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On-line and In-situ **UV/Vis Spectroscopy**

Real time multi parameter measurements with a single instrument

The advantages of online sensors for water quality analysis are becoming ever more widely recognised. The actual number of applications, nevertheless, remains rather limited to this date due to the limited capabilities of the instruments available. The introduction of spectrometric multi parameter probes with low maintenance requirements, however, is now changing the face of online monitoring significantly

Introduction

Surface water quality can change rapidly, e.g. due to weather (heavy rainfall) or contamination events such as oil spills, run-off from fire fighting activities etc. The rapid detection of the contaminants is important to aid in mitigation of possible negative effects on the environment and human health. Online monitoring of the actual water quality, and not just hydrological data, provides the required information for timely recognition of changes. Furthermore, online monitoring can provide a wealth of data on the natural dynamics of water systems that is impossible to obtain using grab sampling; it provides a much better picture of the true changes in water quality, whereas grab samples provide only snapshots of a small number of moments in time. Therefore, the use of on-line instruments is increasingly seen as a big benefit as they provide (near-) continuous information and will miss no quality changes.

These benefits have been recognised as well in water and wastewater treatment, where 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. Furthermore, the monitoring of drinking water, either at the source or in the distribution system, allows identification of low probability / high impact events that might compromise water quality, and as a consequence public health. >

Early identification is the prerequisite for an effective response that reduces or entirely prevents the adverse impact of such a contamination. UV/Vis spectroscopy is a tool that is well suited to perform these types of monitoring.

UV/Vis-spectroscopy

The use of UV/Vis spectroscopy in analytical chemistry dates back to the 1950s and 1960s. It was, however, initially associated with large and expensive laboratory equipment. In the 1980s, the introduction of miniature diode array detectors, combined with powerful microprocessors and state-of-the-art mathematical tools, led to a renaissance of UV/Vis spectroscopy and saw the introduction of compact, relatively low-cost yet still powerful laboratory UV/Vis machines. However, the market for in-situ optical sensors / probes was still - and still is - dominated by relatively simple photometers that are able to measure only one or two wavelengths at a time. Thus, these instruments are limited to measuring one parameter only, and at best employ quite crude and unstable methods to compensate for cross-sensitivities to variations, for example in a water matrix. Examples of widely used applications of these single wavelength instruments in water quality monitoring are the measurement of nitrate, turbidity and organics (indicated as SAC_{254}, Spectral Absorption Coefficient at 254 nm). Reduced cross sensitivity, as well as a wealth of additional information, can be obtained when using the entire absorption spectrum instead of single wavelengths. The developments in electronics and optics over recent years have enabled the marriage between full spectrum UV/Vis spectroscopy and robust, small-scale instruments.

The spectrometer probe

For the purpose of describing the principles behind, and capabilities of, this type of online spectrometers, the spectro::lyser™ will be used as the reference instrument. This spectrophotometer records light transmission in liquid media between 200 - 750 nm. The measurement is performed in-situ, without sampling or sample pre-treatment, thus preventing errors due to sampling, sample transport and storage, etc. A measurement cycle takes between 20 and 60 seconds, making possible a high measuring frequency and detection of rapid changes. For long term stability of the signal produced, a split light beam design is used; one beam passes through the sample while the other travels along a parallel pathway inside the instrument and thus acts as an internal reference. This second beam is used to cancel out fluctuations in light source energy and instrumental fluctuations due to environmental conditions. The instruments are available with different lengths of the measuring compartment, opening up a wide range of applications, from ultra pure water (dissolved organics in the µg/L range) up to concentrated wastewaters (organics and non-dissolved materials in tens of grams/L range).

Figure 1. Example of in-situ application of UV-spectroscopy, river water monitoring

Because neither chemicals nor moving parts for cleaning are necessary for their functioning, a cleaning system using pressurised air is used, the spectrometer can function in harsh environments with little or no maintenance.

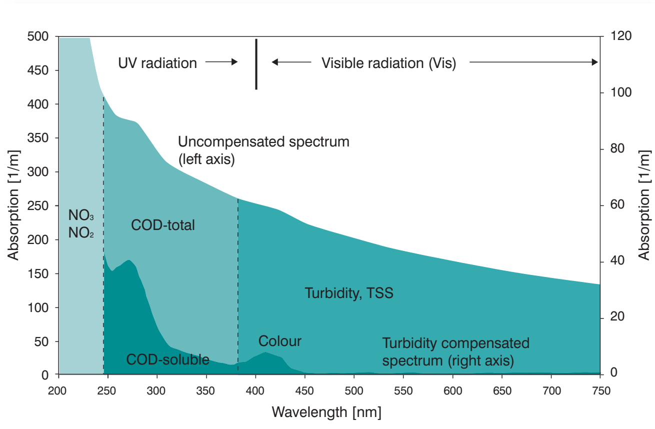

Figure 2. UV-Vis spectrum, and examples of parameters derived out of this spectrum together with their characteristic absorbance profiles

The measurement principle

The absorption spectra, referred to as fingerprints (Figure 2), obtained with such on-line spectrometers are used for the characterisation of the sampled water. Within these fingerprints one can find a huge amount of information about the water composition; they are used calculate specific parameters, such as turbidity, nitrate concentration, and sum parameters such as SAC_{254}, COD, TOC and DOC.[1]

Turbidity due to suspended substances causes light scattering and shading, thus influencing the absorption over the entire fingerprint. This is an important factor that influences in-situ measurements and requires compensation in order to obtain reliable and reproducible readings. The turbidity compensation developed assesses part of the original spectrum and then calculates a function describing turbidity. This function is used to compensate the spectrum for turbidity and for the determination of the turbidity / suspended solids (TSS) level itself. From the compensated fingerprint the levels of dissolved compounds can then be determined, either as sum parameters such as DOC or colour, or as single substances such as benzene or ozone. The latter applications use shape recognition of the characteristic absorption profiles of these substances to ensure a minimum cross-sensitivity to other UV-absorbing species.

Development of the correct algorithms

The wavelengths in the fingerprint used for determining all these parameters have been selected using principal component analysis (PCA) and partial least square regression (PLS) statistical techniques and are based on hundreds of datasets containing both UV/Vis spectra and reference values of these parameters[1], the latter being determined using established and validated laboratory techniques. Characteristic and quantitative relationships between the parameters described above and the absorption at certain wavelengths were thus established. The use of such multi-wavelength algorithms allows much higher specificity than can be achieved with conventional, single or dual wavelength, photometry. As absorption peaks of substances often overlap, no distinction between such substances would be possible with the more primitive systems, whereas multi-wavelength spectroscopy can do so as a matter of course (see Table 1).

One very effective application of on-line spectrometers and the developed spectral algorithms is the replacement of TOC/DOC or COD/BOD (BOD, Biochemical Oxygen Demand) analysers. Classical analysers for these parameters use wet-chemical processes for the determination of levels of organic materials in water. The operation of such analysers requires a huge amount of maintenance, and produces chemical waste as well. Replacing them with spectrometer instruments eliminates these drawbacks, while at the same time increasing availability of measurement results and achieving a precision that is about an order of magnitude better than with the standard DOC analysers[3].

Typical applications

River water monitoring

In an intensive research programme (IMW)[2], on-line spectroscopy has been in use for monitoring the water quality of the Danube river near Vienna for several years now. The monitoring system has registered many fluctuations in the quality of the water, originating from both natural and human influences. For example a daily period in organics and ammonium concentrations was observed (Figure 3) as a result of daily cycles in the composition of the final effluent of waste water treatment plants located upstream from the measuring site.

In this particular application, the results of the monitoring system are transmitted via GSM to a central database collecting results of several monitoring stations. This central database also provides the visualisation of the collected results over the internet and as such is accessible worldwide. Also, because of strongly fluctuating water levels in the Danube, the system was mounted on a trolley so that the installation is fully adjustable to the actual level.

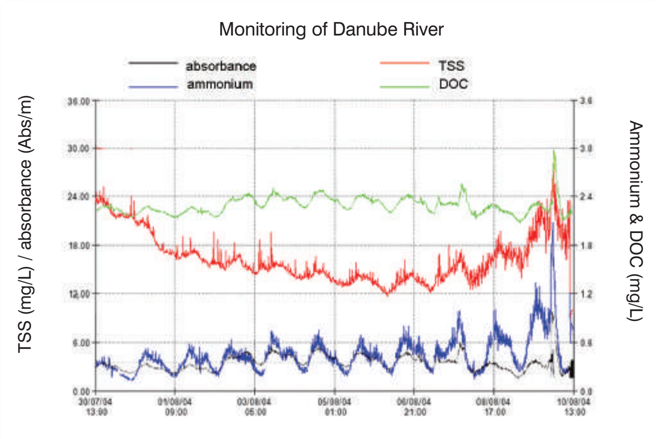

Figure 3. Simultaneous results for ammonium, suspended solids and dissolved organics

Wastewater treatment

On-line UV/Vis spectroscopy is increasingly used to monitor and control wastewater treatment plants. The on-line spectrometers are used to monitor the influent and effluent, determining the loads of organic materials (COD), nitrate and suspended solids (TSS). Monitoring of the effluent helps treatment plants meet the requirements for the discharge of treated water. It also allows assessment of the efficiency of the entire treatment process. Furthermore, spectrometers are applied to control specific steps in the treatment process, most noteworthy the aeration process. During aeration nitrogen compounds are oxidised to nitrate (nitrification). In case of incomplete conversion,

Table 1. Comparison between single wavelength calibration and the multivariate calibration algorithm using PLS for the effluent of a wastewater treatment plant[a]
[a] the numbers show the correlation coefficients R^2 of laboratory values against concentrations calculated from the spectra

Parameter	Nitrate	Nitrite	Soluble COD	TSS
Single wavelength calibration	0.089	0.182	0.213	0.442
Multivariate calibration algorithm	0.993	0.978	0.905	0.848

however, nitrite is formed, which is highly toxic to aquatic organisms. Monitoring of nitrate and nitrite levels in the process can be used to ensure maximum conversion. Compared to the fixed time schedules normally used to steer this process, on-line spectroscopy allows steering of the process in such a way that the time used for each step is reduced to what is truly required, because the progress in the different steps, i.e. nitrification, de-nitrification and settling, can be monitored. This allows a maximisation of the volume of water that can be treated.[3] Also, increased efficiency in the aeration process often makes the amortisation period for the investment in the instruments very short.

Industrial applications / control of spills

The main application of on-line spectroscopy in industry is to be found in the control of wastewater treatment facilities also. Another type of application, however, is the detection of product spills. An example of such an application is hydrocarbon alarms for the petrochemical industry. Spectrometers are used, for example, to monitor total hydrocarbons and benzene concentrations down to levels as low as 10 ppb. A further example is the use of the on-line spectrometer for profiling the spread of contaminants in groundwater at industrial sites, by inserting the instruments into boreholes and recording concentrations at various depths in the groundwater (Figure 4).

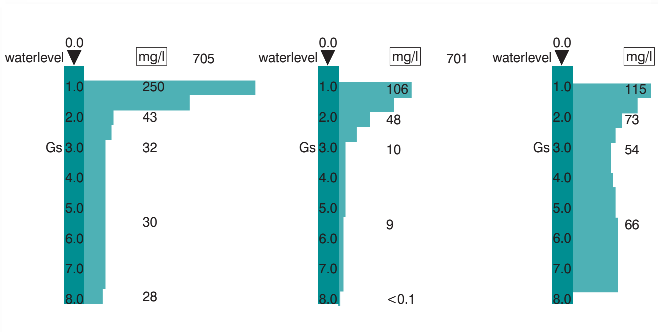

Figure 4. Depth profiles of benzene concentrations (mg/L) in various boreholes. The numbers in the column indicate depth in water column in meters

Advanced features of by online spectrometry

Because the spectrometer probes record the full spectrum, even more advanced features than measuring classical parameters are possible. The development of new variables, so called alarm parameters, that allow for a general assessment of changes in water quality, is possible. Such alarm parameters can be seen as surrogate parameters, which monitor parts of the spectrum for deviations from its known normal shape. This type of shape recognition is a useful strategy to detect changes that will not be picked up by conventional, single contaminant directed, monitoring programmes. As changes due to extreme natural events and anthropogenic changes are typically much faster than gradually occurring natural changes, such as seasonal changes, it is possible to identify unusual water compositions solely on the basis of spectral changes over time. This means not only that contaminants which do not provide very distinct signals can still be detected, because they do incur a change in the absorption spectrum. It also means that in cases where no 'normal' water quality that can serve as a reference is available, 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 the speed of changes in the spectrum. These alarm applications are being applied in river water and drinking water monitoring worldwide.

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Online UV/Vis spectrometry has proven to be a highly capable and valuable tool for monitoring water quality in real time and in the field. Using one instrument only, it is possible to measure several parameters on-line and in various kind of liquids, which is a unique feature amongst online sensor systems. As technology progresses and more experience is gathered, an even further broadening of applications and an increase of the number of parameters that can be measured using this technique will take place.

References

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Author

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