two minutes).

In Figure 2, the fingerprints of the measurements marked in Figure 1 (full red circles) are shown and compared with a typical fingerprint of the plant that shows a shape typical for communal wastewater. The three selected fingerprints were recorded within 18 minutes around 07:00 hours and clearly show different features from the baseline fingerprint. Two peaks, one at 270 nm and another at 360 nm can be observed at 06:44 and 06:52 hours. At 07:02 hours—only 10 minutes later—both peaks have disappeared and another peak at 280 nm is visible, indicating a pronounced change in water quality.

To investigate the origin of these rapid changes of the wastewater composition, some measurements at nearby industrial discharges into the sewer system

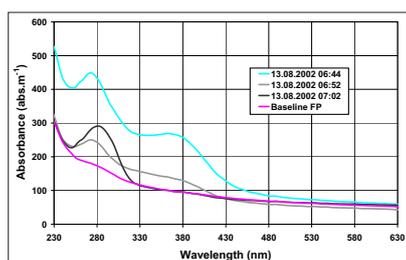


Figure 2. Baseline fingerprint and fingerprints for the times shown in the inset.

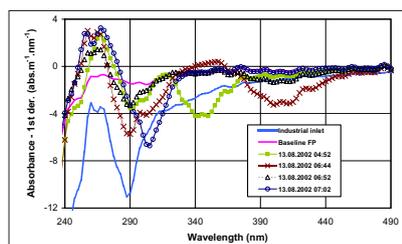


Figure 3. 1st derivative fingerprints of measured wastewater treatment plant influents at different times, the baseline fingerprint and an industrial discharge.

were conducted. Figure 3 compares the 1st derivative of measured fingerprints at the wastewater treatment plant influent at 04:52, 06:44, 06:52 and 07:02 hours, the period when the rapid changes of water quality occurred, with 1st derivative fingerprints of the baseline fingerprint and one measured directly at an industrial discharge. The changing contribution of the industrial inlet to the water composition can be clearly identified in the wavelength region between 255 nm and 295 nm. However, other sources also contribute to the rapid changes of water quality, for example, represented by a peak at about 400 nm at 06:44 hours, at 350 nm at 04:52 hours and at 300 nm at 07:02 hours, respectively, that had to be identified in a consecutive study.

Development of alarm parameters for a sewer network⁵

This second example shows the application of time-resolved delta spectrometry for the development of alarm parameters. Figure 4 shows a 3-D spectral picture of a water body over a period of one day. Peaks, troughs and shoulders can be clearly identified. For this water

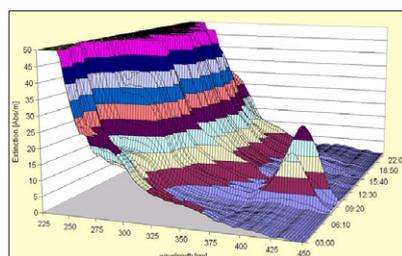


Figure 4. 3D-UV/vis spectra plotted against time.⁵

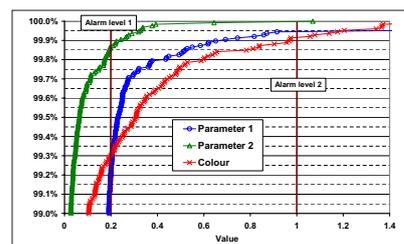


Figure 5. Definition of “Alarm level 1” and “Alarm level 2” for three alarm parameters.⁵

body, a three-month learning period was needed to cover all variations that occurred naturally. For evaluation of the baseline spectrum, only the fingerprints from the periods between the visible peaks were utilised.

The concept of virtual contaminants, as described above, was used for the definition of the alarm parameters generating several groups of virtual contaminants. Occurrence probabilities of the virtual contaminants are calculated off-line and plotted against the normalised spectral derivatives. Figure 5 shows the occurrence probabilities and the defined alarm levels for three virtual contaminants (Parameter 1 and 2, and colour). For example, for the parameter “colour”, the first and second alarm levels are reached at an occurrence probability of 99.3% and >99.9%, respectively.

Experience has shown that the occurrence probabilities of alarm parameters derived from spectral data are, in most cases, different from occurrence probabilities obtained from conventional parameters. In addition, peaks for different contaminants occur at different times.⁵ This enables the detection of events that cannot be detected using conventional parameters.

Conclusions

In this article, it has been shown that UV/vis spectrometry is a promising method to quantify rapid changes in water quality in the inlet of a treatment plant. Measurements with real-time UV/vis spectrometers can, therefore, be a valuable instrument to monitor the influent of treatment plants for integrated management, control of municipal sewer networks and monitoring

of the treatment plant itself, for example, to prevent a possible failure of the plant. Furthermore, it is possible to identify single industrial discharges and it can be expected that even changes in the operational settings of industries can be monitored.

Time-resolved delta spectrometry has been applied for developing alarm parameters. This method to define alarm levels is based on empirical and statistical evaluation of the fingerprints. It can be expected that it is possible to detect events that cannot be detected using conventional parameters when using alarm parameters derived from spec-

tral features, as their occurrence probabilities are, in most cases, different from occurrence probabilities obtained from conventional parameters.

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