

On-line and *in-situ* UV/vis spectroscopy for multi-parameter measurements: a brief review

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Introduction

During 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 ultraviolet visible (UV/vis) spectrometry that enabled the rapid spread of compact, relatively low-cost, yet still powerful, laboratory UV/vis machines. During the 1990s, the technology moved from the laboratory into the field, but still in the form of relatively large, complicated and expensive off-line analysers. However, the market for *in situ* optical sensors/probes was still—and still is—dominated by relatively simple photometers, which are able to measure only one or two wavelengths at a time. These instruments are, thus, limited to measuring one parameter only and they generally 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 UV/vis-spectroscopy in water quality monitoring are the measurement of nitrate, turbidity and organics [spectral absorption coefficient at 254 nm (SAC₂₅₄)]. A lot of additional information, however, as well as reduced cross-sensitivity, can be obtained when using the entire absorption spectrum instead of single wavelengths. The development in electronics and optics over recent years has enabled the marriage between full spectrum UV/vis spectroscopy and small-scale instruments. Moreover, these

developments have allowed the design of robust spectroscopic analysers that can function in harsh environments, such as inside sewer and industrial process streams, with little or no maintenance because neither chemicals nor moving parts for cleaning are necessary for their functioning. As the first compact on-line instruments for use in the field have been on the market for several years now, this article **briefly reviews their capabilities and applications.**

The instruments

For the purpose of describing the principles behind and capabilities of this type of on-line spectrometer, the spectro::lyser (see Figure 1) from the Austrian company s::can Messtechnik will be used as the reference instrument, as this is the most widely used. This spectrophotometer records light attenuation in the wavelength region

between 200 and 735 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 s, making possible a high measuring frequency and detection of rapid changes. In order to combine this high measurement frequency with high accuracy and sensitivity, the instrument is equipped with a Xenon flash lamp as a light source and a concave holographic grating matched with a 256 pixel diode array as detector. 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



Figure 1. Examples of *in situ* applications of UV spectroscopy; process control in a wastewater treatment plant (left) and drinking water monitoring (right).

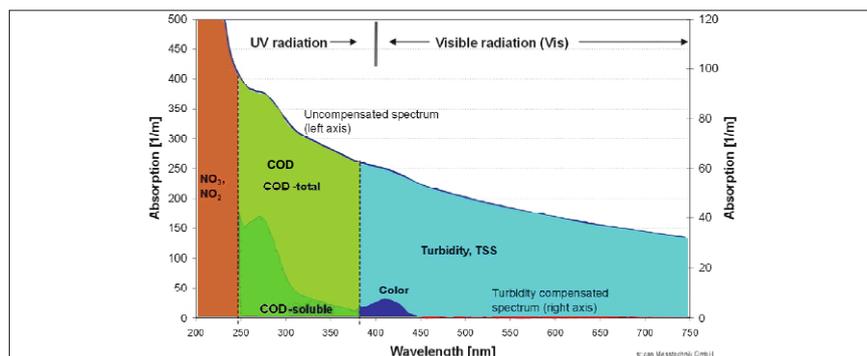


Figure 2. UV/vis spectrum and examples of parameters derived out of this spectrum together with their characteristic absorbance profiles. [chemical oxygen demand (COD); total suspended solids (TSS)].

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 $\mu\text{g L}^{-1}$ range) up to concentrated wastewaters (organics and non-dissolved materials in tens of g L^{-1} range).

Fingerprints

The spectra, referred to as fingerprints (Figure 2), obtained with such on-line spectrometers are used for the characterisation of the sampled water. Within these sometimes almost featureless fingerprints, one can find a huge amount of information about the water composition. The fingerprints are used to monitor changes in the water composition through analysis of the general shape of the spectrum or absorption at a specific wavelength. Furthermore, they are also used to derive more specific parameters, such as turbidity, nitrate concentration and sum parameters such as SAC_{254} , total organic carbon (TOC) and dissolved organic carbon (DOC),^{1,2} which are commonplace in water analysis.

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. An algorithm for compensation of turbidity has been developed, based on a relationship between scattering intensity and wavelength as a function of the particle diameter and the spectral shape caused

by suspended solids.³ The scattering is dependent on wavelength according to λ^x , where x is dependent on a particle diameter.⁴ The turbidity compensation developed utilises the visible range in the original spectrum and fits the function describing turbidity to this spectrum. The resulting compensation is used in two ways, namely for baseline compensation of the fingerprint, which allows the analysis of dissolved components and for the determination of the turbidity/suspended solids (TSS) level itself. From the compensated fingerprint, the total amount of dissolved organic substances and the colour of the sample can then be determined. Furthermore, it is also used to estimate the concentration of single (groups of) substances, such as benzene and toluene. 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. The non-compensated fingerprint is used further for the assessment of the total load of organic matter and the total concentration of nitrate and nitrite.

These two parameters are determined by algorithms that utilise a selected number of wavelengths from the UV range of the fingerprint.

The wavelengths used for determining all these parameters have been selected using principal component analysis (PCA) and partial least square regression (PLS) on hundreds of datasets containing both UV/vis spectra and reference values of these parameters,¹ the latter being determined using established 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.² 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, for example, Table 1).

Typical applications and real case studies

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

Table 1. Comparison between single wavelength calibration and the multivariate calibration algorithm using PLS for the effluent of a wastewater treatment plant.^a

| 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 |

^aThe numbers show the correlation coefficients R^2 of laboratory values against concentrations calculated from the spectra.

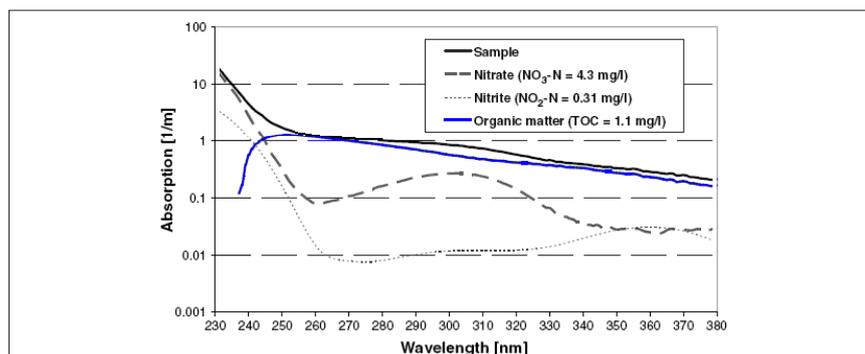


Figure 3. UV spectrum for tap water spiked with nitrite and deconvolution into spectra of nitrate, nitrite and organic matter.²

steps in the treatment process, the most noteworthy being the aeration process. During aeration, nitrogen compounds are oxidised to nitrate (nitrification). In case of incomplete conversion, 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, denitrification and settling can be monitored. This allows a maximisation of the volume of water that can be treated.⁵ Also, increased efficiency in the aeration process often makes the amortisation period for the investment in the instruments very short.

A special application was developed especially for the measurement of nitrite and nitrate simultaneously.² Following measurements of different background

matrices (distilled water, drinking water, wastewater) spiked with nitrate and nitrite (Figure 3), followed by data analysis using PLS, five wavelengths between 230 and 245 nm were selected for both nitrate and nitrite. An algorithm based on the ten wavelengths quantifies these substances independently. As both these compounds have a maximum absorption between 210 and 240 nm and only very weak absorption maxima at 300 nm (nitrate) and 360 nm (nitrite), no distinction between these substances would have been possible with the older two wavelength analysers. Using this algorithm for nitrite analysis, a correlation coefficient of 0.978 with laboratory results and a 95% confidence interval of 0.14 mgL^{-1} at a mean concentration value of 0.94 mgL^{-1} were achieved.

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. 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. Furthermore, the on-line spectrometer has been used to profile the spread of aromatic contaminants in groundwater at an industrial site by inserting the instruments into boreholes and recording concentrations at various depths in the groundwater (Figure 4).⁶

Environmental applications

Monitoring of surface and ground water quality is mainly done using grab sampling and laboratory analyses. On-line measurements will allow for 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. This increased demand for on-line systems has seen the introduction of on-line UV-spectroscopy in river and groundwater monitoring, mainly focusing on monitoring nitrate and organics. One very effective application of on-line UV spectroscopy is the replacement of TOC/DOC or COD/BOD [biochemical oxygen demand (BOD)] analysers. These analysers 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 result and achieving a precision that is about an order of magnitude better than with the standard DOC analysers.²

Drinking water

For applications in drinking water, ranging from monitoring of the raw water used to produce drinking water all the way to the treated product, the standard calibration algorithms for substances like T(D)OC, nitrate, turbidity, organic

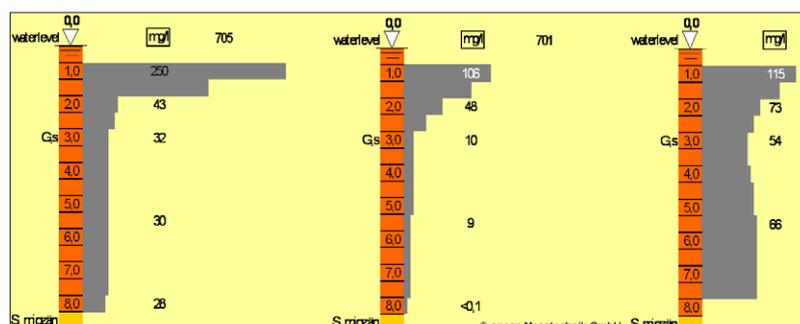


Figure 4. Depth profiles of benzene concentrations (mgL^{-1}) in various boreholes.⁶ The numbers in the column indicate depth in water column in metres.

Table 2. Detection limits for specific organic compounds in drinking water.

| Compound | Detection limit (mg L ⁻¹) |
|-------------------|---------------------------------------|
| PMP ^a | 50 |
| DMMP ^b | 50 |
| Azinphos-methyl | 10 |
| Methamidophos | 1 |
| Oxamyl | 0.1 |
| Mevinphos | 0.1 |
| Aldicarb | 0.1 |
| Benzene | 0.05 |
| Isoproturon | 0.05 |
| Linuron | 0.001 |

^aPMP = pinacolyl methylphosphonate, a simulant for soman

^bDMMP = dimethyl methylphosphonate, a simulant for sarin

substances like aromates, phenols, hydrocarbons and others, can be used to monitor those substances with time and space. The most important applications in this field have been the monitoring of the source water (for example, at Vienna Waterworks where more than 20 monitoring stations are operational) and control of treatment processes (for example, flocculation, membrane filtration and UV disinfection).

One inherent drawback of UV/vis spectroscopy for this type of application is that, although sensitive down to the low ppb-range for many organic pollutants, it will not be selective enough to indicate the type of micropollutant at the level required for quality control of drinking water; as no (chromatographic) separation of the contents is performed; the fingerprints will represent a superposition of all compounds present in the sample. Therefore, a more detailed analysis must followed in cases of elevated signals,

with the observed signal often representing a sum parameter. For monitoring of overall water quality, it is, therefore, a far better strategy to use the UV spectrum in a qualitative way, in order to detect even the smallest changes between the measured spectra and reference spectra at any wavelength. Often, changes will only become evident in differential spectra. Sometimes the detected changes cannot directly be correlated to known substances, but nevertheless provide a sensitive alarm parameter. The capability of UV spectroscopy to detect and identify organic compounds in drinking water in this way was evaluated by spiking water samples with specific contaminants.⁷ This study focused on the detection of toxic compounds, such as pesticides and (simulants for) chemical warfare agents. Drinking water samples, spiked with a selection of compounds that are considered as most likely for use in the event of an intentional contamination of

a drinking water supply, were analysed. For each of the used contaminants, calibration curves were obtained. This showed that compounds with a high UV absorbance could be detected down to a µg L⁻¹ concentration level (Table 2).

A more extensive description of the use of UV/vis spectroscopy in the detection of (unusual) changes in water quality and the use of differential spectra to define quality alarms, can be found in the accompanying article in this issue of *Spectroscopy Europe*.

References

1. G. Langergraber, N. Fleischmann and F. Hofstädter, *Wat. Sci. Technol.* **47(2)**, 63 (2003).
2. L. Rieger, G. Langergraber, M. Thomann, N. Fleischmann and H. Siegrist, *Wat. Sci. Technol.* **50(11)**, 143 (2004).
3. E. Huber and M. Frost, *J. Wat. SRT – aqua* **47**, 87 (1998).
4. G. Langergraber, N. Fleischmann, F. Hofstädter and A. Weingartner, *Wat. Sci. Technol.* **49(1)**, 9 (2004).
5. G. Langergraber, J.K. Gupta, A. Pressl, F. Hofstaedter, W. Lettl, A. Weingartner and N. Fleischmann, *Wat. Sci. Tech.* **50(10)**, 73 (2004).
6. G. Langergraber, N. Fleischmann, F. van der Linden, E. Wester, A. Weingartner and F. Hofstädter, in *In-situ measurement of aromatic contaminants in bore holes by UV/vis spectrometry*, Ed by W. Breh *et al.*, Field Screening Europe 2001. Kluwer Academic Publishers, Dordrecht, The Netherlands, p. 317 (2002).
7. J. van den Broeke, A. Brandt, F. Hofstädter and A. Weingartner, in *Security of Water Supply Systems: From Source to Tap*, Ed by J. Pollert and B. Dedus. Springer Verlag, Dordrecht, The Netherlands, p. 19 (2006).