drinking water and environmental monitoring
1 Introduction

Both national laws and an increasing number of supranational recommendations are prescribing emission limits for reasons of public health. These limits may not be exceeded, and must be controlled as seamlessly as possible, in order that consumers of drinking water are not placed in jeopardy. Furthermore, the quality of raw and/or drinking water must constantly be monitored to be able to perform controlling and/or regulating action or to implement alarms.

In order to prevent any jeopardy to the drinking water consumers’ health, the measured data must be available

1. continuously
2. without delay (in “real time”)

This is the only way to allow quick reaction to changes in the water quality. These requirements can only be fulfilled by online assessment of the raw and drinking water qualities.

Online monitoring in raw and open waters using photometer instruments for individual wavelengths, a state-of-the-art technique for some years now, has proved its value – however, only following sophisticated on-site calibration, and just for individual parameters.

A multitude of laboratory tests has proved that even more accurate and, above all, more selective measurements can be done using a continuous absorbance spectrum reaching from the low UV to visible light. However, compact, robust and submersible UV/VIS spectrometers were not available for field and outdoor analysis before now.

The brand-new s::can submersible spectrometers can be directly immersed into the medium, making it possible for the first time to combine the advantages of probe measurement with those of spectrometry, eliminating such well-known drawbacks as sampling errors, biochemical or physical conversion after sampling, etc. The measuring-technical level thus arrived at opens up completely new vistas.

s::can devices are compact and versatile enough to be used in many conditions, from the 2” bore hole to open rivers and canals, vessels and containers, up to pressure and bypass pipes.

2 Parameters

2.1 Calibration

The s::can calibration methods, developed during many years of co-operative work with university institutes and several chemistry laboratories, make use of the most up-to-date statistical and mathematical procedures.

Three calibration methods can be offered:

1) Polynomial adaptation to known spectra.

We use this method successively for individual substances and sum parameters. The parameters released are characterised by their particular selectivity, and are largely free from cross-sensitivities and reach almost analytical accuracy. Thus, they are instantly and universally applicable without local calibration. Examples are Benzene (Toluene, Xylene), Turbidity and Nitrate.

2) “Global Calibration”, verification by “Local Calibration”

Application-specific universal calibration provided by s::can that should be verified by a few local reference samples. Although this is just as precise, it is not as accurate and/or selective as the first method. Higher selectivity can be achieved, however, with precise “Local Calibration”. Clearly advantageous over established UV or Nitrate photometer probes.

3) Validated advanced calibration

If a very accurate analytical-like measurement is wanted, an automated state-of-the-art method using PCA (principal component analysis) and PLS (partial least square fit) can be used. The output will be a validated, extremely robust and accurate parameter set for all parameters at the same time, provided that all occurring matrices were sampled at least once. All the spectral information is used simultaneously. The procedure is software-driven.
2.2 Organic Carbon Compounds

The parameters for assessment of organic pollution (COD, BOD5, TOC, etc.) are sum parameters whose measurement procedures evince various drawbacks: reproducibility, comparability, measurement ranges, cross-sensitivities, use of chemicals, etc. Nevertheless they cannot be considered as to be absolutely “true” parameters. For this reason, increased interest has been shown in the past few years – by privates and authorities as well – in substitute measurement methods, if they provide the great advantage of time-continuity.

In terms of its methodical approach, process spectrometry features the advantage of not indirectly measuring consumed oxygen, but rather of directly measuring the concentration of oxidable organically bound carbon. Comparison of the standard deviations of i.e. DOC lab measurements with spectral measurement values will result in substantially less dispersion for the spectral parameters; the uncertainties pertaining to the DOC (above all in the lower concentration region) are well known. Thanks to lower dispersion, when determined via UV/VIS spectrometry, a lower detection limit can be achieved.

For these reasons, the SAC254 (Spectral Absorbance at 254 nm) has long been an acknowledged parameter for the description of organic carbon compounds in drinking-water analysis (i.e. after DIN38404). However, the choice of this wavelength was made above all for historical rather than analytical reasons. In most cases, organic matter generates the strongest signal at other wavelengths. Furthermore, validated spectral calibration allows much more accurate and robust measurements, as shown in figure 1, where single wavelength measurement is compared to spectral calibration.

The comparison of DOC concentrations with data gained from UV-spectrometry of various natural water samples always yields correlations $r^2 > 0.95$.

As regards BTX, Hydrocarbons, phenols, etc., even concentration changes of down to 10 ppb are detectable with high selectivity and reproducibility using s::can’s high-resolution UV instrument.

Aromatics, phenolics, hydrocarbons, and most chromophores with peak $e > 10^4$ will show results comparable to Benzene after calibration.

As a rule, for most situations where a parameter for sensible alarms or control is needed, online UV spectrometry alone will be the ideal solution - from drinking waters to waste waters. However, where results with full parameter security are needed, i.e. for testing a water’s
suitability for drinking water purposes, there is no passing by laboratory validation.

2.3 UV/VIS-Absorbance Spectrum (fingerprints)

A continuous UV/VIS absorbance spectrum features two substantial advantages:
1. Nitrate, turbidity and organic substances can be measured simultaneously
2. Qualitative assessment of water composition is possible

Figure 5 shows the spectra from the east bank (red fingerprint), west bank (blue) and open water (black) of an alpine lake.

The differences visible in the absorbance spectra in the wavelength range of 215 to 350 nm become even more distinct using the “Delta-Spectrometry” method. Comparison of the east and west bank spectra to the fingerprint of the free water body will yield the difference (delta) spectra shown in the upper right corner of the graph above. Due to differing substance groups, the spectra take various shapes within the range determinant for the relevant organic substance. This method is capable of capturing very small variations in water composition, which is of particular benefit in early warning systems based on the s::can software ana::larm.

2.4 Turbidity

The correlation between turbidity and the spectro::lyser™ values in natural water yields very good results (cf. Figure 11), lying throughout at 0.95 to 0.99 from 0.05 FTU up to several 100 FTU.

2.5 Nitrate

The correlation between concentrations of nitrate and spectral extinction parameters results in always excellent correlation coefficients.

Nitrate produces a particularly strong signal which can be particularly easily detected. The measuring precision lies in the µg - range, the measuring ranges are from dozen up to hundreds mg/l NO₃-N, depending on the measuring path length.
3 Advantages of Process Spectrometry in Comparison with Simple Photometer Probes

- **Cost efficiency**
  Even at minimum performance, the continuous UV/VIS spectrum enables simultaneous measurement of the parameter equivalents of organic carbon, nitrate and turbidity, for which reason only one s::can spectrometer is required, instead of merely three photometer probes.

- **Lower cross-sensitivity on turbidity, coloration, window deposits, etc.**
  Potentially interfering variables, which are not detectable using conventional one- or dual-wavelength probes, can nearly always be compensated with the help of spectral information. In cases of high solid-matter or fat content, the automatic cleaning unit is connected via an external pressure line and guarantees absolute drift-less measurements.

- **thus greater precision**
  Since cross-sensitivity is substantially reduced by this means, heterodyning of measuring signals due to interference/noise is significantly less than with simple photometer probes.

- **higher selectivity**
  The individual substances and/or substance groups sought can be allocated to significant spectra, for which reason they can be selectively identified.

- **greater reproducibility**
  These s::can spectrometer advantages result in very high reproducibility as well as the benefit of universal applicability without the absolute necessity of local calibration.

- **Calibration matching other substances and substance groups**
  Aside from the usual parameters (D(T)OC, BOD, nitrate, turbidity), other parameters can also be made available using calibration software from the UV/VIS spectrum.

- **Quantitative and qualitative readouts**
  In addition to the calibrated parameters, the qualitative spectral information (fingerprint) can be directly applied for alarm and control systems, etc. With the s::can software ana::larm qualitative and quantitative differentiation of carbon fractions is possible for more detailed assessment of the water, e.g. from pollution sources.

4 Other Advantages of s::can Instruments

- **Extreme dynamic range**
  A special feature of all spectro::lyser™ is their extreme dynamic range ( > 1:1000 or e.g. 1 to 1000 mg/l DOC_eq). The universal 35 mm configuration allows measurements in groundwater, river water, lake water, drinking water, etc. With the new 100 mm measuring path, changes of 10 µg/l DOC are detectable, and/or individual substances such as BTX, phenols, olefins, etc. are distinguishable.

- **Long-term stability**
  Dual-beam measurement enables all changes in the measurement system to be compensated. In addition, the spectral compensation of biological growth on windows allows the long-term stable measurement of dissolved substances, which is the basis for continuous monitoring of water quality and for the safe and precise operation/control of treatment plants.

- **No maintenance necessary**
  Virtually no maintenance is necessary because no moving parts or ageing equipment is in use.

- **Field and Outdoor Applicability**
  UV/VIS spectrometry technology to this date has never been available in such a compact design, enabling the use of the spectro::lyser™ even in tight spatial situations. Owing to the lightweight, robust design (all surfaces are anodised), and the absence of movable components coming into contact with the medium, as well as due to the 12-volt supply w. sleep mode option, the instrument is also suitable for use under rough conditions and can be supplied by solar power.

- **Flexible measuring process**
  Intelligent evaluation algorithms adapt the hardware (exposure time, oversampling, etc.) and the measuring parameters to altered conditions of the medium.

- **High operational safety ...**
  ... thanks to implemented self-test procedures.

- **Ease of use**
  Besides calibration, no setting whatever is possible. The user remains unaffected by the complexity of the mathematical processes running in the background, i.e. he need not manipulate the measurement procedure, he merely receives the definitive measurement figures.
5 Application of spectro::lyser™ in drinking- and natural waters

5.1 Assessments and parameters

- Measurement of UV/VIS spectra over a wavelength range of circa 200 – 750 nm
  - compensation of turbidity
  - simultaneous determination of various substances
  - differentiation between various carbon fractions
  - detection of hazardous pollution of raw water
  - detection of polluters and irregular charges
  - early detection of threats to water quality - alarm systems
  - evaluation of efficiency of drinking water treatment processes

- Calibration to the following parameters:
  - organic substances (calibration to T(D)OC, BOD, SAC254, SAC280, SAC330)
  - turbidity
  - nitrate (with UV-probe)
  - BOC (bioaccessible organic carbon), and with that
  - tendency for hygienic problems in drinking water networks
  - single substances: Aromatics, phenolics, hydrocarbons, and most chromophores with peak $e > 10^4$ will show good results comparable to Benzene after calibration.

5.2 Equipment and installation

- selection of measuring path length depending on substance concentration
  - 35 mm for surface waters and polluted ground waters
  - 100 mm for low detection limits in drinking waters and ground waters
  - other lengths available for special applications

- recommended measuring points
  - in the raw water (groundwater, surface water, bank filtrate, etc.)
  - before water collection
  - along water treatment
  - prior to feed into the water supply
  - along the supply network
  - at points of consumer use (tap)

(see chapter 7.7)
5.3 Parameter ranges for clean waters and drinking waters

Typical measuring ranges - cross-sensitivities are empirical estimations and always depend on the character of the matrix!

Strong variations in the background matrix always have a disturbing influence.

<table>
<thead>
<tr>
<th>Parameter Matrix</th>
<th>Extinction / m</th>
<th>measurement compared to</th>
<th>typ. DOC</th>
<th>typ. COD</th>
<th>typ. NO3-N</th>
<th>typ. Benzene* (polynomial fit)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detector</td>
<td>min. max. at 250 nm</td>
<td>min. max. min. max. min. max. min. max. min. max. min. max. min. max. min. max. min. max. min. max. min. max.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Absolute UV-Vis</td>
<td>0,005 2,5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Absolute UV</td>
<td>0,002 3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>35 mm UV-Vis</td>
<td>0,1 70</td>
<td>0,1 40 0,2 120 0,05 10 0,1 5 --- --- --- --- --- --- --- ---</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>35 mm UV</td>
<td>0,06 90</td>
<td>0,1 40 0,2 150 0,05 20 0,1 10 --- --- --- --- --- --- --- ---</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*other aromatics, phenolics, hydrocarbons, chromophores with peak ε > 10^4 will show comparable results after calibration.

All specifications for single measurements with accuracy set “high”; can be improved by oversampling with √n measurements.

5.4 Some selected references

s::can references Q2/2005

List not complete - selection of s::can systems sold to customers; no trials listed;
6 Additional features of s::can measuring systems

6.1 System integration
1. Our interface terminal con::stat allows total system integration and most advanced visualisation and provides analogue and digital interfaces to all kind of other sensors and control systems. Complete monitoring stations can be programmed to completely meet customer’s needs concerning visualisation, process control and data exchange.
2. The instrument can be operated and read with any commercial notebook/pc computer via the USB-interface and our proprietary software.
3. The instrument is also operable in data-logger mode without any additional periphery. However, no continuous data access is possible in this mode.
4. In addition, s::can offers a waterproof field-case (accumulator) for stand-alone operation in the field.

6.2 Operation and data transfer
- Measurement values can be integrated into automated processes (control, alarm, databases) via most known standard interfaces.

6.3 Simultaneous water-level measurement
- Sensor for pressure-measurement integrated in the instrument and the software.
- Estimation of flow-through if level-flow relation is known
- Fully automatic determination of vertical concentration profiles e.g. in groundwater levels or lakes.

6.4 Simultaneous temperature measurement
- Sensor for temperature measurement integrated in the instrument and the software.

6.5 Networking of multiple devices
- Multiple measurement points can be united to a centrally operable network. Together with its associates, s::can supplies the complete equipment.
7 Some reference measurements

7.1 OnLine Measurement in a Ground Water Well

Turbidity- and carbon peaks, always together with Nitrate valleys, result from the influence of a nearby river. The spectro:lyser™ has been working for 8 months so far with 100,0 % availability and no maintenance work whatsoever.

Figure 7: Time-series of Nitrate, SAC, Turbidity and DOC_eq in a ground-water well with strongly fluctuating water quality.

7.2 OnLine Measurements at the Tap

The NO3-N, SAC 254 and turbidity series (cf. Figure 6) originate from a measuring point in an urban water-supply network. While the nitrate concentration in the course of the week remains at a stable level, changes are detectable in the SAC 254 and turbidity.

Figure 6: Time series of nitrate, turbidity and SAC 254 in a water-supply network.
7.3 Measurement of ozone during water treatment

Figure 8 clearly shows the spectral peak of ozone at 260 nm. This peak is used to quantify the ozone concentration down to 0.05 mg/l, thus ensuring that the oxidation agent does not reach the network.

Furthermore, this application allows the easy distinction during oxidation between carbon compounds (and/or their variations), and ozone, thanks to the spectral information available.

![Absorbance spectra of ozone in drinking water](image1)

Figure 8: Absorbance spectra of ozone in drinking water

![Correlation between spectral O3 and conventional O3](image2)

Figure 9: Correlation between spectral O3 and conventional O3
7.4 Measurements in raw water/river water/bank filtrate

Figure 10 shows the spectra of river water (red fingerprint) and its filtrate following a river bank passage of 3 m (green) and 9 m (blue). The filter effect is clearly detectable in the reduction of the spectral extinction within the wavelength range from 250 to 500 nm. In this spectral region, absorbance is primarily effected by organic carbons, which are for the most part removed by the filter.

![Absorbance spectra of surface water after various filtration path lengths](image)

**Figure 10:** Absorbance spectra of surface water after various filtration path lengths

Figure 11 compares two turbidity time series measured in surface water. Over a period of more than two weeks (all together eight months), there was absolutely no deviation between the measuring values of the s::can device and those of a well proven and recognised device.

![Turbidity time series in surface water](image)

**Figure 11:** Turbidity time series in surface water
7.5 “Derivative spectrometry” used as a sensitive alarm parameter

Figure 12, below, clearly shows the benefit of derivative spectrometry in alarm systems. The ever-returning shoulder at 420 nm in the absorbance spectrum, delineated by the thick, red, drawn-out curves, is barely identifiable. The lower illustration displays the first derivation of the spectra, and here the peak is very clearly discernible. The data originate from the point of discharge of industrial waste water into a river (blue/green colour from an oil mill). The s:can software ana:lar is using these and similar methods for the detection of minimum changes of the water quality.

Figure 12: Derivative spectra of a dominant discharge into a body of running water
### 7.6 Detection of small concentrations using “delta spectroscopy”

1) Use of distilled water as reference
   - Y-axis scaled maximally

2) Zoom enlargement of the dimension axis by a factor of 20

The extinction value at 254 nm ("classical" SAC) does not reflect at all the organic matter in the water!

3) Zoom enlargement by a further factor of 10 - total factor is now 200

4) In order to make the difference more distinct, the drinking water is used as a reference, so that a peak in the range of the organic carbon (typical humic matter) now becomes visible in the bank filtrate. The DOC can now be calibrated to match this peak.
7.7 Measuring Benzene in Groundwater

- Using new mathematical procedures, an extremely selective and accurate method for measuring aromatic compounds in the widest variety of matrices was found and subsequently validated by an independent laboratory.
- At a measuring path of 100 mm, the measuring range of Benzene and also other aromates extends from 50 to 50,000 ppb.
- The measuring method can be applied in natural waters just as in processes, whereby the process measurement will tend to be simpler and even more accurate, due to less complex matrices.

Figure 14 and 15: Spectrum of Benzene in ground water (14), and Benzene calibration result (15).
7.8 Derivative Spectrometry for Identification of Manure Pollution

*Figure 16* shows absorption spectra of clean ground water, and of the same water polluted by 3 liquid manures. The spectral fingerprints of the manures are quite similar but not identical. Concentrations are clearly different. A slight shoulder around 280 nm can be distinguished.

![Figure 16: Absorptionsspektren von Grundwasser](image1)

In order to be able to better distinguish the manure from other sources of pollution, the 1st order derivative is utilised. In *figure 17*, the peak around 290 nm is now clearly visible. Other sources of organic carbon, like natural humic substances (blue line), do not provide this 1st order peak.

![Figure 17: Derivative spectra derived from figure 16](image2)
7.9 Evaluation of Contaminated Sites and Ground Waters

The investigation and monitoring of contaminated ground-waters can be greatly enhanced by measuring contaminant concentration profiles with the help of the spectro::lyser™. The optional integrated pressure sensor allows the measurement of concentration profiles in real-time. Today, this is the only method to measure such profiles without disturbing the sample. See application lists for parameters and concentration ranges.

*Figure 18* shows a selection of different well profiles in the central and surrounding area of a highly contaminated site. Under consideration of the geographical position, a three-dimensional evaluation of the Benzene contamination was done. The monitoring and comparison of time-dependent trends in the wells helps to evaluate the size and location of the contamination, and to monitor the effects of remediation activities. All needed software to run one or more probes is provided by s::can on a most advanced and user friendly level and runs on all s::can terminal units.

*Figure 18: Vertical profiles of Benzene concentration in bore holes.*
Figure 19 represents a simplified application scheme of s::can spectrometer probes for the evaluation of the threatening potential and for long time monitoring underneath suspect zones and contaminated sites. The “Delta Spectrometry” method (see chapt. 7.5) allows the evaluation and monitoring of “additional pollution” from the suspected zones, i.e. during remediation projects.

Figure 19: Method for the evaluation and monitoring of contaminated ground water by in situ and online spectrometry
7.10 Application’s profile from source water to drinking water

Figure 20: Application’s profile from source water to drinking water