Use of In-situ UV/Vis spectrometry in Water Monitoring in Vienna

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Abstract
On-line optical instruments for water quality measurements can be found in all types of applications, from drinking water to wastewater. Traditionally, these instruments measure one or two wavelengths in the visible or UV range of the spectrum, but more advanced instruments that measure the full range of UV and visible light with high resolution have now established themselves on the market. These advanced spectrometer probes can measure multiple parameters, such as turbidity, nitrate and sum organics, simultaneously and in real time with a high frequency. In Vienna, Austria, such instruments are in use to monitor all aspects of the urban water chain: from clean spring water in the mountains all the way to the Danube. The different demands and specifics of these very diverse applications have been covered with a single technology solution which is described in this contribution.

1. INTRODUCTION
The advantages of online sensors for water quality analysis are becoming more widely recognised. 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 real dynamics of water systems that is impossible to obtain using grab sampling; it provides (near-) continuous information and will miss no quality changes, whereas grab samples provide only snapshots of the water composition on a limited number of points in time.\(^1\)\(^2\) Therefore, the use of on-line instruments is increasingly seen as a benefit by very different water disciplines.

The online advantage has been widely recognised in water and wastewater treatment, where changes of concentration and/or composition of raw, influent or treated 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 optimisation of operational practices as well as 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.\textsuperscript{1,3} The actual and widespread use of advanced online sensors, nevertheless, remains rather limited to this date due to the limited capabilities and / or high maintenance requirements 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. Already since the 1990’s, single and dual wavelength instruments have found widespread applications in water quality monitoring for the measurement of nitrate, turbidity and organics as indicated by the spectral absorption coefficient (SAC\textsubscript{254}). These instruments are, however, limited to measuring one parameter only and they are cross-sensitive to non-target substances and also sensitive to variations in a water matrix.\textsuperscript{4,5} Much additional information, as well as reduced cross sensitivity, can be obtained when using the entire absorption spectrum instead of single wavelengths.\textsuperscript{6,7,8} The use of UV/Vis spectroscopy for such purposes has been reported since the 1950s, for some examples see references 9, 10, 11 and 12. Nevertheless, only recent developments in electronics and optics have enabled the marriage between full spectrum UV/Vis spectroscopy and robust, small scale instruments (Figure 1).\textsuperscript{13}

The current generation of UV/Vis spectrometer probes can function in hostile environments, such as sewers and industrial process streams, with little or no maintenance, because neither consumables, nor spare parts nor moving parts are necessary for their functioning. As a result, the last years have seen the introduction of such instruments in the complete cycle of water used for human consumption and industrial applications.

An illustrative example of the deployment of online UV/Vis spectrometer probes in all possible types of applications in an urban water cycle can be found in the city of Vienna (Austria). Here, UV/Vis spectrometry is being used to monitor and control water quality all the way from the mountain springs which provide the city with its drinking water to the final effluents of the waste water treatment plant and the receiving waters of the Danube.\textsuperscript{14}

Using the city of Vienna as an illustration, this paper presents the possibilities offered by the current spectrometer probes in these diverse application types and the associated operational challenges.
Fig. 1 - Examples of in-situ submersed applications of UV/Vis-spectroscopy in Vienna; process control in waste water treatment (left) and drinking water monitoring (right).

2. MATERIALS AND METHODS

2.1 The Instrument
The spectrometer probe used in the applications in Vienna described herein is the spectro:lyser™ of the Austrian company s::can Messtechnik (Figure 2). This spectrophotometer records light attenuation between 200 and 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 typical measurement cycle takes between 20 and 60 seconds, making possible a high measuring frequency. For long term stability of the signal, a split light beam design is used; one beam passes through the sample while the other travels along a parallel pathway inside the instrument. This second beam is used to cancel out any fluctuations in light source as well as instrumental fluctuations due to environmental conditions. Operation of the probe under battery power is possible, enabling operation in remote locations.
The optical pathlength of the instrument, which determines the distance the light travels through the medium, can be adapted to cope with different types of water compositions. A long pathlength increases the precision of the instrument, but reduces the maximum absorption (in Abs/m) it can measure. The optical pathlength used in the applications described herein varies from 100 mm in drinking water to 0.5 mm in wastewater aeration tanks.

2.2 Spectral Information

The spectra obtained from the spectrometer probe are used for the characterisation of the sampled liquid. From the spectrum, a large number of parameters can be derived. Some examples of parameters that can be calculated based on spectral information are: turbidity, nitrate, nitrate and sum organics (e.g. BOD, COD, TOC, DOC),\textsuperscript{8} ozone,\textsuperscript{15} and hydrogen sulphide.\textsuperscript{16} Furthermore, using information from the full spectrum, the interfering effects on the measurement from light scattering, e.g. caused by turbidity,\textsuperscript{17} air bubbles or suspended particles,\textsuperscript{18} can be compensated. The wavelengths used for determining all these parameters have been selected using principal component analysis (PCA) and partial least square regression (PLS) on datasets containing both UV/Vis spectra and reference values for these parameters,\textsuperscript{6} the latter being determined using established laboratory techniques.\textsuperscript{3} Characteristic and quantitative relationships between the parameters described above and the absorption at certain wavelengths were thus established.

3. VIENNA’S DRINKING WATER

Mountain springs in geological regions consisting of Karst formations are the main source for the drinking water supply of the city of Vienna, Austria. The water quality from these springs
is normally of such high quality that only minimal treatment, disinfection before the water enters the distribution network, is required. The quality of the raw water, however, can show instabilities as a result of heavy rainfall; storm weather can lead to rapid increases in turbidity, dissolved organic substances as well as bacteria numbers in an unpredictable way. In order to ensure water quality and security at all times, it is vital to monitor the water in these springs continuously and detect changes immediately as the raw water quality is obviously one of the prime factors determining the final quality of the drinking water.

Before 2001, only a few major springs were being monitored online. Complete buildings equipped with power supply, pipe installations and special housings had to be built for the instrumentation for monitoring SAC$_{254}$, TOC, turbidity, conductivity, DO and pH as well as radioactivity. Sample pre-treatment had to be installed prior to some measuring devices. Thus the investment and operation of the monitoring stations, which required regular maintenance, lead to high total costs of ownership. Both the total costs as well as geographical location of some of the springs prohibited setting up of a monitoring network that covered all essential springs. The introduction of the submersible spectrometer probe allowed Vienna Waterworks to establish this much desired monitoring network.

3.1 Instrument Validation

Before establishing this monitoring network based on the spectrometer probes, several periods of long-term validation took place to prove the comparability of spectral and conventional measurements as well as the equivalence between spectrometer probes.

For verification of the inter-instrumental comparability, 12 instruments were installed for six months at one spring in 2002. This validation was repeated in 2007, when 10 instruments were installed at the same spring for one month. In both cases the equivalence of the spectrometers was confirmed; Table 1 presents the results from the evaluation in 2007.
Table 1: Intercomparability between 10 spectrometer probes installed in a single spring between the 15th of September and 15th of October 2007.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Rangea</th>
<th>Measured Range</th>
<th>Median of differenceb</th>
<th>Standard Deviationc</th>
<th>95% Conf.d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Turbidity (FTU)</td>
<td>0 - 52</td>
<td>0 - 1.75</td>
<td>0.18</td>
<td>0.12</td>
<td>0.24</td>
</tr>
<tr>
<td>NO3-N (mg/L)</td>
<td>0 - 5.25</td>
<td>0.78 - 0.93</td>
<td>0.025</td>
<td>0.005</td>
<td>0.01</td>
</tr>
<tr>
<td>SAC 254 (abs/m)</td>
<td>0 - 25</td>
<td>0 - 0.41</td>
<td>0.001</td>
<td>0.019</td>
<td>0.04</td>
</tr>
</tbody>
</table>

A measurement frequency of one measurement per minute was used, resulting in a total of 4087 measurements per probe per parameter for this assessment. 10 instruments, A - J were evaluated. Instrument B showed a brief event, most likely caused by low water level causing the instrument to be only partially submersed. The results during the event were removed as outliers by deleting the 25 values with the strongest deviation for these parameters and only for this probe (0.6% of the total number of measurements collected with probe B). System specifications in this application: For each parameter and each measurement the median of the difference between the result from two adjacent probes was calculated. The overall comparability is indicated by the average value over all these medians. Overall standard deviation, calculated over all differences determined for adjacent probes. 95% Confidence interval, calculated over all differences calculated for adjacent probes.

Operation of the instruments in parallel with existing particle counters, turbidity meters and single wavelength SAC254 analysers yielded the following results; between the single wavelength SAC254 analyser, performed after membrane filtration, and the SAC254 obtained from the spectrometer probe, using the spectral turbidity compensation but no physical filtration, a squared correlation coefficient $R^2$ of 0.96 was obtained. The equivalence between turbidity from a classical 90° nephelometer and the spectrometer probe in these Karst springs was also determined, with identical results being obtained during the evaluation period apart for the measurements on the 22nd of March (Figure 3), where the nephelometer reached its upper detection limit but the spectrometer probe continued to report the still increasing turbidity.
Fig. 3 - Comparison of turbidity measurements obtained from a nephelometer employing light diffraction at a 90° angle, and the spectrometer probe measuring attenuation at 180°.

During the same study, the results from the spectrometer probe were also compared to those from two particle counters; the Abakus Mobil Fluid from Klotz Analytische Messtechnik and the WPC 2000 from ART Instruments, Inc. This comparison was undertaken to investigate the relationship between particle counts, SAC$_{254}$ and Coliforms present in the water. Although the correlation amongst these parameters was too weak for exact quantitative statements on Coliform levels, it was found that the combination of turbidity and SAC$_{254}$ is useful as an early warning parameter. Furthermore, a strong correlation ($R^2$ of 0.98) was found between the smallest size classes measured by the particle counters (2-5 µm) and the turbidity from the spectrometer probe.

3.2 Operational Experience from the Monitoring Network

At present Vienna Waterworks operates online monitoring systems for turbidity, SAC$_{254}$, Nitrate, TOC, DOC, temperature and electric conductivity in springs, catchments of various springs and essential points in the transportation network. The results from these monitoring systems are transferred in real time to a number of central stations. By means of this early warning system the operational staff of the specific central stations manages the raw water sources 24 hours a day: Whenever the readings exceed specific limits, the water of the spring of concerned will be disconnected from the water catchment system. Real time monitoring has shown that the quality of the spring water can vary rapidly (Figure 4) and that online monitoring of multiple parameters is indeed necessary to ensure that springs are timely
disconnected in case storm weather affects their quality. Figure 4 also shows that monitoring only a single parameter provides an incomplete picture of the quality; turbidity responds very rapidly but returns to background levels while there remains an elevated level of organics in the water, whereas SAC\textsubscript{254} properly represents the duration of the event, but responds too late to the onset of the event.

![Graph showing water quality changes](image)

**Fig. 4 - Example of the water quality changes triggered by a heavy rainfall event.**

Online monitoring by UV/Vis spectrometry has now become a fundamental part of the water quality management system of Vienna Waterworks, with one instrument being able to provide readings for multiple crucial water quality parameters, and 30 monitoring stations have been equipped with the spectrometer probes.

4. **VIENNA'S SEWER SYSTEM**

After use, Vienna's water is collected in and transported through a 2200 km long sewer system that drains an area of 260 km\textsuperscript{2} and services a population of 1.8 million people. The sewers not only collect the used drinking water, but are also used to collect and transport storm water. Although flow measurements comprise the majority of the online monitoring performed in this part of the water chain in Vienna, UV/Vis spectrometry has also found a place.
4.1 COD measurements in Sewer Systems

A prime application of spectrometer probes in wastewater monitoring in sewers is the measurement of COD. Although the measurement itself is easily performed, the operational difficulties of operating any type of instrument inside sewer are substantial; such a system should be able to cope with high and low flows and water levels (storm water, dry periods), deposits, sediment erosion, clogging and/or damage by foreign materials, etc. When the spectrometer probes were first deployed in sewer systems, extensive studies were performed in Vienna and in Graz on the suitable operational practices.\(^{19}\) The first challenge to be dealt with is providing the probe with water from a representative sampling location, despite strongly varying water levels and flow velocities. Two solutions were tested: mounting of the probe in a floating pontoon which ensures it always measures the upper water layer. The second solution was the installation of the probe in a measuring flume, which is continuously fed with wastewater from the sewer a peristaltic pump. Although both setups provide good quality data, it was found that the operation of a measurement flume needs substantially more maintenance as reduced flow rates in the flume lead to sedimentation in the flume. The monitoring station in Vienna has now been operated successfully since November 2004, and provides online measurements for total suspended solids (TSS) and COD.

4.2 Hydrogen Sulphide prevention.

Under low flow conditions and long retention times, the dissolved oxygen level in the sewage can decrease due to biological transformation of organic matter. This consumes the available oxygen, as well as nitrate, and causes the redox potential (ORP) of the water to fall. As a result, anaerobic conditions arise, under which bacteria will continue the degradation of organic matter but amongst others produce hydrogen sulphide.\(^{20}\) Accumulation of hydrogen sulphide in the sewage poses significant problems, as it is toxic, foul smelling and upon exposure to oxygen can be transformed into sulphuric acid.\(^{21}\) The latter is responsible for corrosion of concrete and metal structures in the sewer network and waste water treatment plants.

In several parts of Vienna's sewer system the formation of hydrogen sulphide is actively prevented by the addition of iron nitrate to the wastewater. The iron stimulates the precipitation of sulphur compounds and the nitrate raises the ORP level and thus prevents anaerobic conditions.\(^{22}\) The iron nitrate dosing control is based on online measurement of the nitrate concentrations in the aqueous phase of the sewage. Here the UV/Vis spectrometer monitoring the raw sewage water in-situ provides accurate nitrate measurement in the
required 0 - 50 mg/L concentration range. The turbidity compensation employed has proven crucial in the extremely changeable wastewater matrix and allowed the achievement of a correlation with an $R^2$ of 0.95 with reference analytics. The correlation presented in Figure 5 is based on a so-called Global Calibration, provided ex-works from the manufacturer for the standardised application in untreated waste water, without calibration of the spectrometer for this specific matrix (Figure 5).

Furthermore, recently an algorithm has been developed that allows the monitoring of both nitrate and hydrogen sulphide directly in the waste water using one spectrometer probe. Using this new algorithm, it will be possible to further improve the on-line process control of hydrogen sulphide prevention via nitrate salts.

![Figure 5 - Correlation for NO3-N in the aqueous phase of the sewage. On the x-axis results from a non-calibrated spectrometer probe or plotted and on the y-axis results from reference analyses. The dashed lines represent the 95% confidence interval.](image)

**5. VIENNA MAIN WASTEWATER TREATMENT PLANT**

Vienna’s main sewage treatment plant is designed to process wastewater for a population equivalent of 4.0 million and is able to clean 680,000m³ of wastewater per day. The preliminary mechanical purification of the wastewater collected in the sewers of Vienna removes up to 30% of the organic pollution. Subsequently, micro-organisms break down the dissolved pollutants in four primary-stage aeration tanks. 15 secondary-stage aeration tanks take care of nitrification and denitrification. Finally, wastewater is separated from sludge in secondary sedimentation tanks, with most of the sludge being returned to the aeration tanks to
increase the concentration of micro-organisms and to maintain a stable decomposition process. Following secondary clarification the treated water is discharged into the Danube Canal. Particularly challenging in this application are the strongly variable water compositions, caused by different operational modes, as well as the dosing of ferric(III)chloride and organic polymers for flocculation and phosphate removal.

At Vienna's main sewage treatment plant spectrometer probes are in use to monitor NOx-N and total solids in the primary and secondary aeration tanks as well as COD, NO3-N and total solids in the plant influent. In the case of the secondary aeration tanks, the control of sludge recirculation can be controlled by the nitrogen measurements from the spectrometer probes. As this plant operates 27 instruments, uniformity and accuracy were verified before initial deployment by operation of five instruments in parallel in one denitrification tank and three in one nitrification basin, determining the inter-comparability as well as correlation to laboratory results (Figure 6); the observed average difference in the nitrate readings between instruments installed adjacent to one another was 2.5%. This average difference expressed as percentage of the 0 - 20 mg/L total measurement range in this application is 0.8%, or less than 0.17 mg/L. The changes in nitrate concentration observed during the period of this test were the result of operational changes carried out by the operators of the plant. No interferences to the nitrate measurements as a result of these changes were observed.
The results for the NOx-N were made possible by the development of a special spectral algorithm, facilitated by the availability of the full UV and visible spectrum provided by the spectrometer probe. This algorithm compensates cross-sensitivities resulting from the added flocculation agents and made possible the accurate measurement of NOx-N in the nitrification and denitrification basins. A squared correlation coefficient of 0.89 was obtained between calibrated spectrometer probes and colorimetric test kits, for a dataset that combines measurements from such diverse processes as aeration and non-aerated denitrification.

Since the start of operations with the spectrometer probes at the Main Wastewater Treatment Plant, 3 years ago, all NOx-N measurements provided by the spectrometer probes are based on one single initial calibration. The accuracy of these readings is periodically verified and re-approved. Besides visual inspection and trivial cleaning of surfaces there is no regular maintenance performed on these spectrometer probes.

6. DANUBE

The final receiving body for Vienna’s water is the Danube river. The quality of its water is continuously monitored by a station located 3.5 km downstream from Vienna’s main wastewater treatment plant. Besides the spectrometer probe, for monitoring solids, organics and nitrates, additional probes are integrated in this station, such as ISE probes for nitrate and ammonium, pH, dissolved oxygen and conductivity sensors. To cope with variations in water level in the Danube of up to 7 meter, the monitoring devices have been mounted on a movable trolley as mounting on a floating pontoon was not possible due to intensive shipping traffic. This monitoring station, as well as two others, is linked to a central station for data collection and visualization of monitoring results. The configuration of individual monitoring devices can be performed remotely over the central station and collected results can be accessed via an internet platform. This station was developed in the IMW project and was started up in January 2003.

During the initial operation phase, all sensors were calibrated on the water matrix. Subsequently, all electrochemical sensors required a 2 - 4 weekly calibration. This frequent maintenance is the result of the sensitivity of the membranes of ion selective- and gas electrodes towards fouling and damage as well as aging effects. Maintenance on the
spectrometer probe, which employs automatic cleaning with compressed air to prevent fouling, was much less frequent as it has neither replaceable parts nor needs consumables and the possible instrumental causes for drift in results are automatically compensated by considering the spectral measurement of the internal light beam. This was clearly shown when directly comparing spectral and ion selective measurement of nitrate: over the course of two weeks the ISE showed a drift of up to 0.6 mg/L, necessitating recalibration, as well as a significant number of measurement outliers. The readings from the spectrometer probe were free and outlier free over the same period.  

An important issue that had to be addressed in this monitoring station was the protection of the instruments from physical damage and excessive fouling. Besides the already mentioned trolley system, deflectors were placed around the sensors preventing damage by and congestion of drift wood, as well as damage by ice floes.

7. **Bank Filtration and Artificial Recharge in VIENNA**

Apart from applications in the well-known chain of urban water activities, in Vienna a major application of online monitoring is the measurement of groundwater quality in the vicinity of a hydropower plant. During construction of a new power plant by VERBUND-Austrian Hydro Power AG, a sealing wall system that prevents excessive infiltration into groundwater from the river was constructed. To retain ground water dynamics, bank filtered water is pumped from extraction wells to infiltration wells or pumped back from the infiltration wells into the Danube. Protection of ground water quality is ensured by monitoring the quality of the bank filtered water used for the artificial recharge and to stop infiltration in case of unacceptable water compositions. More than a dozen water quality monitoring stations are operated along the Danube to safeguard the waters hydrodynamically affected by the operation of the plant. As the evaluation of the impact on the water systems after construction of the plant requires long term continuous monitoring, online systems were implemented to ensure the best possible coverage of any changes in water quality. Sum organics in the bank filtrate water was selected as a key measurement parameter, and SAC254 was formally allowed to be used as the indicator parameter as an equal option to DOC. This decision to use SAC254 was based on previous operational experience with high availability of spectrometer probes, but it was also shown that at this site that the correlation between the DOC content of the water and the SAC254 measurement was very high ($R^2 > 0.81$) when the discharge of the
Danube was low (Figure 7). But, although the dynamics in the concentration of organic materials in the bank filtrate is strongly linked to the discharge in the Danube, no direct relationship with the water level could be determined.

![Graph](image)

**Fig. 7 – Relation between Danube water level and organic materials, indicated by SAC254, in bank filtrate water.**

Over the period September 2001 - November 2003, long term trials were performed to assess availability as well as performance of the spectrometer probe in this application. Over this period the spectrometer probe achieved 97% availability (50149 out of a possible 51815 half hourly averages recorded), whereas a DOC cabinet analyser operated in parallel showed an availability of 75%. Furthermore, the precision in the spectrometer measurements was significantly higher than that obtained with the analyser (Figure 8). This allowed the detection of small changes in water composition that were traced back to changes in water level but which could not be discerned in the results form the analyser due to its higher measurement noise.
Fig. 8 - Comparison of the results of online measurement of SAC254 from a spectrometer probe and DOC measured in parallel using a cabinet analyser.

After the successful conclusion of the two year testing period, four spectrometer probes have been in operation for the continuous measurement of water quality both in the river Danube as well as in the bank filtrate.

8. Summary and Conclusions

In this paper, an overview of all types of applications in Vienna where the submersible UV/Vis spectrophotometer from s:can is in use has been provided. These applications range from monitoring of drinking water quality in mountain springs to nitrate monitoring in the sewer network and aeration basins of Vienna's main waste water treatment plant. Although these very different applications pose disparate challenges to an online monitoring system, the design of the spectrometer probe allows successful application of one instrumental design under all these conditions. The only adaptation of the systems to these different environments are the optical pathlength of the measurement cell and the spectral algorithms for calculation of parameters from the spectrum, which have been developed and optimised for the different standardised applications.

Vienna is the single most elaborate example, where many different applications can be found within a single urban conglomerate. The Viennese example, however, is indicative
of what can be achieved in other places as well, as the measurement principles and technologies used here are not restricted to any specific geographical or environmental conditions; online UV/Vis spectrometry is a powerful principle that facilitates efficient and economical monitoring of multiple parameters and in this way provides valuable insight, in real time, into water compositions in widely differing matrices as well as into their dynamic behaviour.

References


14 Suitability of UV/Vis spectroscopy in these applications was verified and proven in the EU project "Management of sensible water uses with the help of innovative sensor technology" (LIFE99 ENV/A/403)


Innovative Messtechnik in der Wasserwirtschaft - IMW, 2003. A project funded by the Austrian Ministry of Agriculture, Forestry, Environment and Water Management, city of Vienna, city of Graz, the water authorities of Lower Austria and Styria, EBS / Main Wastewater Treatment Plant Vienna. www.imw.ac.at