

## A Compact Submersible UV-Vis-Spectrometer for Multi-Parameter Measurements

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Submersible process spectrometers can solve many of the demanding measuring tasks of the water treatment industry at the same time. The spectro::lyser, a new probe spectrometer goes directly into rivers, wastewater or the process stream of any industry and can sense a wide range of substances whether it be nitrates, organics, solids, colour, toxic chemicals, milk-, paper- or petro-chemicals, and others. The unit can run off a battery pack and has a built in data logger capable of recording many months of information. What follows is a close-up look at the potential of this, the new generation of probe spectrometers, which promise significant technological progress that could have a deep impact on the water treatment industry – even to the water security.

### History and state of the art

During the eighties, the introduction of miniature diode array detectors, combined with powerful microprocessors and state-of-the-art mathematical tools, lead to a renaissance of UV-Vis spectrometry and enabled the rapid spread of compact, relatively low-cost yet still powerful laboratory UV-Vis machines. During the nineties, the technology moved from the lab to the field, but still offered as part of relatively large and expensive off-line auto-analysers produced by several manufacturers.

### The next generation: submersible spectrometers

A young Austrian company, s::can Messtechnik, Vienna, were the first to put UV-Vis spectrometry into a small probe, named the “spectro::lyser”. Compared to the conventional photometer probe, a great deal of proprietary know-how from the areas of optics, electronics, mechanics, software and mathematics was squeezed into this new tool, yet it's still so simple, anyone can use it. Since 1999, the instrument has been placed in so many applications that most segments of the water industry appear on the company's reference list. By now, nearly a thousand spectro::lysers have been put to applications from industrial waste waters to ultra pure waters, many of them without ever leaving the water, so it's clear that this instrument not only represents large technological progress, but that it also has proven to work very reliably under real world conditions.



Fig. 1: The spectro::lyser

## The new technology

The instrument utilises no chemicals, no membrane, no pumps, no filters, no wipers, nothing but 12 V low power energy. There are no moving parts and is built to run without ever leaving the water, with almost zero operating costs.

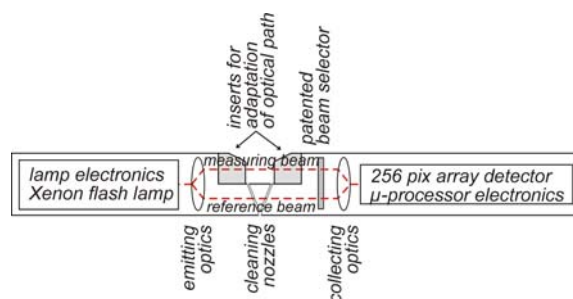


Fig. 2: How it works

The patented 2-beam optical design works by blasting UV light from a high-energy long-life Xenon lamp directly onto the matrix. The Zeiss 256 pixel diode array detector at the opposite side monitors the entire optical spectrum--from UV to the visible--and with the help of advanced chemometric algorithms running in the onboard computer, the smallest amounts of various pollutants can be quantified, even in a complex matrix. The interface is digital and can be connected to any PC or data acquisition / SCADA system.

## Yardsticks for online instruments

Three most important criteria for on-line and in-situ instruments are suggested as follows:

1. Good correlation with the reference method
2. No sample preparation needed
3. Fast response

As long as standard stock solutions of known concentration are used for calibration, readings in the range of 95 - 99 % correlation to reference methods should be no problem for well working instruments. However, tests conducted by several European university institutes with real world waste waters of unknown composition for total solids (TSS) as an example, suggest that any specification with better than a 10 % prediction error amounts to a case of wishful thinking, since this is the typical total error of the reference method itself (including sampling, transport and storage). For the COD, and even more for the BOD, prediction accuracy will not be much better, and will in fact be worse if non-filtered samples are examined. At the same time some international tenders specify accuracies between 1 or 5 %, which can not be met for methodological reasons. The now discussed ISO/WD 15839 could be a first step in the right direction to resolve this discrepancy.

The second criterion is met by the spectro::lyser with the help of an automatic cleaning device: Researchers in Switzerland, Germany and Austria approved that the "sand blasting" effect of the applied high pressure water/air mixture is more effective for keeping the sapphire windows clean than any wiper, ultrasonic or other cleaning device, which tend to "smear" windows. The spectro::lyser cleaning system has been working perfectly in sewer systems or in extremely greasy liqueurs such as of milk (see fig.3) or meat industries, making possible the online COD measurement in the factory effluent.

## Waste water applications

On-line measuring instruments are increasingly sought after for the control and operation of waste water treatment plants. Their chief advantages over cabinet analysers include lower initial and operating costs. The spectro::lyser is an instrument which allows the simultaneous measurement of Nitrate, Nitrite, COD\_tot, COD\_solved, BOD, SAC after DIN38404 and turbidity / total solids (TSS). By performing tasks from the characterisation of predominant emitters and their integral matrix in the WWTP influent

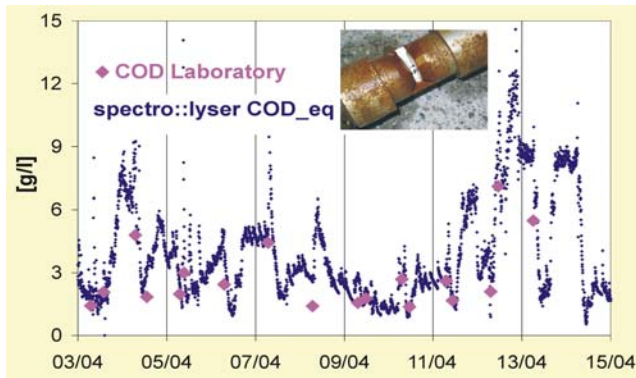


Fig. 3: Effluent of an industrial dairy

water, to the control of the biological processes in the aeration tank, and plant emission monitoring, the instrument provides almost all of the online parameters that are necessary for the monitoring and control of the complete waste water system. It can easily be used to trace and identify illegal charges i.e. into sewer systems or receiving waters. As one example for all of these applications, the measurement in the influent of a medium size German WWTP is showed in fig. 4. Zooming into one week of this plant's monitoring, the fine resolution of measurement and the independence of the parameters can be evaluated. A daily period can clearly be distinguished, weekly and monthly periods can be seen at larger time scales.

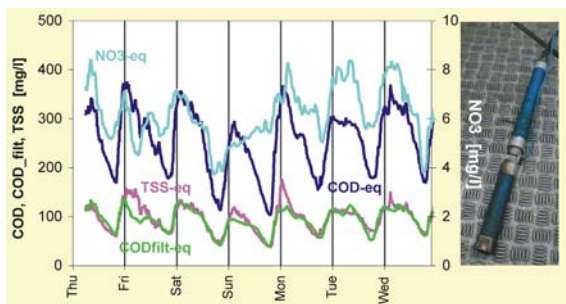


Fig. 4: One week in the influent of a waste water treatment plant

### Sewer system applications

Inlet monitoring informs but measuring the same parameter in the sewer system enables the treatment plant engineer to act and not to react. For sewer system measuring stations even under harshest conditions, a very robust, almost maintenance-free, non-clogging carbon-fiber ponton can be applied, and an explosion-proof version of the spectro::lyser is available. The controlled and holistic operation of the complete waste water system based on parameters like COD, solids, or Nitrate, under consideration of sewer systems, emitters, treatment plants, stormwater discharges and receiving rivers have become a reality. Upcoming scientific publications give evidence of this new potential.

Fig. 6 illustrates the result of such a campaign in the sewer system. Parameters such as COD, COD-filtrated, NO<sub>3</sub>, UV<sub>254</sub>, and TSS can be monitored online – by using just one small probe.

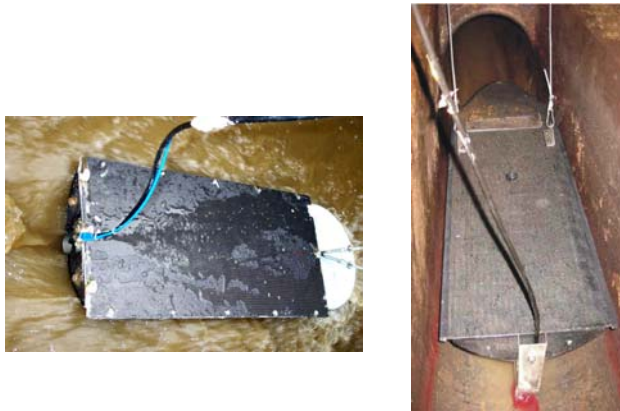


Fig. 5: Floating installation in the sewer system

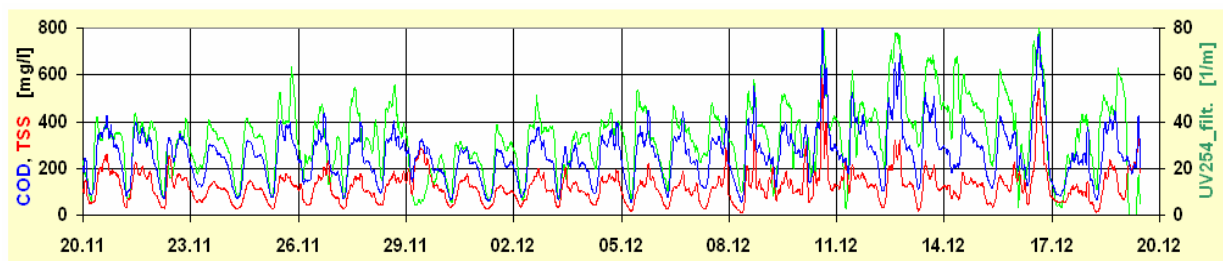


Fig.6: Monitoring several parameter in the sewer system

### Hydrocarbon alarm systems

After having seen the suitability for monitoring those conventional parameters, the question followed: what about additional parameters? Is the spectro::lyser able to see accidents or other irregularities that are invisible for COD analysers or UV monitors? As an answer, in fig. 7, a set of UV-Vis differential spectra is plotted against time, as taken by the spectro::lyser in a sewer system. Many irregularities that have a harmful potential for the plant and environment can be identified. Peaks that result from hydrocarbon spills (in the U range, red arrows) or colour emissions (in the visible range, blue arrows) were detected. Such measurements are fed online into very simple but sensitive alarm software that triggers adequate activities of plant staff on different levels - like automatic sampling, or urgency visits at site.

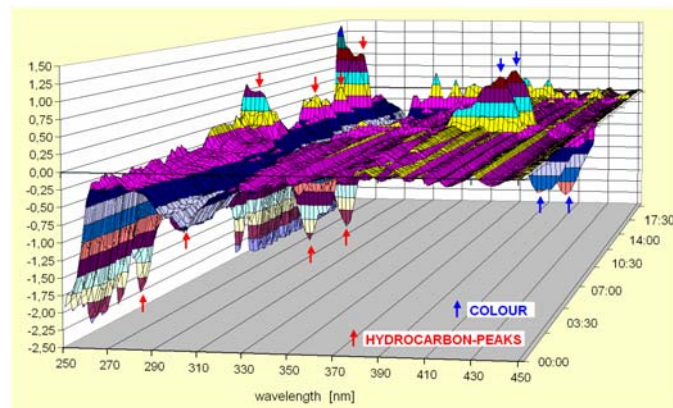


Fig. 7: A set of UV-Vis differential spectra plotted against time

### The aeration basin

A more simple application for the spectro::lyser is the simultaneous measurement of NO<sub>3</sub>-N and COD<sub>eq</sub> directly in the aeration basin for control purposes, as pictured in Fig. 8.

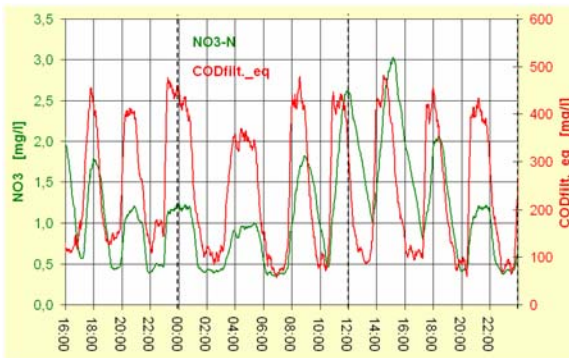


Figure 8: Simultaneous NO<sub>3</sub>-N and COD measurements in the aeration tank

The accuracy is much higher than necessary for control purposes, and clearly higher than of the wide spread photo-optical probes. Unlike the latter, the cross-sensitivity of the measured parameters is almost zero. On-board pre-calibrations for many different applications, including several industrial waste waters, allow the start of measurement within a few minutes, often even without local calibration.

### Monitoring of Nitrite, Nitrate, COD<sub>soluble</sub> and TSS in the effluent of a WWTP

Swiss and Viennese researchers succeeded at the monitoring of NO<sub>2</sub>, NO<sub>3</sub>, COD<sub>soluble</sub> and TSS in the effluent of a WWTP – all by one instrument (Rieger et al., 2004\*).

A UV spectro::lyser with 10 mm open pathlength was located in the secondary clarifier effluent of a Swiss WWTP. 256 wavelengths are measured simultaneously between 210 and 400 nm with a resolution of < 1 nm. This high resolution / narrow range instrument is needed to distinguish between NO<sub>3</sub> and NO<sub>2</sub> at the disadvantage of restricted but still acceptable TSS accuracy. Spectral ranges of some measured substances are pictured in figure 9.

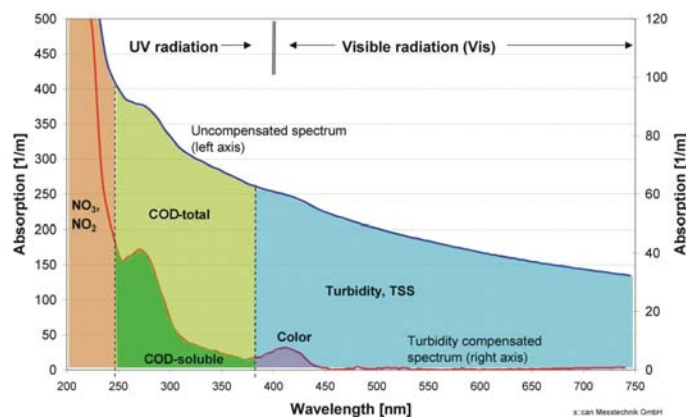


Figure 9: Measured substances and their spectral ranges

The calibration of the spectrometer is based on a chemometric PCA/PLS model correlating the concentrations of the required determinants to UV spectra. An improved algorithm uses different optimal numbers of principal components for each parameter. However, this is only one of the methods that are provided by s::can Messtechnik, Vienna.

### Environmental applications - replacing organic carbon analysers

One very effective application of process UV spectrometry is the replacement of TOC/DOC or COD/BOD analysers. The correlation to the normalised methods for carbon parameters is always according to DIN 38404, moreover, the precision is about an order of magnitude better than with standard DOC analysers (Figure 9). The comparison to a University institute's laboratory DOC reached an  $r^2$  of 0,99, and was limited only by the lab method's standard deviation. In river bank filtrate and ground water applications, spectro::lyser have been running for more than a year without missing one single measurement and without leaving the water.

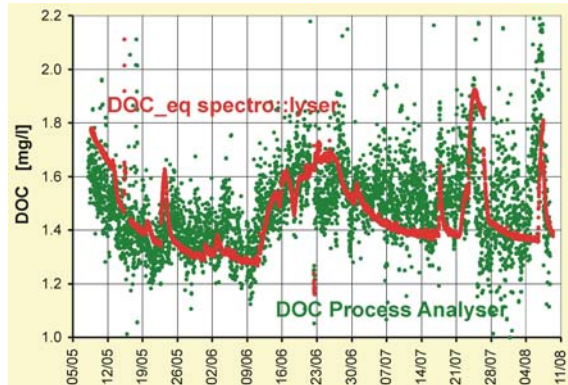


Fig. 9: Comparison of spectro::lyser with DOC process analyser

Other spectro::lysers run reliably under extreme conditions i.e. high in the Austrian mountains - as the main sensors of an alarm system of a large drinking water utility- , or in the Brazilian Amazonas river - in the heart of an international carbon research project - , or in Swiss ground water - to protect a local drinking water system.

The cost saving is about a factor of 2 to 3 for the purchase and installation, and around 2.500 Euro per year for maintenance compared to conventional DOC online analysers (more in exposed regions), and even more compared to COD analysers. This is one reason that several utilities in Europe are now, step-by-step, replacing their DOC process analysers with spectro::lyser systems. With the optional built-in level meter, it can be utilised to measure and plot in-situ concentration profiles of many substances in bore holes, lakes, or tanks.

### Calibration

In order to be able to take full advantage of the spectral information, new methods were developed by s::can together with University partners, allowing both to use the instrument in a very simple and robust "plug-and-play" modus, but also to explore the full potential of UV-Vis chemometry. In addition, a powerful off-line analysis software tool allows to visualise all data of the measuring period and to follow all spectral changes using advanced methods like derivative spectrometry and difference spectrometry. New calibrations can be tested off line and data can be corrected with new-found algorithms retrospectively.

### System integration

A powerful industrial PC (IP65) is available, which serves as the basis and brain for complete monitoring stations, including networks of spectro::lysers: A large colour display and a touch panel allow menu-driven, user-friendly communication with the spectro::lysers and any other digital (RS485) or 4-20 mA sensors of different makes, as well as the operation of distributed systems, either via telephone, radio, GSM, or GPRS telemetry. The LabView™ based system is open for the interconnection to existing SCADA systems, data bases, or for integration into any third party remote data acquisition system.

### **Drinking water protection**

Exactly the same method, developed by s::can and their University partners, is used in river basin and ground water monitoring systems that protect drinking water plants against any kind of irregularities, like natural disasters or terrorist attacks. As one example of many, a network based on 10 independent stations was recently installed by s::can at a large European water works.

### **Water Security and Alarm Systems based on UV-Spectrometry**

The prevention against conventional anthropogenic risks like from accidental discharges into drinking water systems has been good practice for drinking water managers since long time. However, the threat of intentional discharges is relatively new and has become more offensive to our minds since the terrible terrorist attacks of September 11. In addition, the horrible Tsunami catastrophe of December 26 in Southern Asia with its immense deterioration of drinking water sources and infrastructure showed us that we should not forget about the immanent natural risks that our drinking water systems are exposed to every day.

### **Sensors for early warning and alarm systems**

There is a new and urgent need for the instrumental identification of contaminants in a stage as early as possible forming the vital basis for any following intervention activity including treatment and operations decisions. Methodically, we can distinguish between

1. measurement of specific substance concentrations by: advanced process analysers (GC/MS, AOX, LC/MS etc.); time resolved optical methods, like UV, IR, ATR or fluorescence spectrometry, including application of special reactive coatings
2. direct measurement of toxicity by: microbial culture methods; caged organisms (mussels, fish etc.); bacteria; daphnids
3. immuno-optical, immuno-assay technologies, “electronic noses”
4. monitoring of broadband characteristics with the help of diverse physical and chemical sensors and tracking of deviations from a pre-defined reference status

The reference or baseline is normally generated from historical samples, i.e. by state-of-the-art “black box” statistical methods. Such a system must be “trained”, which is a tricky task that will always lead to unacceptable false alarm probability as long as non-selective surrogate parameters like pH, conductivity, turbidity, DOC, Nitrate etc. are available. Even after long training periods, no information is hidden in a set of non-selective signals that can tell the manager if a DOC increase of + 1 mg/l is to be considered “good” – i.e. by natural fluctuation - or “bad” – i.e. by a contamination. However, a contamination mirrored by an increase of 1 mg/l of DOC could easily be very harmful to drinking water consumers – so how can water managers rely on such a alarm parameter? No successful real-case studies are available today proving the practicability of such an approach.

Without more sensitive and at the same time much more selective sensors, alarm systems will not be very useful for practical applications. There used to be a wide gap between the non-selective, low-sensitive sensors and analysers, on the one hand, and sophisticated, highly selective, expensive analysers etc. Real-time UV-spectrometry exactly fills this gap, and no other instruments are known today that could provide a comparable specific suitability for alarm systems.

s::can Messtechnik, Vienna, have developed a completely new method to detect slightest changes and deviations from the “normal” reference state of a water, instrumentally based on their well-proven spectro::lyser instruments described above, and on their water security and alarm software package. Their alarm software has been specifically developed for the purpose during many years of testing and practical experience. Compared to other known on-line instruments, the 100 mm optical path version it is extremely sensitive which renders it

most suitable for applications embedded in alarm systems. Changes at a low ppb level of DOC-equivalents can be traced.

One strategy is to use the standard calibration algorithms for substances like T(D)OC, Nitrate, Turbidity, organic substances like benzenes, phenols, hydrocarbons, and others, and to monitor those substances with time and space. Specifications are given in the relevant technical notes. With this, the spectro::lyser can replace several complicated and expensive on-line analysers at the same time. One drawback is that, although UV-Vis-spectroscopy is sensitive down to the low ppb-range for many organic pollutants, it will not be selective enough to indicate the type of micro pollutant at the drinking water level. Therefore, a closer analysis must follow in cases of elevated signals. However, the signal will often represent a sum parameter, but also as such; it will be orders of magnitude more sensitive than i.e. DOC measurements.

The better strategy is 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 that become only evident in differential spectra. Sometimes the detected changes can not directly be correlated to known substances, but nevertheless provide a sensitive alarm parameter. Immediately, actions can be started, like shutting down valves in order to prevent that potentially dangerous substances can enter the drinking water system, depending on the level of exceed. Next action would be to (automatically) take a sample and find out in the lab about the origin of the spectral anomaly.

There are several ways to exploit the provided spectral information:

- qualitative interpretation of spectral deviations from a site specific reference spectrum (peaks, shoulders, gradients, analysis of derivative spectra)
- changes of spectral features over time (anthropogenic changes, like from spills, are typically faster than natural changes)
- compare spectral differences between measuring points of a measuring network - we call this "delta spectrometry", and it is explained in the appendix.

### **The sensor contribution**

For the time being, real-time UV-spectrometry seems to be the method that, in comparison with other chemical and biological systems, covers most of the needs of alarm systems. The new sensor consists of several state of the art components from different sectors of technologies (optics, electronics, data processing, telemetry). A software controlled system provides the telemetric control and data transfer from several field sensors to a central main processor, which again is connected to the data bank / management system. As an additional benefit, through the detailed knowledge about the evolution of water quality parameters over space and time, non-alarming but chronic polluter identification can be brought forward.

### **How to Define Alarms vs. the Baseline of "Normality"**

As for all alarm systems, a well defined approach to quality data interpretation is needed for each individual case. Specific baselines must be evaluated, and deviations of such that lead to an alarm must be defined. It is always a most difficult task, when using unselective and low specified surrogate parameters like i.e. turbidity, to distinguish between the "normal" baseline variations originating from natural occurrences, and the often only small peaks that origin from other influences or impacts.

Because of the multidimensional information provided, UV spectrometry offers a much higher information potential about the "normal" baseline than single signals like turbidity or DOC. A new approach for baseline definition - geographically resolved "Delta Spectrometry": A "reference" is measured in real time at a point where unimpaired water quality can be guaranteed, near the source of the system, or after the controlled treatment.

At strategically chosen sampling points in the monitoring network, (spectral) water quality is measured in real-time and sent to the central station where the data (spectra) are again compared in real time, in order to detect any change or deviation between sampling point and the reference with highest possible resolution.

### **Conditions for Early Warning and Alarm Parameters / Instruments / Systems**

- quick response to suspect quality changes
- real-time measurement
- high sensitivity, at the same time low false alarm probability
- clear interpretability of signal and alarms, reproducibility
- broad band response to diverse contamination sources
- robustness and long term stability of sensors and stations under harsh conditions
- remote accessibility
- low costs, allowing multi-point systems to cover larger areas, basins and distributions networks
- high security access, secure data exchange, high security reserves on all levels

less important:

- parameter selectivity
- compliance to analytical laboratory norms

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